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Acceleration Effects of Phosphine Ligands on the Rhodium-Catalyzed Dehydrogenative Silylation and Germylation of Unactivated C(sp^3)–H Bonds

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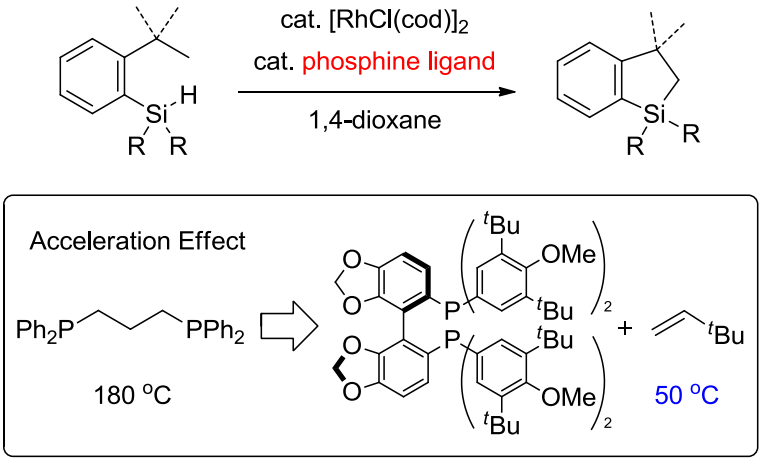


ABSTRACT: The current work describes the marked rate of acceleration caused by phosphine ligands on the rhodium-catalyzed dehydrogenative silylation and germylation of unactivated C(sp^3)–H bonds. Reactivity was affected by the steric and electronic nature of the phosphine ligands. The use of the bulky and electron-rich diphosphine ligand, (*R*)-DTBM-SEGPHOS, was highly effective to yield the dehydrogenative silylation products

selectively in the presence of a hydrogen acceptor. An appropriate choice of C_2-symmetric chiral diphosphine ligand enables the asymmetric dehydrogenative silylation via the enantioselective desymmetrization of the C(sp^3)–H bond. The unprecedented catalytic germylation of C(sp^3)–H bonds with dehydrogenation was also examined with the combination of the rhodium complex and a wide bite angle diphosphine ligand to provide the corresponding 2,3-dihydrobenzo[*b*]germoles in good yield.

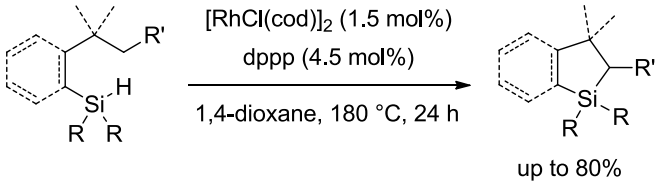
INTRODUCTION

Investigation of new catalyst systems for the improvement of reaction efficiency and selectivity is one of the most important research topics in synthetic chemistry. Transition metal-catalyzed dehydrogenative silylation of C–H bonds is a straightforward, atom-efficient, and environmentally friendly method for the synthesis of organosilicon compounds, and has received intensive interest.[1-3] In addition to the unique function of organosilicon compounds themselves, they can be used as useful intermediates because silyl groups can be easily converted to various functional groups by Hiyama cross-coupling[4] and Tamao–Fleming oxidation,[5] *etc*. Although organosilicon compounds can be synthesized via bond forming reactions with reactive functional groups, molecules containing the proper substituents are not always readily available and sometimes must be prepared through additional synthetic steps from commercially available building blocks. Thus, the development of efficient silylation methods for ubiquitous C–H bonds is highly desirable. There are many reports on the dehydrogenative silylation of aromatic C(sp^2)–H bonds without any directing groups,[1] whereas silylation of aliphatic C(sp^3)–H bonds is still limited from the viewpoint of substrate scope.[6-9] In most cases, activated C(sp^3)–H bonds at the benzylic position,[7] or located adjacent to boron or nitrogen atoms,[8] are used as substrates. Generally, C(sp^3)–H bonds are highly unreactive due to their thermal stability and low polar nature.

Seminal work on the dehydrogenative silylation of unactivated C(sp^3)–H bonds was reported by Berry *et al*.[9a] They found Ru(*p*-cymene)$(H)_2(SiEt_3)_2$ and Cp*Rh$(H)_2(SiEt_3)_2$ (Cp* =

η^5-C_5Me_5) complexes were effective for the dehydrogenative silylation of the C(sp^3)–H bond adjacent to a silicon atom. Since then, Tilley *et al*. reported that the rare-earth-metal complex, Cp^*_2ScH, could catalyze the dehydrogenative silylation of methane gas (150 atm) with H_2SiPh_2.[9b] These works clearly imply that π-coordinated six-electron-donor ligands are highly important to overcome this unfavorable thermodynamic transformation. Recently, Hartwig *et al.* disclosed the iridium-catalyzed hydroxyl group-directed dehydrogenative silylation of C(sp^3)–H bonds, in which the phenanthroline-based nitrogen ligand, 3,4,7,8-tetramethyl-1,10-phenanthroline was reported to be optimal.[9c] The utility of nitrogen ligands can be understood by considering the fact that nitrogen and oxygen containing heterocycles have been frequently employed as directing groups for dehydrogenative C–H bond silylation,[7c,7e,8,9f] since the seminal work on C–H bond functionalization by Murai *et al*.[10] In contrast, the use of phosphorus atom-based ligands on the dehydrogenative silylation of C(sp^3)–H bonds is limited to the reactions with $RhCl(CO)(PMe_3)_2$,[7a] $Ni(PEt_3)_4$,[7b] and $Ru(H)_2(CO)(PPh_3)_3$.[8a] Nevertheless, phosphorus ligands have been well investigated as one of the most important and effective ligands in modern organic synthesis.[11]

In 2013, we reported the rhodium-catalyzed synthesis of 2,3-dihydrobenzo[*b*]siloles via the intramolecular dehydrogenative silylation of 2-alkylphenylsilanes (eq 1).[9d] The combination of $[RhCl(cod)]_2$ and bidentate phosphines, was found to be effective to construct five-membered silicon-containing heterocycles. Although the silylation occurred even at less reactive secondary C(sp^3)–H bonds,[9a,d-f] the reaction required high temperature to overcome the low reactivity of the C–H bond, which detracts from its synthetic utility. Recently, Hartwig *et al*. reported that rhodium or iridium complexes with C_2-symmetric bisphosphines are useful for hydroarylation of olefins and dehydrogenative silylation of C(sp^2)–H bonds. These studies stimulated us to reexamine the reaction conditions of dehydrogenative silylation of C(sp^3)–H bonds carefully to improve the reaction efficiency. We envisioned that the precursors, 2-alkylphenylsilanes, are suitable to study the effect of phosphine ligands, since they do not contain any heteroatoms, such as nitrogen and oxygen, which potentially coordinate with a metal center.



