Regio- and Stereochemistry on the Electrophilic Trapping of Allylic Samariums Generated by Reductive Cleavage of Allylic Ethers with $(C_5Me_5)_2Sm(thf)_n$

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The C−O bond of allylic benzyl ethers was selectively cleaved with $Cp^*_2Sm(thf)_n$ to give allylic samarium complexes in good yields. Facility of their bond fission has been found to be comparable to that of the corresponding propargylic ethers intermolecularly, but lower intramolecularly. Regio- and stereochemistry on the electrophilic trapping of the allylic complexes thus generated remarkably depended on the nature of the electrophiles. They reacted with carbonyl compounds exclusively from the most substituted terminus of the allylic moieties to yield blanched homoallylic alcohols with anti diasteroselectivity. On the other hand, trapping with silyl chlorides produced linear allylic silanes. Here, a plausible mechanism to account for the difference is proposed.

Introduction

Allylic organometallics are useful reagents in organic synthesis, and thus, extensive studies on their preparation, structure, and reactivity have been reported.[1] Of the allylic metals, allyllanthanides used for synthetic reactions can be generated in situ by various methods, which include halogen−metal exchange of allylic halides using samarium diiodide[2] or cerium amalgam,[3] reduction of allylic phosphates with samarium diiodide,[4] and transmetalation such as allylic lithium with cerium trichloride[5] and allylic palladium with samarium diiodide.[6] However, the structure of these reagents has not been confirmed unambiguously. On the other hand, well-defined allylic complexes with cyclopentadienyl (Cp) and pentamethylcyclopentadienyl (Cp*) ligands are prepared from alkenes with $[Cp^*_2LnH]$ (Ln = La, Nd)[7] or Cp^*_2Sm[8] and allylmagnesium bromide with Cp_2LnCl (Ln = Sm, Ho, Er).[9] However, their reactivity has been rarely investigated,[10] and synthesis and characterization of di- and trisubstituted allyl complexes have not been explored.[11]

In regard to regioselectivity on allylation of carbonyl compounds with allylic lanthanides, it has been concluded that the reaction takes place from the least substituted terminus to yield linear products.[2−6] Only one exception to this category is observed for the reaction with the Cp complexes in which blanched products are formed selectively.[10] Research addressing the stereoselectivity on their addition to a prochiral center has been limited.[4]

In previous papers, we have reported a selective C−O bond cleavage of allylic,[12] propargylic,[13] and vinylic ethers[14] with $Cp^*_2Sm(thf)_n$ leading to allyl-, allenyl-, and vinylsamarium complexes, respectively. Moreover, it has been found that allenylsamarium complexes thus generated exhibit a completely opposite regiochemistry in the reaction with electrophiles to the corresponding complexes prepared by transmetalation, as shown in Scheme 1.[13, 15]

These results prompted us to study further regio- and stereochemistry on the electrophilic trapping of allylic lanthanides. We report herein full details of the generation of allylic samarium complexes by reductive C−O bond cleavage and their structure and regio- and stereoselectivities.

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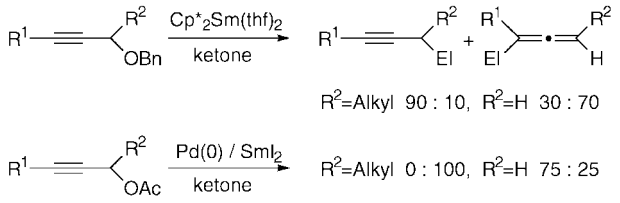
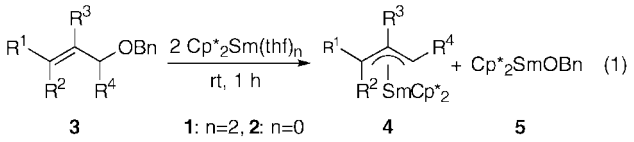
Scheme 1



Results and Discussion

Generation of Allylic Samarium Complexes. When allyl benzyl ether (**3a**) was added to a solution of 2 equiv of $Cp^*_2Sm(thf)_2$ (**1**) in cyclohexane at room temperature, the color of the mixture changed immediately to deep red. Hydrolysis of the mixture gave benzyl alcohol in 83% yield along with **3a** (10%) and Cp*H (>99%), but allyl alcohol and toluene were not formed at all. In the gas phase, propene was detected by GC. These results clearly indicate that the C−O bond between the allyl and benzyloxy moieties is cleaved exclusively. Monitored by NMR, allylsamarium **4a** and samarium benzyl oxide **5** were generated in the mixture in equimolar amounts (82%). The reaction with nonsolvated samarocene, Cp^*_2Sm (**2**), instead of **1**, gave **4a** and **5** quantitatively. Similar results were obtained in the reactions using other hydrocarbon solvents such as benzene, toluene, and hexane.

