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Ligand-Controlled, Complementary Stereoselectivity in the Platinum-Catalyzed Intramolecular Silaboration of Alkenes

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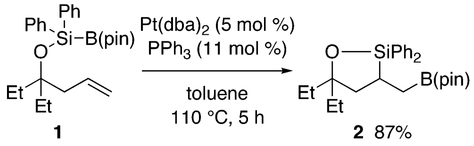
Silicon-tethered intramolecular reactions have received much attention in organic synthesis.[1] The merits of the silicon-tethered cyclizations involve an easy installation of tethered silyl moieties, an accelerated rate of reaction, and an easy disconnection of the tethered group for further transformation. Particular attention has been paid to the stereochemical aspects of silicon-tethered reactions. These tethered reactions often show high stereoselectivity because of the cyclic conformations, making these reactions attractive from a synthesis perspective. A high stereoselectivity has been achieved in transition metal-catalyzed intramolecular hydrosilylation,[2] bis-silylation,[3] and silylformylation.[4] It should be noted that these stereoselections mainly rely on the structure of the reactant, and only one of the two diastereomers is usually accessible via such a substrate-controlled stereoselection. It is desirable to explore stereoselective cyclizations that can provide either stereoisomer selectively, although such reactions are still not common.[5]

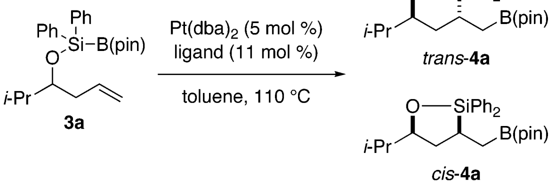
Platinum-catalyzed silaboration of alkenes offers a convenient access to compounds containing both boryl and silyl groups, which are potentially useful intermediates for the synthesis of acyclic compounds.[6,7] However, the silaboration of aliphatic alkenes suffers from the formation of significant amounts of the isomer, that is, 1-boryl-1-silylalkane, along with the major formation of 2-boryl-1-silylalkane. In the course of our study on the stereoselective construction of organic molecules via silaboration,[8] we were interested in developing the intramolecular silaboration of alkenes, which would allow introduction of boryl and silyl groups into the carbon−carbon double bond in both regio- and stereoselective manners. Herein, we describe an interesting stereochemical aspect of intramolecular silaboration of borylsilanyl homoallyl ethers catalyzed by a platinum catalyst.

A toluene solution of 4-(borylsiloxy)-4-ethyl-1-hexene (**1**)[9] was heated to 110 °C in the presence of $Pt(dba)_2$ (5 mol %) and PPh_3 (11 mol %) (eq 1). The intramolecular silaboration took place to afford the five-membered cyclic silyl ether **2** in 87% yield. Unlike the corresponding intermolecular reaction, no isomeric products were formed in appreciable amounts in the reaction. For an efficient reaction, it was found to be crucial to use a catalyst with a P/Pt ratio greater than 2:1. Use of a catalyst with a lower P/Pt ratio (1.1:1) or one that had no ligands resulted in a lower yield (57% and 8%, respectively) for the formation of **2**. As observed in the intermolecular reaction, $Pd(PPh_3)_4$, $Pd(dba)_2/2PPh_3$, and $Pd(dba)_2$ were totally inactive for the intramolecular silaboration.



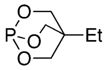
(1)

Table 1. Effects of Ligands on the Stereoselectivity in the Intramolecular Silaboration of **3a**[a]

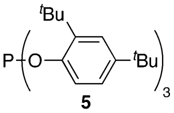


entry	ligand	yield (%)[b]	trans:cis[d]
	Phosphines		
1	PPh_3	69[c]	74:26
2	**$PCyPh_2$**	88[c]	**87:13**
3	PCy_2Ph	95	65:35
4	PCy_3	73	70:30
5	$PEtPh_2$	86	72:28
6	$PMePh_2$	73	47:53
7	$P(2\text{-biphenyl})Cy_2$	70	14:86
	Phosphites		
8	etpo	86	75:25
9	$P(OMe)_3$	70	68:32
10	$P(OEt)_3$	99	60:40
11	$P(O^iPr)_3$	65	56:44
12	$P(OPh)_3$	74	27:73
13	**5**	90[c]	**7:93**

[a] **3a** (0.24 mmol), $Pt(dba)_2$ (12 μmol), and ligand (26 μmol) were stirred in toluene (0.3 mL) at 110 °C. [b] ^{1}H NMR yield. [c] Isolated yield. [d] Determined by ^{1}H NMR and HPLC.