(1)

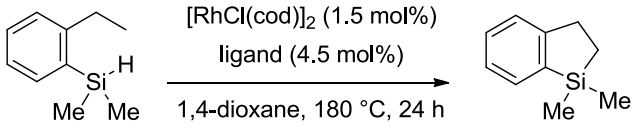
The present study describes the acceleration effect of phosphine ligands on the rhodium-catalyzed dehydrogenative silylation of C(sp^3)–H bonds. Bulky and electron-rich C_2-symmetric diphosphine ligands were found to be effective, and the reaction temperature was markedly decreased compared with our previous report.[9d] The proper choice of phosphine ligands also enabled the unprecedented enantioselective silylative desymmetrization as well as the dehydrogenative germylation of C(sp^3)–H bonds.

RESULTS AND DISCUSSION

The effect of phosphine ligands on the dehydrogenative silylation of 2-(dimethylsilyl)ethylbenzene **1a** was first studied with a catalytic amount of $[RhCl(cod)]_2$ in 1,4-dioxane at 180 ^oC (Table 1). The monodentate phosphine ligands, such as PPh_3, PCy_3, $PMePh_2$, and P(*o*-Tol)$_3$, were ineffective, and the yields of 2,3-dihydrobenzo[*b*]silole **2a** were less than 30% (entries 1-4).[12] In contrast, bidentate diphosphines were found to be effective (entries 5-8). Employing dppp and dppbz as ligands, **2a** was obtained in 70% yields (entries 6 and 8). On the other hand, nitrogen-based bidentate ligands, including TMEDA and 1,10-phenanthroline, previously reported as effective ligands for the iridium-catalyzed hydroxyl group-directed dehydrogenative silylation,[9c] were less reactive, with more than half of starting hydrosilane **1a** recovered (entries 9 and 10). Although the typical C_2-symmetric bisphosphines, BINAP and (*R*)-SEGPHOS, were less effective, the yield was increased to 72% when electron-rich and wide-bidentate phosphine, (*R*)-DTBM-SEGPHOS, was used as a ligand. The catalytic activity of other rhodium and iridium precursors, $[Rh(OMe)(cod)]_2$, $[IrCl(cod)]_2$, and $[Ir(OMe)(cod)]_2$, with (*R*)-DTBM-SEGPHOS was also tested and the

combination of $[RhCl(cod)]_2$ and (*R*)-DTBM-SEGPHOS was found to be the most effective.

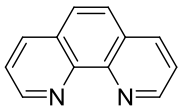
Table 1. Effect of ligands on the dehydrogenative silylation of the C(sp^3)–H bond



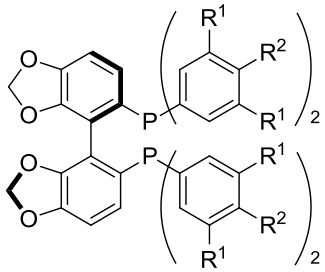
1a **2a**

entry	ligand	recov. of **1a**[a] / %	yield of **2a**[a] / %
1[b]	PPh_3	78	18
2[b]	PCy_3	17	19
3[b]	$PMePh_2$	18	10
4[b]	P(*o*-Tol)$_3$	28	29
5	dppe	0	50
6	dppp	11	70
7	dppf	0	44
8	dppbz	0	70
9	TMEDA	67	7
10	1,10-phenanthroline	44	29
11	*rac*-BINAP	0	38
12	(*R*)-SEGPHOS	54	23
13	(*R*)-DTBM-SEGPHOS	0	72

[a] Determined by ^{1}H NMR.
[b] Ligand 9 mol%.



1,10-phenanthroline

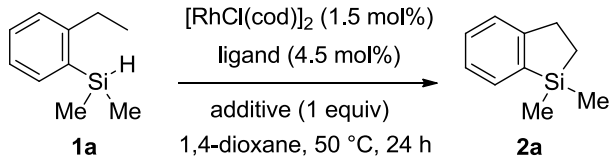


(*R*)-DTBM-SEGPHOS (R^1= ^{t}Bu, R^2 = MeO)
(*R*)-SEGPHOS (R^1 = R^2 = H)

Based on these results, we chose dppp, dppbz, and (*R*)-DTBM-SEGPHOS as ligands and studied other parameters further. We found the efficiency of the reaction was significantly improved by the addition of hydrogen acceptors, and the reaction temperature could be markedly decreased from 180 ^{o}C to 50 ^{o}C. For example, 2,3-dihydrobenzo[*b*]silole **2a** was isolated in 77% yield when 1 equiv of 3,3-dimethyl-1-butene was added under the reaction

conditions described in Table 1, entry 13 (Table 2, entry 1). On the other hand, the reaction did not occur at all even with 3,3-dimethyl-1-butene, when dppp or dppbz were employed as ligands at 50 °C (entries 2 and 3). Although norbornene can be used as a hydrogen acceptor, the yield was decreased to 40% due to the competitive hydrosilylation of **1a** with norbornene (entry 4). Other hydrogen acceptors, including 1,5-cyclooctadiene and 1,4-cyclohexadiene, were totally ineffective with most of **1a** recovered (entries 5 and 6). The expected 2,3-dihydrobenzo[*b*]silole **2a** was not obtained when the reaction was examined without adding any hydrogen acceptor (entry 7).

Table 2. Effect of hydrogen acceptors



1a **2a**

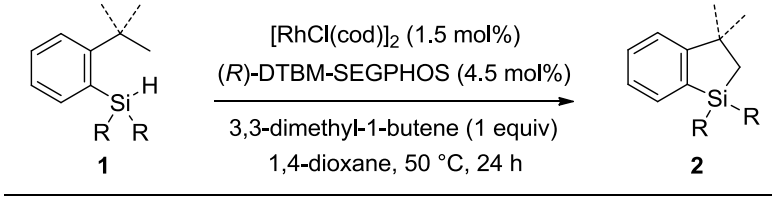
entry	ligand	additive	yield of **2a**[a] / %
1	(*R*)-DTBM-SEGPHOS	3,3-dimethyl-1-butene	81 (77)
2	dppp	3,3-dimethyl-1-butene	0
3	dppbz	3,3-dimethyl-1-butene	0
4	(*R*)-DTBM-SEGPHOS	norbornene	40
5	(*R*)-DTBM-SEGPHOS	1,5-cycloocatdiene	0
6	(*R*)-DTBM-SEGPHOS	1,4-cyclohexadiene	0
7	(*R*)-DTBM-SEGPHOS	———	0

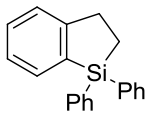
[a] Determined by ^{1}H NMR. Isolated yield is in parenthesis.