Various allylic samarium complexes **4** were generated in NMR tubes from the corresponding ethers **3** with **1** and **2** (eq 1 and Table 1). Monosubstituted allylic ethers



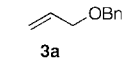
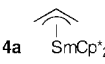
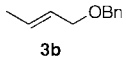
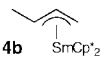
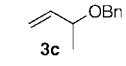
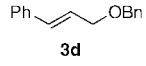
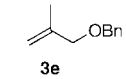
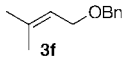
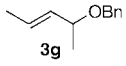
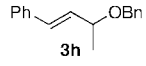
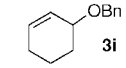
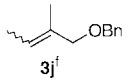
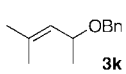
3b−**e** were readily converted to **4b**−**e** in high yields. Of the disubstituted ethers **3**, those with (*Z*)-substituents, **3f** and **3i**, changed to the complexes **4f** and **4i** at slower rates than those with (*E*)-substituents, **3g** and **3h**. In the reaction of **3j**, the (*E*)-isomer changed to **4j** smoothly, whereas the (*Z*)-isomer remained unchanged for 20 h. Trisubstituted ether **3k** did not react at room temperature, but elevated temperature promoted the reaction to afford **4k** in 36% yield, which was probably formed by a spontaneous isomerization of the expected trisubstituted allylic complex.

With respect to the leaving group, benzyl ether can be substituted by alkyl and allyl ethers. Thus, cinnamyl methyl ether and diallyl ether gave the complexes **4d** and **4a**, respectively, together with the corresponding alkoxides. However, reaction of crotyl acetate and crotyl methoxymethyl ether with **1** gave a complex mixture, in which **4b** was not detected by NMR.

Structures of the allylic samariums **4** were determined by ^{1}H NMR. Allylsamarium **4a**, generated with $Cp^*_2Sm(thf)_2$ (**1**), showed coalescent signals for both the four terminal protons and two C_5Me_5 at δ 5.70 and 1.16, respectively.[8] In contrast, when **4a** was prepared with Cp^*_2Sm (**2**), the anti and syn terminal protons appeared at δ 7.09 and 3.65, respectively, and two C_5Me_5 were separated at δ 1.24 and 1.04. Apparently, **4a** in the former reaction is a fluxional η^3-complex, caused by the coordination of THF, whereas a static η^3-complex is formed in the latter.[16] As with **4a**, structures of the complexes **4b**−**e**,**j**−**k** generated with **1** were determined to be fluxional and those with **2** to be static.[17] However, 1,3-disubstituted complex **4g** prepared by both reactions showed the same spectra, wherein two C_5Me_5 were split at δ 1.15 and 1.12. Thus, **4g** would exist as a static η^3-complex, since two allylic termini are secondary and unfavorable for η^1-bonding. Geometry of the terminal substituents was determined to be syn by the fact that trapping of **4** with electrophiles gave (*E*)-olefinic products selectively (vide infra). In contrast, the spectra of **4f** and **4i** were different from those of others: signals for the central protons of the allylic moieties at ca. δ 15 were shifted to higher field. Therefore, they are likely to be η^1-complexes.[7]

The present reductive cleavage of allylic ethers provides some advantage for the generation of allylic lanthanides, despite contamination of the alkoxides. For

Table 1. Generation of Allylic Samariums 4 from Benzyl Ethers 3 with Samarocenes 1 and 2[a]