etpo



5

Borylsilanyl ether **3a**, prepared from secondary homoallylic alcohol,[9] was then subjected to intramolecular silaboration (Table 1). The reaction of **3a** successfully gave the cyclic product **4a** in 69% yield after a reaction time of 6 h (entry 1). The trans/cis ratio was found to be 74:26, which is in sharp contrast to the *cis*-selectivity observed in related transition metal-catalyzed intramolecular addition reactions, such as hydrosilylation,[2] bissilylation,[3] and silylformylation.[4] To optimize the reaction conditions, several phosphines were tested in the intramolecular silaboration of **3a** (entries 2−7). Like PPh_3, trans-selective cyclization proceeded in the reaction using phosphines such as $PCyPh_2$, PCy_2Ph, PCy_3, and $PEtPh_2$ (65:35−87:13, entries 2−5). We found that a platinum catalyst bearing $PCyPh_2$ ligands afforded the highest trans-selectivity (87:13, entry 2). However, it is interesting to note that a cis-selectivity was observed when the reaction was carried out in the presence of $P(2\text{-biphenyl})Cy_2$ (14:86, entry 7).

The reversal of the selectivity prompted us to examine results using other ligands, such as phosphites (entries 8−13). We found that a clear relationship existed between the bulkiness of the phosphite and the trans/cis selectivity. While a platinum catalyst

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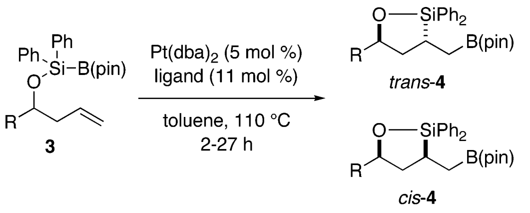
Table 2. Intramolecular Stereoselective Silaboration of Alkenes[a]

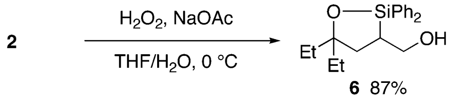


substrate	product	PCyPh$_2$ yield (%)[b]	PCyPh$_2$ trans:cis[c]	**5** yield (%)[b]	**5** trans:cis[c]
3b (R = Me)	**4b**	71[d]	81:19	93	7:93
3c (R = *i*-Bu)	**4c**	79	82:18	83	6:94
3d [R = Ph(CH$_2$)$_2$]	**4d**	76	84:16	82	8:92
3e (R = Ph)	**4e**	80	88:12	83	7:93
3f (R = *t*-Bu)	**4f**	96	92:8	85	6:94

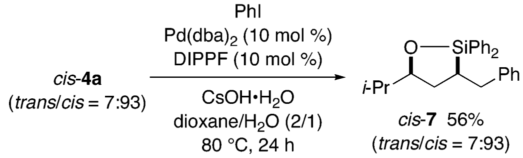
[a] **3** (0.24 mmol), Pt(dba)$_2$ (12 μmol), and ligand (26 μmol) were stirred in toluene (0.6 mL) at 110 °C for 8−27 h (PCyPh$_2$ as ligand) or for 2−12 h (**5** as ligand). [b] Isolated yield. [c] Determined by ^{1}H NMR, HPLC, and GC. [d] Isolated as 80% pure material.

bearing a sterically less-hindered phosphite ligand, such as etpo and P(OMe)$_3$, showed moderate trans preference (entries 8 and 9), the cis selectivity was extended using a catalyst having a more bulky ligand, such as P(OPh)$_3$ (entry 12). So far, we have found that sterically hindered **5** is the catalyst of choice for cis-selective silaboration (7:93, entry 13).

The optimized conditions using either the trans-selective Pt/PCyPh$_2$ catalyst or the cis-selective Pt/**5** catalyst were employed for the intramolecular silaboration of **3b**−**f** (Table 2). In the presence of the Pt/PCyPh$_2$ catalyst, the intramolecular silaboration of **3b**−**f** took place at 110 °C within a period of 27 h to give the corresponding trans products **4b**−**f** in 71−96% yields. The trans/cis ratios depended on the steric bulkiness of the R. On the other hand, reactions using the Pt/**5** catalyst proceeded faster than the Pt/PCyPh$_2$ catalyst system, affording the product in 82−93% yield with high cis-selectivities (trans/cis = 8:92−6:94). The stereoselectivity did not depend on the structure of **3**, in contrast to the Pt/PCyPh$_2$ catalyst system.