Next, several 2-alkylphenylsilanes were subjected to the current optimized reaction conditions (Table 3). Diphenylsilane **1b** was converted to the corresponding 2,3-dihydrobenzo[*b*]silole **2b** in 76% yield with a slightly higher temperature. Reactions with 2-ethylarylsilanes **1c** and **1d** having anisyl or naphthyl groups gave **2c** and **2d** in good yields even at 50 °C. C(sp^3)–H bonds of 2-*tert*-butylphenylsilane **1e** and 2-isopropylphenylsilane **1f** were also silylated effectively, affording the expected silacycles **2e** and **2f** in 90% and 83% yields, respectively. The effect of the substituents on the silicon

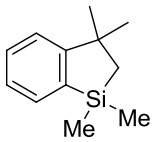
was also examined to find that diethyl and diphenylsilanes **1g** and **1h** could also be used as silicon sources.[13]

Table 3. Rhodium-catalyzed dehydrogenative silylation of **1** leading to 2,3-dihydro-1*H*-benzo[*b*]siloles **2**

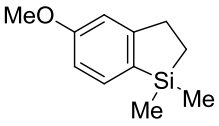




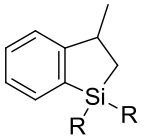
2b 76%[a]



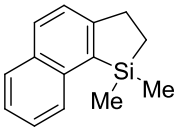
2e 90%[a]



2c 74%



R = Me **2f** 83%
Et **2g** 88%[a]
Ph **2h** 92%[b]

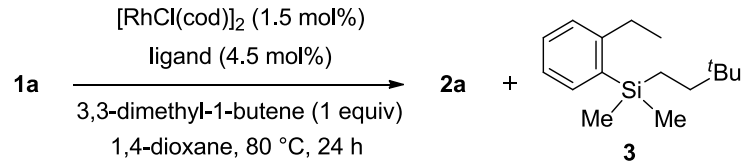


2d 83%

[a] At 80 °C. [b] At 65 °C.

To obtain insight into the ligand effects, the reaction of **1a** was reexamined in the presence of several phosphine ligands and 3,3-dimethyl-1-butene at 80 °C. Representative results are shown in Table 4. All the phosphine ligands except (*R*)-DTBM-SEGPHOS afforded a mixture of the desired 2,3-dihydrobenzo[*b*]silole **2a** and the hydrosilylated product **3** (entries 1-4). In fact, the combination of rhodium and phosphine ligands has been previously reported as an effective catalyst for the hydrosilylation of olefins.[14] In sharp contrast, formation of hydrosilylated product **3** was not observed, furnishing only **2a** in 83% yield, when (*R*)-DTBM-SEGPHOS was used with 3,3-dimethyl-1-butene (entry 5). This result clearly indicates that (*R*)-DTBM-SEGPHOS can selectively accelerate dehydrogenative silylation of C(sp^3)–H bonds even in the presence of olefins without producing hydrosilylated adducts.

Table 4. Competition between intramolecular dehydrogenative silylation and intermolecular hydrosilylation



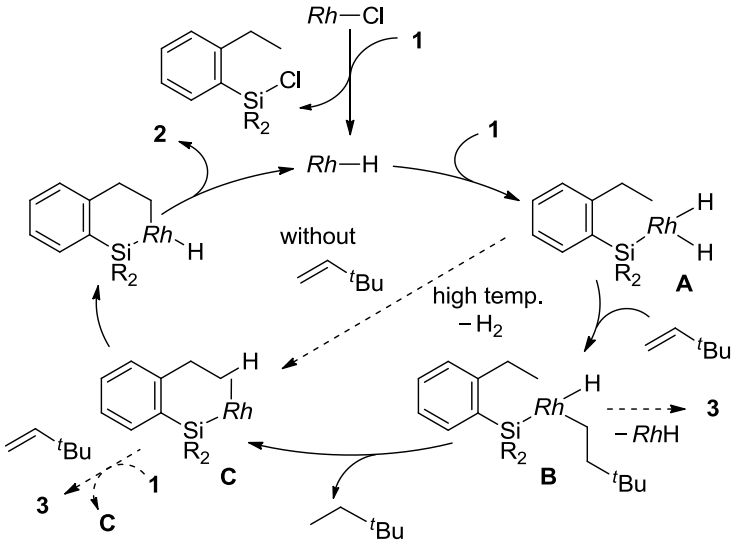
entry	ligand	yield of **2a**[a] / %	yield of **3**[a] / %
1[b]	PPh_3	42	15
2	dppp	39	6
3	dppbz	31	52 (50)
4	*rac*-BINAP	22	18
5	(*R*)-DTBM-SEGPHOS	83	0

[a] Determined by ^{1}H NMR. Isolated yield is shown in parenthesis. [b] Ligand 9.0 mol%.

Based on these observations, Scheme 1 presents a plausible mechanism for the current dehydrogenative silylation of unreactive C(sp^3)–H bonds. First, a rhodium hydride species is generated via the oxidative addition of hydrosilane **1** to the rhodium precatalyst followed by the reductive elimination of chlorosilane.[15] This rhodium hydride species is subsequently added to the Si–H bond of **1**, and the resulting intermediate **A** then reacts with 3,3-dimethyl-1-butene to form intermediate **B**. Reductive elimination of H and 3,3-(dimethyl)butyl groups on the rhodium center affords intermediate **C**, whereas that of silyl and 3,3-(dimethyl)butyl groups produces hydrosilylated product **3**. Because sterically bulky silyl and 3,3-(dimethyl)butyl groups tend to keep their distance from each other, the reductive elimination to form **C** might be energetically more favorable. In the absence of a hydrogen acceptor, 3,3-dimethyl-1-butene, intermediate **A** is directly converted to intermediate **C** via the reductive elimination of H_2. Generally, this step is thermodynamically unfavorable, and therefore requires additional heating to 180 ^oC as shown in Table 1 and our previous report.[9d] Rhodium silyl species **C** can potentially react with 3,3-dimethyl-1-butene to proceed hydrosilylation leading to **3**. However, the electron-rich rhodium center with a strongly electron-donating (*R*)-DTBM-SEGPHOS ligand should favor the oxidative addition of C(sp^3)–H bonds to the rhodium center over the hydrosilylation, which is usually promoted by the electron-deficient metal complex.[16] This is consistent with

the results shown in Table 4. Moreover, the intramolecular oxidative addition of C(sp^3)–H bonds to the rhodium center can be also facilitated by the steric effect of the ligand, due to the bulky (*R*)-DTBM-SEGPHOS overhanging outside. The subsequent reductive elimination provides 2,3-dihydrobenzo[*b*]silole **2** along with the regeneration of the rhodium hydride species.