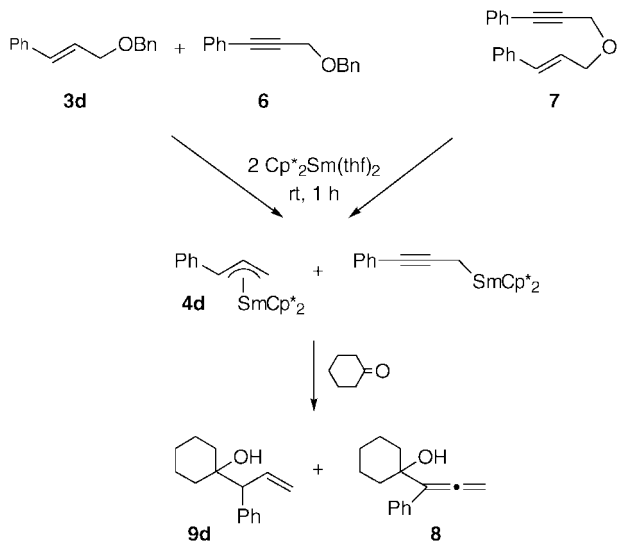
run	allylic benzyl ether	solvent[b]	allylic samarium	yield (%)[c,d]
1	 **3a**	A	 **4a**	82 (quant)
2	 **3b**	A	 **4b**	86 (quant)
3	 **3c**	A	**4b**	80
4	 **3d**	A	 **4d**	95 (quant)
5	 **3e**	B	 **4e**	86 (quant)
6	 **3f**	B	 **4f**	80[e]
7	 **3g**	A	 **4g**	82 (quant)
8	 **3h**	B	 **4h**	91
9	 **3i**	B	 **4i**	50[e]
10	 **3j**[f]	B	 **4j**	42[e]
11	 **3k**	B	 **4k**	36[g]

[a] NMR tube reaction. [b] (A) C_6D_{12}; (B) C_6D_6. [c] Yield with **1**, determined on the basis of the ratio of **4** to **3**. [d] The numbers in parentheses are the yields with **2** in C_6D_6, except for **3g** (C_6D_{12}). [e] Measured after stirring for 20 h. [f] *E*:*Z* = 45:55. [g] Measured after stirring for 5 h at 80 °C.

(16) It has been reported that a static $Cp^*_2Sm(\eta^3\text{-}C_3H_5)$ is changed to a fluxional complex by addition of THF, which occurs through a THF adduct; see ref 8.

(17) Since ^{1}H NMR spectra of **4a**,**b**,**d** are similar to those of the monomeric complexes reported, they seem to be monomeric and separated from benzyl oxide **5** in solution; see ref 8.

Scheme 2

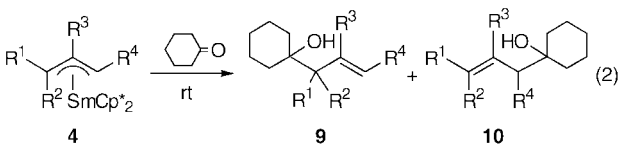


88% (51 : 49) from a 1:1 mixture of **3d** + **6**
94% (18 : 82) from **7**

example, this reaction produces the allylic complexes **4** cleanly, since the starting ethers **3** are unreactive to **4**. On the other hand, reactions of allyl and methallyl chlorides with **1** and **2** give **4a** and **4e** in lower yields than Cp^*_2SmCl or untractable mixtures under the reaction conditions. Moreover, the complexes having various substituent patterns can be prepared from readily available allylic ethers, owing to the regiospecific C−O bond fission. These results exhibit a marked contrast to the reductive cleavage of vinylic ethers, in which the regioselectivity depends on the substituents: benzyl vinyl ethers leading to enolates and tolyl species and methyl vinyl ethers to vinylic samariums and methoxide.[14]