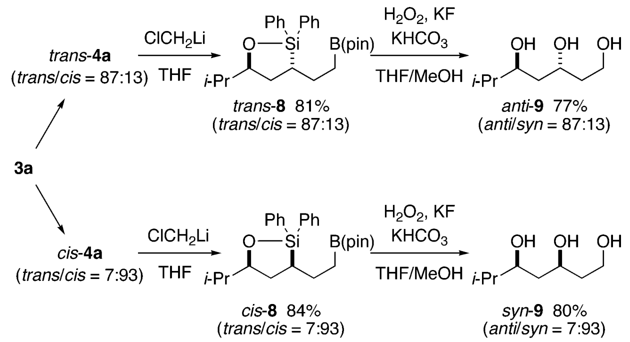
(2)



(3)

The present intramolecular silaboration reactions allow regioselective introduction of a boryl group onto the terminal carbon with the stereoselective formation of a five-membered oxasilacycle. The selective conversion of the boryl group into hydroxy and aryl groups was carried out (eqs 2 and 3).[10] The reaction of **2** with H$_2$O$_2$ under the basic conditions gave the alcohol **6** in 87% yield. The sp^2−sp^3 Suzuki−Miyaura cross-coupling of *cis*-**4a** with iodobenzene afforded the product *cis*-**7** in 56% yield by applying the Hartwig conditions using a palladium catalyst bearing 1,1′-bis(diisopropylphosphino)ferrocene (DIPPF).[11] These two reactions took place selectively at the terminal C−B bonds without cleavage of the oxasilacycles.

Scheme 1. Complementary Synthesis of a Pair of Diastereomers of 1,3,5-Triol **9**



Intramolecular silaboration was further utilized for the complementary synthesis of a pair of diastereomers of the 1,3,5-triol **9** (Scheme 1). The reaction of *trans*-**4a** with ClCH$_2$Li led to a one-carbon homologation,[12] giving **8** in 81% yield. Under Tamao conditions,[13] oxidation of both the C−B and C−Si bonds of **8** afforded the *anti*-1,3,5-triol **9** in 77% yield. The analogous homologation/oxidation of *cis*-**4a** afforded *syn*-**9** in high yield. These results demonstrate that either diastereomer is accessible from the same starting compound only by choosing the appropriate ligand in the platinum-catalyzed intramolecular silaboration.

In conclusion, we have demonstrated the Pt-catalyzed intramolecular silaboration of borylsilanyl homoallyl ethers, in which the diastereoselectivity of the products was highly dependent on the phosphorus ligand of the platinum catalyst. A mechanistic investigation and synthetic applications are now being carried out.

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Supporting Information Available: Experimental details and characterization data of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Bols, M.; Skrydstrup, T. *Chem. Rev.* **1995**, *95*, 1253. (b) Fensterbank, L.; Malacria, M.; Sieburth, S. McN. *Synthesis* **1997**, 813. (c) Gauthier, D. R., Jr.; Zandi, K. S.; Shea, K. J. *Tetrahedron* **1998**, *54*, 2289.

(2) (a) Tamao, K.; Nakajima, T.; Sumiya, R.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6090. (b) Tamao, K.; Nakagawa, Y.; Arai, H.; Higuchi, N.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 3712.

(3) (a) Murakami, M.; Suginome, M.; Fujimoto, K.; Nakamura, H.; Andersson, P. G.; Ito, Y. *J. Am. Chem. Soc.* **1993**, *115*, 6487. (b) Suginome, M.; Yamamoto, Y.; Fujii, K.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 9608.

(4) (a) Leighton, J. L.; Chapman, E. *J. Am. Chem. Soc.* **1997**, *119*, 12416. (b) Zacuto, M. J.; O'Malley, S. J.; Leighton, J. L. *Tetrahedron* **2003**, *59*, 8889.

(5) Curtis, N. R.; Holmes, A. B. *Tetrahedron Lett.* **1992**, *33*, 675.

(6) Suginome, M.; Nakamura, H.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2516.

(7) For recent reviews on bismetalation, see (a) Beletskaya, I.; Moberg, C. *Chem. Rev.* **2006**, *106*, 2320. (b) Suginome, M.; Ito, Y. *Chem. Rev.* **2000**, *100*, 3221.

(8) (a) Suginome, M.; Ito, Y. *J. Organomet. Chem.* **2003**, *680*, 43. For recent examples, see (b) Suginome, M.; Ohmura, T.; Miyake, Y.; Mitani, S.; Ito, Y.; Murakami, M. *J. Am. Chem. Soc.* **2003**, *125*, 11174. (c) Ohmura, T.; Suginome, M. *Org. Lett.* **2006**, *8*, 2503.

(9) The substrates **1** and **3** were synthesized by the reaction of homoallylic alcohols with (chlorodiphenylsilyl)pinacolborane in the presence of pyridine. See the Supporting Information for details.

(10) For a recent review on synthetic utilities of alkyl boronates, see Crudden, C. M.; Edwards, D. *Eur. J. Org. Chem.* **2003**, 4695.

(11) Lawrence, J. D.; Takahashi, M.; Bae, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 15334.

(12) Sadhu, K. M.; Matteson, D. S. *Organometallics* **1985**, *4*, 1687.

(13) Tamao, K.; Nakagawa, Y.; Ito, Y. *Org. Synth.* **1994**, *73*, 94.

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