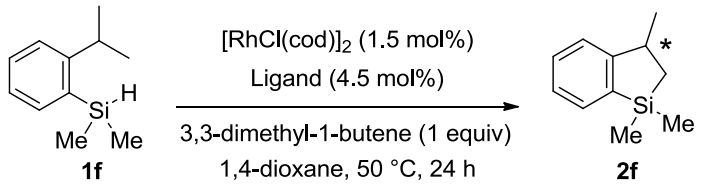
Scheme 1. Proposed reaction mechanism (phosphine ligand is omitted for clarity)

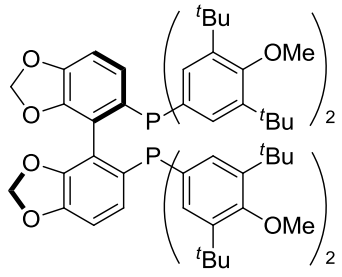


We further examined this unprecedented rhodium-catalyzed enantioselective desymmetrization of C(sp^3)–H bonds via dehydrogenative silylation (Table 5).[17,18] Treatment of 2-(isopropyl)silylbenzene **1f** with (*R*)-DTBM-SEGPHOS afforded the corresponding 2,3-dihydrobenzo[*b*]silole **2f** in 81% yield and 21% *ee*. Because enantiomers of **2f** were not separated by HPLC methods using a chiral stationary phase, the *ee* was determined by the HPLC analysis of diol **4**, which could be readily converted from **2f** by Tamao–Fleming oxidation (Scheme 2).[5] To increase the *ee*, the effect of other chiral diphosphine ligands was tested. Among the phosphines examined, high yield, as well as better enantioselectivity, was observed in the reaction catalyzed by the rhodium complex with (*R*)-DTBM-Garphos. These studies also confirm that ligands having electron-rich biaryl backbones were much more reactive, as revealed by a comparison of the reactions with (*R*)-DTBM-SEGPHOS and (*R*)-DTBM-Garphos to those with (*R*)-3,4,5-MeO-BIPHEP.

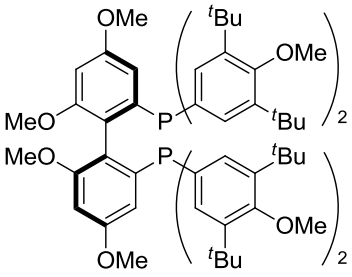
Although the enantioselective silylative cyclization of diethyl and diphenylsilanes **1g** and **1h** were also examined, *ee*'s were less than 10% (data not shown).

Table 5. Rhodium-catalyzed enantioselective C(sp^3)–H bond silylation with chiral diphosphines

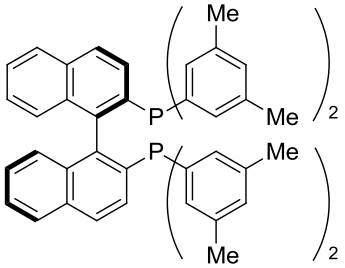




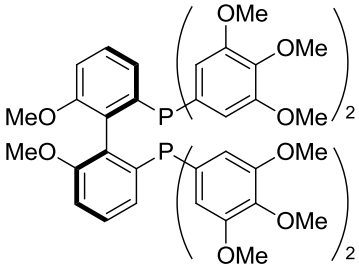
(*R*)-DTBM-SEGPHOS
81% (21% *ee*)[a]



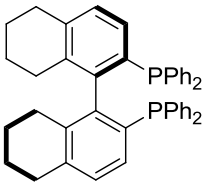
(*R*)-DTBM-Garphos
83% (37% *ee*)[a]



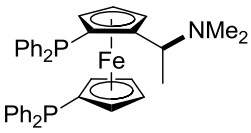
(*R*)-DM-BINAP[b]
61% (10% *ee*)[a]



(*R*)-3,4,5-MeO-MeOBIPHEP[b]
65% (4% *ee*)[a]



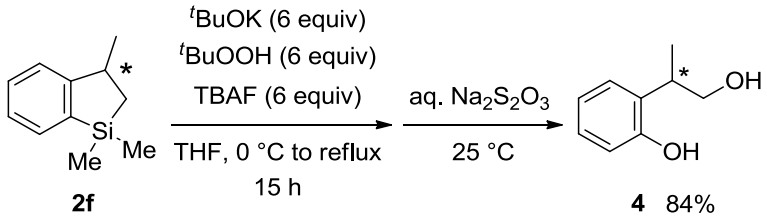
(*R*)-H_8-BINAP (100 °C)[b]
17%[c]



(*R*)-(*S*)-BPPFA[b]
20%[c]

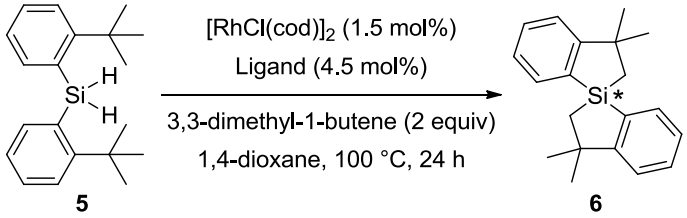
[a] Determined on a CHIRALPAK OD column with hexane / 2-propanol = 9 / 1 as the eluent. [b] At 100 °C. [c] Determined by ^{1}H NMR.

Scheme 2. Transformation of the 2,3-dihydrobenzo[*b*]silole **2f**



With (*R*)-DTBM-SEGPHOS as a ligand, dihydrosilane **5** provided 1,1'-spirosilabiindane **6** in 73% yield with 27% *ee* (Table 6, entry 1). This is a rare example of the catalytic construction of tetraorganosilicon stereocenters.[19] The reaction proceeded via the sequential twofold dehydrogenative silylation of C(sp^3)–H bonds. The chirality of the spirosilabiindane is thought to be determined at the first dehydrogenative cyclization. (*R*)-DTBM-Garphos, which was the best ligand in the enantioselective dehydrogenative silylation of **1f**, produced both lower yield and *ee*, although the starting dihydrosilane **5** was consumed completely (entry 2). Further screening of the catalyst revealed that changing the ligand to (*R*)-H_8-BINAP increased the *ee* up to 39%, albeit with only moderate yield of **6** (entry 3). Fortunately, the yield was improved to 75% without deterioration of the *ee* when the catalyst loading was increased (entry 4). As mentioned above, strongly electron-donating (*R*)-DTBM-SEGPHOS was the most effective for the silylative cyclization of 2-alkylphenylsilanes **1**. This is probably because oxidative addition of C(sp^3)–H bonds can be selectively promoted by the electron-rich phosphine ligand compared with the competitive hydrosilylation with 3,3-dimethyl-1-butene. In the reaction of **5**, however, (*R*)-H_8-BINAP also worked as an efficient promoter (entry 1 vs 3). The difference might be explained by considering the fact that the bulky 2-*tert*-butylphenyl group on the silicon atom prevented intermolecular hydrosilylation, and facilitated intramolecular C(sp^3)–H bond silylation selectively. In fact, no hydrosilylated product was observed under any of the conditions described in Table 6.