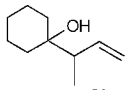
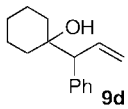
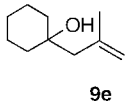
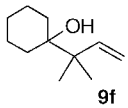
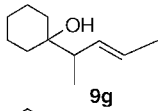
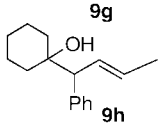
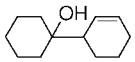
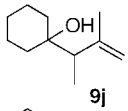
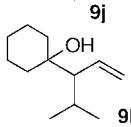
The facility of the C−O bond cleavage of allylic ethers was compared with that of propargylic ethers (Scheme 2). Treatment of a mixture of allylic benzyl ether **3d** and propargylic benzyl ether **6** with **1** (1:1:2), followed by trapping with cyclohexanone, gave homoallylic alcohol **9d** and allenyl alcohol **8** in 88% total yield with a 51:49 ratio. The products **9d** and **8** were derived from **3d** and **6** via allylic and propargylic samarium complexes, respectively (vide infra). In contrast, the two alcohols **9d** and **8** were obtained in 94% total yield with an 18:82 ratio by the reaction of allyl propargyl ether **7**. The intramolecular reaction suggests that the propargylic C−O bond is cleaved four times faster than the allylic one. The result of the intermolecular reaction can be interpreted by assuming that the ratio is determined by the relative coordination rate of the two ethers **3d** and **6** to the samarocene **1**, not by the facility of their C−O bond fission. That is, this process is irreversible and the two rates are nearly equal.

Electrophilic Trapping of Allylic Samarium Complexes. Allylic samariums **4**, generated in situ from **3** and **1** in toluene, were trapped with cyclohexanone in order to study their regiochemistry (eq 2 and Table 2).



(2)

Table 2. Reaction of Allylic Samariums 4 with Cyclohexanone[a]

run	allylic samarium	time (h)	product	yield (%)[b]
1	**4b**[c]	20	 **9b**	99
2	**4b**[d]	20	**9b**	99
3	**4d**	20	 **9d**	99
4	**4e**	12	 **9e**	60[e]
5	**4f**	20	 **9f**	47
6	**4g**	20	 **9g**	65
7	**4h**	3	 **9h**	82
8	**4i**	6	 **9i**	38 (78)
9	**4j**	6	 **9j**	40 (89)
10	**4k**	3	 **9k**	21 (58)

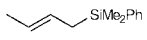
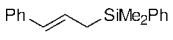
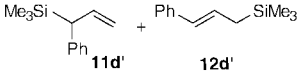
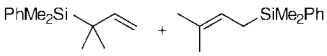
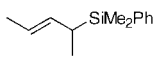
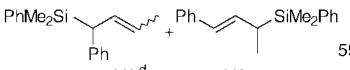
[a] Two equivalents of cyclohexanone were used. [b] Isolated yields. Conversion yield is given in parentheses. [c] Generated from **3b**. [d] Generated from **3c**. [e] One equivalent of cyclohexanone was used.

All reactions, except for runs 4, 6, and 8, took place from the most substituted termini of the allylic moieties to give homoallylic alcohols **9** exclusively, and the other regioisomers **10** were not detected. In addition, the olefinic geometry of the products **9g** and **9h** was *E*. High selectivity was particularly demonstrated by the reaction of **4h**, in which only one isomer **9h**, of the four possible products, was formed in 82% yield.

Interestingly, the present regioselectivity is opposite to that observed for allylic lanthanides generated by transmetalation[5,6b] and halogen−metal exchange,[2a,3a] wherein ratios of the least to the most substituted homoallylic alcohols were about 100:0 and 60:40, respectively.[18] In addition, a 1,3-disubstituted allylic species corresponding to **4h** was reported to yield the other regioisomer **10h** exclusively.[6b] The difference is not caused by the solvent effect, because the reaction of **4d**

(18) Allylic samariums, generated from allylic phosphates with SmI_2, showed no definite regio- and stereospecificity in the reaction with carbonyl compounds; see: ref 4.

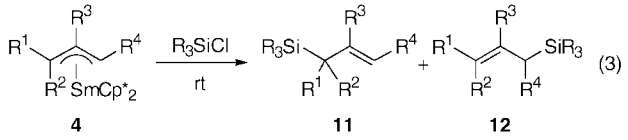
Table 3. Reaction of Allylic Samariums 4 with Dimethylphenylsilyl and Trimethylsilyl Chlorides

run	allylic samarium	product	yield (%)[a]	ratio of **11** : **12**
1	**4b**[b]	 **12b**	73	0 : 100
2	**4d**	 **12d**	63	0 : 100
3	**4d**	 **11d′** **12d′**	59	16 : 84
4	**4f**	 **11f** **12f**	66 (60)[c]	25 : 75 (10 : 90)[c]
5	**4g**	 **12g**	40	
6	**4h**	 **11h**[d] **12h**	59 (32)[e] (54)[c]	42 : 58 (41 : 59)[e] (62 : 38)[c]

[a] Total isolated yield. [b] Generated from **3b**. [c] The reaction was carried out at −78 °C for 6 h. [d] *E*:*Z* = 75:25 at 80 °C, 79:21 at room temperature, and 100:0 at −78 °C. [e] The reaction was carried out at 80 °C for 3 h.