Table 6. Rhodium-catalyzed sequential two-fold dehydrogenative silylation of C(sp^3)–H bonds of **5** leading to 1,1'-spirosilabiindane **6**



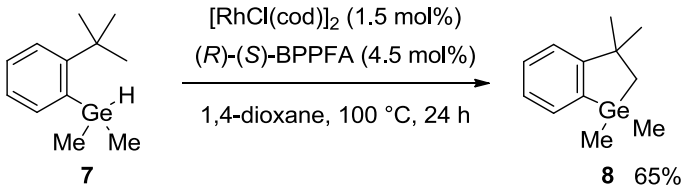
5 **6**

entry	Ligand	yield of **6** / %	*ee* of **6** / % ee[a]
1	(*R*)-DTBM-SEGPHOS	73	27
2	(*R*)-DTBM-Garphos	20	25
3	(*R*)-H_8-BINAP	54	39
4[b]	(*R*)-H_8-BINAP	75	40

[a] Determined on a CHIRALPAK OD column with hexane / 2-propanol = 9 / 1 as the eluent. [b] $[RhCl(cod)]_2$ 3 mol% and (*R*)-H_8-BINAP 9 mol%.

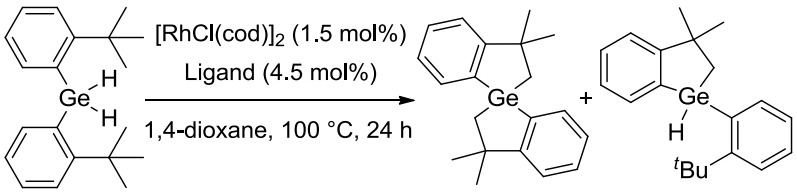
In contrast to the well-studied bond formation reactions between second- or third-row elements and hydrogens, much less attention has been paid to the dehydrogenative functionalization of C–H bonds involving bonds between the fourth-row elements and hydrogens.[20] The present successful result on the catalytic dehydrogenative silylation of C(sp^3)–H bonds further stimulated us to examine dehydrogenative germylation of unactivated C(sp^3)–H bonds. When (*R*)-DTBM-SEGPHOS was used as a ligand together with 3,3-dimethyl-1-butene at 100 ^oC, the yield of the expected 2,3-dihydrobenzo[*b*]germole **8** was low (15%) with the decomposition of the precursor 2-germyl-*tert*-butylbenzene **7**. After further screening of the phosphine ligands, (*R*)-(*S*)-BPPFA was found to be effective to afford **8** in 65% yield (Scheme 3).[21] It should be noteworthy that the reaction does not require a hydrogen acceptor, 3,3-dimethyl-1-butene.[22] This result is in good agreement with the previous our report on the dehydrogenative germylation of C(sp^2)–H bonds.[20b] Under the same reaction conditions, dihydrogermane **9** afforded 1,1'-spirogermabiindane **10** in 68% yield via the sequential twofold dehydrogenative germylation of C(sp^3)–H bonds (Table 7). In contrast, when (*R*)-DTBM-SEGPHOS was used in place of (*R*)-(*S*)-BPPFA, dehydrogenative germylation occurred only one time to furnish selectively 2,3-dihydrobenzo[*b*]germole **11** in 88% yield without forming 1,1'-spirogermabiindane **10**.[23]

Scheme 3. Rhodium-catalyzed synthesis of 2,3-dihydrobenzo[*b*]germole **8** via the dehydrogenative germylation of C(sp^3)–H bond



7 **8** 65%

Table 7. Rhodium-catalyzed dehydrogenative germylation of C(sp^3)–H bonds of dihydrogermane **9**



9 **10** **11**

entry	Ligand	yield of **10** / %	yield of **11** / %
1	(*R*)-DTBM-SEGPHOS	0	88
2	(*R*)-(*S*)-BPPFA	68	11

CONCLUSION

The work described herein is the acceleration effect of phosphine ligands for the dehydrogenative silylation of C(sp^3)–H bonds. Proper choice of diphosphine ligands and hydrogen acceptors is highly important. Among the phosphines examined, bulky and electron-donating (*R*)-DTBM-SEGPHOS was found to be the most effective to facilitate the dehydrogenative silylation of C(sp^3)–H bonds while suppressing the competitive hydrosilylation of a hydrogen acceptor, 3,3-dimethy-1-butene. By employing bulky and electron-rich C_2-symmetric diphosphine ligands, asymmetric desymmetrizations of 2-(isopropyl)silylbenzene or dihydrosilane via the silylative cyclization were achieved. Although the *ee* was low, this is the rare example of the asymmetric dehydrogenative

functionalization of C(sp^3)–H bonds. Furthermore, the use of (*R*)-(*S*)-BPPFA enabled the unprecedented catalytic germylation of C(sp^3)–H bonds with dehydrogenation. Expansion of these observations to enantioselective C(sp^3)–H and C(sp^2)–H bond functionalization is underway in our laboratory.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out in dry solvent under an argon atmosphere. 1,4-Dioxane was purchased from Wako Pure Chemical Industries and was dried by the usual methods, distilled, and degassed with an argon gas for 20 min before use. $[RhCl(cod)]_2$ was purchased from Kanto Chemical Co. (*R*)-DTBM-SEGPHOS, (*R*)-DTBM-Garphos, (*R*)-H_8-BINAP were purchased from Sigma-Aldrich. (*R*)-(*S*)-BPPFA was purchased from Tokyo Chemical Industry. Other chemicals obtained from commercial suppliers were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer (100 MHz for ^{13}C NMR) at 25 °C. Proton chemical shifts are reported with a residual solvent peak ($CDCl_3$ at δ7.26 ppm) as an internal standard. Carbon chemical shifts are reported relative to $CDCl_3$ at 77.00 ppm. The following abbreviations are used; br s: broad singlet, s: singlet, d: doublet, t: triplet, q: quartet, sept: septet, m: multiplet. The mass analyzer type used for High resolution mass spectrometry (HRMS) was orbitrap. Melting points were determined with a micromelting point apparatus without corrections. The analytical data for (2-alkylaryl)silanes **1a**-**1e** and **1h**, and 2,3-dihydro-1*H*-benzo[*b*]siloles **2a**-**2e** and **2h** have been reported previously by our group.[9d]

Procedure for the Preparation of (2-Alkylphenyl)silanes. To a mixture of magnesium turnings (243 mg, 10 mmol) and chlorosilane (10 mmol) in THF (10 mL) was added 2-alkylbromobenzene (8.0 mmol) at 25 ^{o}C. The mixture was refluxed for 1 h, and then quenched with saturated NH_4Cl solution and extracted with Et_2O for three times (20 mL × 3). The combined organic layer was dried over $MgSO_4$, and the organic solvent was removed

under reduced pressure. The residue was purified by flash column chromatography on silica gel with hexane as the eluent to give the corresponding (2-alkylphenyl)silanes.

2-(Dimethylsilyl)isopropylbenzene (**1f):** A colorless oil (87% yield, 1.24 g, 7.0 mmol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.39 (d, J = 4.0 Hz, 6H), 1.29 (d, J = 6.8 Hz, 6H), 3.19 (sept, J = 6.8 Hz, 1H), 4.58 (sept, J = 4.0 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H). ^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$): δ -2.7, 24.4, 33.6, 124.7, 125.3, 129.8, 134.6, 135.0, 154.9. IR (neat / cm^{-1}): 3057, 3007, 2962, 2927, 2868, 2119, 1589, 1473, 1458, 1382, 1363, 1249, 1120, 1070, 1029, 883, 837, 773, 763, 748, 731, 711, 644. HRMS (FAB^{+}): calcd for $C_{11}H_{18}Si$ ($[M]^{+}$) 178.1178; found. 178.1177.

2-(Diethylsilyl)isopropylbenzene (1g): A colorless oil (84% yield, 1.39 g, 6.7 mmol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83-0.89 (m, 4H), 1.00 (t, J = 7.4 Hz, 6H), 1.25 (d, J =7.2 Hz, 6H), 3.13 (sept, J = 7.2 Hz, 1H), 4.34 (quint, J = 3.2 Hz, 1H), 7.16 (t, J = 6.2 Hz, 1H), 7.29-7.38 (m, 2H), 7.44 (d, J = 7.6 Hz, 1H). ^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$): δ 4.2, 8.4, 24.4, 33.7, 124.7, 125.1, 129.7, 133.2, 135.4, 155.2. The analytical data match those reported in the literature.[23]

2-(Diphenylsilyl)isopropylbenzene (1h): A colorless oil (80% yield, 1.94 g, 6.4 mmol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (d, J = 6.8 Hz, 6H), 3.13 (sept, J = 6.8 Hz, 1H), 5.62 (s, 1H), 7.14 (t, J = 6.8 Hz, 1H), 7.31-7.43 (m, 9H), 7.54 (d, J = 6.8 Hz, 4H). ^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$): δ 24.1, 34.2, 125.1, 125.3, 127.9, 129.6, 130.6, 130.9, 133.8, 135.8, 137.0, 155.8. The analytical data match those reported in the literature.[24]

Di(2-*tert*-butylphenyl)silane (5): A colorless oil (51% yield, 1.21 g, 4.1 mmol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.48 (s, 18H), 5.52 (s, 2H), 7.12 (dt, *J* = 1.2, 7.6 Hz, 2H), 7.37 (dt, *J* = 1.2, 7.6 Hz, 2H), 7.42 (dd, *J* = 1.2, 7.6 Hz, 2H), 7.54 (dd, *J* = 1.2, 8.0 Hz, 2H). ^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$): δ 32.1, 37.5, 124.9, 125.8, 129.7, 130.8, 139.9, 157.2. IR (neat / cm^{-1}): 2986, 2965, 2904, 2869, 2176, 2138, 1586, 1472, 1430, 1363, 1247, 1127, 1116, 1057, 967, 880, 869, 764, 739, 613. HRMS (FAB^+): calcd for $C_{20}H_{28}Si$ ($[M]^+$) 296.1960; found. 296.1952.

Preparation of 2-(dimethylgermyl)-*tert*-butylbenzene 7. To a solution of 2-*tert*-butylbromobenzene (852 mg, 4.0 mmol) in Et_2O (5.0 mL) was added ^{n}BuLi (3.0 mL, 4.8 mmol, 1.6 M in hexane) dropwisely at -78 ^{o}C. After stirred for 10 mins, dichlorodimethylgermane (833 mg, 4.8 mmol) was added, and the mixture was gradually warmed to 25 ^{o}C. After stirring for overnight, the resultant mixture was added to a suspension of $LiAlH_4$ (304 mg, 8.0 mmol) in Et_2O (20 mL) at 25 ^{o}C, and stirred for further 6 h. The mixture was quenched with H_2O (3.0 mL), *aq*. NaOH (15 wt%, 3.0 mL), and H_2O (1.0 mL). The resultant suspension was filtered through celite, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with hexane as the eluent to afford the 2-(dimethylgermyl)-*tert*-butylbenzene **7** (94% yield, 891 mg, 3.8 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.50 (d, *J* = 3.2 Hz, 6H), 1.44 (s, 9H), 3.19 (sept, *J* = 3.2 Hz, 1H), 7.19 (dt, *J* = 0.8, 7.2 Hz, 1H), 7.28 (dt, *J* = 1.2, 8.0 Hz, 1H), 7.45 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 1H). ^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$): δ -1.6, 32.0, 37.1, 125.1, 125.2, 128.2, 135.4, 139.0, 155.5. IR (neat / cm^{-1}): 2966, 2912, 2060, 1469, 1465, 1437, 1424, 1395, 1363, 1249, 1237, 1112, 847, 833, 766, 732,

712, 597. HRMS (FAB$^+$): calcd for $C_{12}H_{20}Ge$ ([M]$^+$) 238.0777; found. 238.0762.

Di(2-*tert*-butylphenyl)germane (9): A colorless oil (56% yield, 766 mg, 2.2 mmol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.46 (s, 18H), 5.77 (s, 2H), 7.12 (dt, J = 0.8, 7.2 Hz, 2H), 7.32-7.38 (m, 4H), 7.55 (dt, J = 1.2, 7.8 Hz, 2H). ^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$): δ 32.0, 37.3, 125.2, 126.0, 129.0, 133.6, 138.8, 156.1. IR (neat / cm^{-1}): 2989, 2964, 2358, 2084, 2047, 1471, 1363, 889, 792, 762, 732. HRMS (FAB$^+$): calcd for $C_{20}H_{28}Ge$ ([M]$^+$) 342.1403; found. 342.1420.