(run 3 in Table 2) in THF, a common solvent used for other methods, gave **9d** as a sole product in 73% yield. There is also a possibility that samarium benzyl oxide **5**, generated together with **4** by this method, may alter the regioselectivity. Thus, cinnamylsamarium **4d** without **5** was prepared by the reaction of allylbenzene with **1** in toluene[8] and trapped with cyclohexanone. However, only **9d** was obtained in 35% yield along with an aldol product, 2-(1-cyclohexenyl)cyclohexanone (30%).

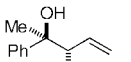
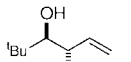
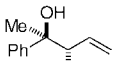
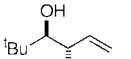
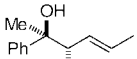
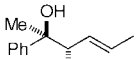
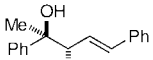
Regioselectivity on the reaction of allylic samariums **4** with dimethylphenylsilyl and trimethylsilyl chlorides was investigated (eq 3), and these results are summarized in Table 3. Crotylsamarium **4b** reacted with dimethylphe-



(3)

nylsilyl chloride exclusively from the least substituted terminus to give linear crotylsilane **12b** in 73% yield. Similarly, only linear product **12d** was formed in the reaction of cinnamylsamarium **4d** with $PhMe_2SiCl$ (Table 3, run 2). Substitution of the trapping agent with Me_3SiCl decreased the selectivity to yield a mixture of **11d′** and **12d′** in a ratio of 16:84 (Table 3, run 3). The regioselectivity of **4f** was 25:75 at room temperature and 10:90 at −78 °C, which was contrary to the expectation that competition between tertiary and primary termini of the allylic moiety of **4f** should exhibit higher selectivity than that between the secondary and primary termini of **4b** and **4d**. In the case of **4h**, the selectivity was very low in contrast to the reaction with cyclohexanone, and it depended on the reaction temperature slightly. The olefinic geometry of the products **11** and **12** was exclusively *E* as mentioned above, except for **11h**.

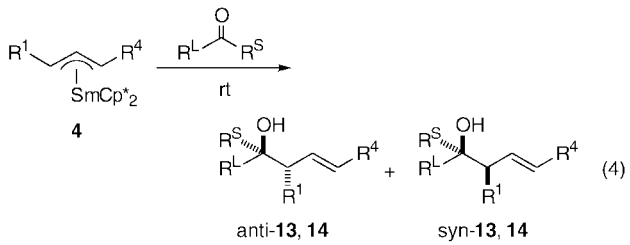
Table 4. Reaction of Allylic Samariums 4 with Acetophenone and Pivalaldehyde

run	allylic samarium	carbonyl compound[a]	major product	yield (%)[b]	ratio of anti : syn
1	**4b**	A	 **13b**	99	79 : 21
2	**4b**	B	 **14b**	83	96 : 4
3	**4d**	A	 **13d**	96	85 : 15
4	**4d**	B	 **14d**	98	100 : 0
5	**4g**	A	 **13g**	76	59 : 41
6	**4h**	A	 **13h**  **13h′**	65[c] 15[c]	85 : 15 66 : 34

[a] (A) Acetophenone; (B) pivalaldehyde. [b] Total isolated yield. [c] GC yields of **13h** and **13h′** were 73% and 16%, respectively.

As a whole, regioselectivity on the trapping with the silyl chlorides is reversed to that with cyclohexanone, giving rise to the least substituted allylic silanes **12** predominantly. This unique duality seems to be induced not only by the Cp* ligand but also by the allylic structure itself, since allylsamariums generated from allylic palladium and SmI_2[6b,19] and allenylsamariums having a Cp* ligand[13] exhibit the same regioselectivity, respectively, in both reactions with ketones and silyl chlorides.