General Procedure for Rhodium-Catalyzed Dehydrogenative Silylation and Germylation of Unactivated C(sp^3)–H Bonds. A flame dried sealed tube was charged with $[RhCl(cod)]_2$ (1.8 mg, 3.8 μmol), phosphines (11 μmol) and 1,4-dioxane (0.25 mL), and the resulting mixture was stirred at 25 ^{o}C for 30 min. 2-Alkylphenylsilanes or 2-alkylphenylgermane (0.25 mmol), 3,3-dimethyl-1-butene (21.0 mg, 0.25 mmol) was added to the mixture, and stirred at 50 or 100 ^{o}C for 24 h. The solvent was removed in vacuo and the residue was subjected to flash column chromatography on silica gel with hexane as an eluent to give the corresponding 2,3-dihydro-1*H*-benzo[*b*]siloles or 2,3-dihydro-1*H*-benzo[*b*]germole.

1,1,3-Trimethyl-2,3-dihydro-1*H*-benzo[*b*]silole (2f): A colorless oil (83% yield, 36.5 mg, 0.21 mmol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.26 (s, 3H), 0.34 (s, 3H), 0.67 (dd, J = 6.0, 14.8 Hz, 1H), 1.28 (dd, J = 6.8, 14.8 Hz, 1H), 1.34 (d, J = 6.8 Hz, 3H), 3.30-3.32 (m, 1H), 7.21 (t, J = 6.8 Hz, 1H), 7.28 (d, J = 6.8 Hz, 1H), 7.34 (t, J = 6.8 Hz, 1H), 7.51 (d, J = 6.8 Hz,

1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ -1.7, -0.6, 21.6, 25.2, 38.4, 124.6, 125.7, 129.4, 131.8, 139.7, 157.8. IR (neat / cm^{-1}): 3055, 2993, 2956, 2897, 1591, 1560, 1452, 1438, 1406, 1367, 1296, 1247, 1195, 1174, 1128, 1078, 1056, 1022, 997, 920, 844, 802, 769, 756, 723, 694, 644. HRMS (FAB^+): calcd for $C_{11}H_{16}Si$ ($[M]^+$) 176.1021; found. 176.1029. The *ee* of **2f** was determined by HPLC analysis after the derivatization leading to diol **4** by Tamao oxidation (see below for the detail).

1,1-Diethyl-3-methyl-2,3-dihydro-1*H*-benzo[*b*]silole (2g): A colorless oil (88% yield, 44.9 mg, 0.22 mmol); ^1H NMR (400 MHz, $CDCl_3$): δ 0.61 (dd, J = 6.0, 14.8 Hz, 1H), 0.74-0.84 (m, 4H), 0.93-1.04 (m, 6H), 1.29 (dd, J = 8.0, 14.8 Hz, 1H), 1.35 (d, J = 6.8 Hz, 3H), 3.29 (sext, J = 6.8 Hz, 1H), 7.19 (t, J = 7.2 Hz, 1H), 7.28-7.36 (m, 2H), 7.51 (d, J = 6.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 5.0, 5.6, 7.6, 7.7, 17.6, 25.2, 38.3, 124.6, 125.4, 129.3, 132.4, 137.8, 158.4. IR (neat / cm^{-1}): 3055, 2995, 2954, 2910, 2873, 1591, 1560, 1456, 1438, 1413, 1371, 1298, 1255, 1232, 1126, 1085, 1060, 1006, 956, 756, 682, 665, 624. HRMS (FAB^+): calcd for $C_{13}H_{20}Si$ ($[M]^+$) 204.1334; found. 204.1344.

3-Methyl-1,1-diphenyl-2,3-dihydro-1*H*-benzo[*b*]silole (2h): A colorless oil (92% yield, 69.1 mg, 0.23 mmol); ^1H NMR (400 MHz, $CDCl_3$): δ 1.17 (dd, J = 6.0, 14.8 Hz, 1H), 1.38 (d, J = 6.8 Hz, 3H), 1.79 (dd, J = 7.6, 14.8 Hz, 1H), 3.46 (sext, J = 6.8 Hz, 1H), 7.26-7.28 (m, 1H), 7.31-7.40 (m, 8H), 7.53-7.55 (m, 2H), 7.60-7.61 (m, 2H), 7.66 (d, J = 7.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 20.5, 24.9, 38.4, 124.8, 126.1, 127.8, 127.9, 129.5, 130.0, 133.1, 135.1, 135.2, 158.9. The analytical data match those reported in the literature.[12b]

2-(Dimethyl(3,3-dimethylbutyl)silyl)ethylbenzene (3): A colorless oil (50% yield with dppbz as a ligand (see Table 4, entry 3), 31.0 mg, 0.13 mmol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.31 (s, 6H), 0.72-0.77 (m, 2H), 0.85 (s, 9H), 1.15-1.19 (m, 2H), 1.25 (t, *J* = 7.4 Hz, 3H), 2.75 (q, *J* = 7.4 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H). ^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$): δ -1.5, 10.6, 16.4, 28.8, 28.9, 31.1, 37.9, 124.8, 127.9, 129.2, 134.7, 136.9, 150.1. IR (neat / cm^{-1}): 3057, 2954, 2866, 1589, 1541, 1508, 1390, 1363, 1249, 1219, 1159, 1128, 1083, 1060, 1041, 1006, 929, 885, 837, 819, 775, 754, 731, 682, 632. HRMS (FAB^+): calcd for $C_{16}H_{28}Si$ ($[M]^+$) 248.1960; found. 248.1967.

3,3-Dimethyl-1-sila-1,1-spirobiindane (6): A colorless oil (75% yield, 54.8 mg, 0.19 mmol); The *ee* was determined to 39% on a Daicel CHIRALPAK OD column with hexane as the eluent (flow rate = 0.50 mL/min). Retention time for the major enantiomer was 16 min, and that for the minor enantiomer was 13 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (d, *J* = 15.2 Hz, 2H), 1.34 (d, *J* = 15.2 Hz, 2H), 1.41 (s, 6H), 1.51 (s, 6H), 7.18-7.22 (m, 2H), 7.41-7.44 (m, 6H). ^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$): δ 29.2, 33.65, 33.69, 43.3, 123.3, 126.0, 130.3, 133.0, 135.5, 163.0. IR (neat / cm^{-1}): 3045, 3005, 2996, 2952, 2881, 2860, 1966, 1927, 1589, 1559, 1462, 1439, 1402, 1379, 1360, 1285, 1257, 1188, 1138, 1098, 1064, 1030, 946, 869, 856, 767, 734, 729, 708. HRMS (FAB^+): calcd for $C_{20}H_{24}Si$ ($[M]^+$) 292.1647; found. 292.1626.

1,1,3,3-Tetramethyl-2,3-dihydro-1*H*-benzo[*b*]germole (8): A colorless oil (65% yield, 38.5

mg, 0.16 mmol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.47 (s, 6H), 1.17 (s, 2H), 1.34 (s, 6H), 7.19-7.22 (m, 1H), 7.31-7.33 (m, 2H), 7.51 (d, J = 7.6 Hz, 1H). ^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$): δ -0.98, 30.6, 33.6, 44.4, 123.5, 125.8, 128.9, 132.1, 141.1, 159.4. IR (neat / cm^{-1}): 3065, 3053, 2956, 2907, 2862, 1587, 1464, 1439, 1411, 1379, 1360, 1283, 1255, 1235, 1187, 1123, 1056, 1030, 860, 833, 797, 766, 728, 672, 667, 601, 582, 552. HRMS (FAB^{+}): calcd for $C_{12}H_{19}Ge$ ([M+H]$^{+}$) 237.0699; found. 237.0694.

3,3-Dimethyl-1-germa-1,1-spirobiindane (10): A colorless solid (68% yield with (*R*)-(*S*)-BPPFA (Table 7, entry 2), 67.8 mg, 0.17 mmol); mp 83.4-83.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (s, 12H), 1.42 (d, J = 12.4 Hz, 2H), 1.51 (d, J = 12.4 Hz, 2H), 7.20 (dt, J = 1.6, 7.0 Hz, 2H), 7.38 (dt, J = 1.2, 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H). ^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$): δ 30.0, 33.3, 33.7, 43.8, 123.6, 126.0, 129.5, 132.8, 137.6, 160.3. IR (KBr / cm^{-1}): 3054, 2960, 2905, 1584, 1456, 1436, 1380, 1359, 1261, 1251, 1157, 1121, 1050, 1030, 771, 766, 745, 730, 670. HRMS (FAB^{+}): calcd for $C_{20}H_{25}Ge$ ([M+H]$^{+}$) 339.1168; found. 339.1158.

3,3-Dimethyl-1-(2-*tert*-butylphenyl)-2,3-dihydro-1*H*-benzo[*b*]germole (11): A colorless oil (88% yield with (*R*)-DTBM-SEGPHOS (Table 7, entry 1), 74.8 mg, 0.22 mmol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (s, 6H), 1.35 (d, J = 13.2 Hz, 1H), 1.36 (s, 9H), 1.52 (d, J = 13.2 Hz, 1H), 5.74 (d, J = 4.4 Hz, 1H), 6.92 (t, J = 7.2 Hz, 1H), 7.10-7.18 (m, 3H), 7.26 (d, J = 3.6 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 7.2 Hz, 1H). ^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$): δ 31.3, 32.3, 33.2, 33.5, 37.2, 44.3, 124.0, 125.2, 125.8, 126.2, 128.9, 129.4, 133.7, 134.6, 136.7, 137.0, 156.1, 160.6. IR (neat / cm^{-1}): 3052, 2956, 2864, 2054, 1586, 1464,

1439, 1395, 1380, 1362, 1282, 1249, 1189, 1171, 1125, 1112, 1052, 1031, 792, 764, 737, 724, 686, 668, 637. HRMS (FAB$^+$): calcd for $C_{20}H_{26}Ge$ ([M]$^+$) 340.1246; found 340.1251.

Derivatization of 2f for the Determination of the *ee*. To a solution of *t*-BuOK (135 mg, 1.2 mmol) in THF (1.4 mL) was added *tert*-butyl hydroperoxide (0.22 mL, 5.0~6.0 M in decane) at 0 ^oC, and stirred for 10 mins. A solution of **2f** (35.2 mg, 0.20 mmol) in THF (1.0 mL) and TBAF (1.2 mL, 1.0 M in THF) was added, and the mixture was stirred at 70 ^oC for 15 h. The resultant mixture was cooled down to 25 ^oC and $Na_2S_2O_3 \cdot 5H_2O$ (*ca.* 650 mg) in water (6.0 mL) was added. After stirred for 30 min, the reaction mixture was quenched with saturated NH_4Cl solution and extracted with Et_2O for three times (15 mL × 3). The combined organic layer was washed with 5 wt% of citric acid, and dried over $MgSO_4$. The organic solvent was removed under reduced pressure, and then the residue was purified by flash column chromatography on silica gel with hexane as the eluent to give 2-(2-hydroxy-1-methylethyl)phenol **4** (25.6 mg, 0.17 mmol, 84% yield) as a colorless oil. The *ee* was determined to 37% on a Daicel CHIRALPAK OD column with hexane / 2-propanol (*v* / *v* = 9 / 1) as the eluent (flow rate = 0.5 mL/min). Retention time for the major enantiomer was 21 min, and that for the minor enantiomer was 23 min. ^1H NMR (400 MHz, $CDCl_3$): δ 1.32 (d, *J* = 7.2 Hz, 3H), 3.22-3.28 (m, 1H), 3.74 (dd, *J* = 7.6, 9.6 Hz, 1H), 3.95 (dd, *J* = 3.6, 9.6 Hz, 1H), 6.88-6.91 (m, 2H), 7.11-7.16 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 15.6, 36.8, 69.4, 117.1, 120.7, 127.7, 127.8, 130.5, 154.8. The analytical data match those reported in the literature.[12b]

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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21. Effect of other ligands in the absence of 3,3-dimethyl-1-butene at 100 ^{o}C: dppp, 15%; dppbz, 19%; dppf, 47%; (*R*)-H_8-BINAP, 32%; (*R*)-H_8-BINAP, 35%. 2,3-Dihydrosbenzo[*b*]germole **8** was obtained in 42% yield at 80 ^{o}C with (*R*)-(*S*)-BPPFA.

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23. Effect of other ligands at 100 ^{o}C: (*R*)-DTBM-Garphos, 0% of **10** and 70% of **11**; (*R*)-H_8-BINAP, 20% of **10** and 30% of **11**; dppp, 51% of **10** and 33% of **11**; dppf, 5% of

10 and 80% of **11**; (*R*)-SEGPHOS, 6% of **10** and 78% of **11**. The *ee* of **10** and **11** were less than 10% with these ligands. For example, the *ee* of **11** was 3% (Table 7, entry 1) and **10** was 5% (entry 2), respectively.

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