Next, stereoselectivity in the reaction of allylic samariums **4** with acetophenone and pivalaldehyde was investigated (eq 4, Table 4). Reaction with the ketone gave



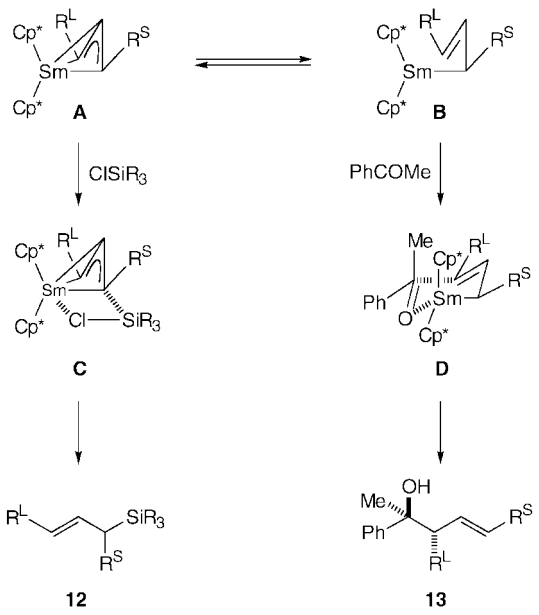
(4)

homoallylic alcohols **13** in good yields with moderate selectivity in favor of the anti isomer (ca 80:20), except for **13g**.[18] Better anti selectivity was obtained with the aldehyde (Table 4, runs 2 and 4). Of course, regiochemistry here was identical to that with cyclohexanone. But in the reaction of **4h**, two regioisomers **13h** and **13h′** were formed in a ratio of 82:18 (Table 4, run 6).

Regio- and stereochemistry of allylic samariums **4** would be accounted for as follows (Scheme 3). The complexes **4**, generated by the treatment with $Cp^*_2Sm(thf)_2$ (**1**), are fluxional, that is, in equilibrium between

(19) Sugino, A.; Hanamoto, T.; Inanaga, J. 12th Annual Meeting of the Rare Earth Society of Japan, Tokyo, May 18−19, 1995, Abstract 2PA-40.

Scheme 3



η^3- and η^1-complexes **A** and **B**. When ketones and aldehydes are used as trapping agents, the equilibrium shifts to the η^1-complexes **B**, since the carbonyl oxygen coordinates to samarium metal more tightly than THF.[20] In this case, the least substituted η^1-complexes could be formed preferentially. Therefore, C−C bond formation takes place from the most substituted terminus of the allylic moieties via six-membered transition state **D**, which leads to the blanched homoallylic alcohols **13** with anti diastereoselectivity.

In contrast to the carbonyl compounds, silyl chlorides are a less coordinating electrophile and would react directly with the η^3-complexes **A** via four-membered transition state **C**. Accordingly, silyl chlorides approach the least substituted terminus of the allylic system to yield the linear allylic silanes **12** selectively. Thus, regioselectivity with less bulky trimethylsilyl chloride was lower than that with dimethylphenylsilyl chloride (Table 3, runs 2 and 3). Alternatively, the reaction of **B** via the four-membered transition state may yield **12**. Although the two mechanisms cannot be distinguished clearly, the former process seems to be more likely, because the static complex **4d**, prepared from **3d** and Cp^*_2Sm (**2**), gave the same results as did the fluxional complex **4d** (Table 3, run 2). The decreased selectivity of **4f** on the trapping with $PhMe_2SiCl$ (Table 3, run 4), compared to **4b** and **4d**, could be attributed to its structure, which presumably exists as an η^1-complex based on NMR spectra. Thus, minor regioisomer **11f** would be formed by S_E2' reaction.

Although there is no mechanistic proposal for the predominant formation of linear homoallylic alcohols from allylsamariums prepared by other methods,[2,3,5,6] these results could be rationalized by the four-membered transition state. In fact, recent ab initio molecular orbital study on the reaction of $Cp_2Sm(\eta^3\text{-}C_3H_5)$ with formaldehyde demonstrates that the four-membered transition state is more favorable than the six-membered one.[21] Deviation of our results with carbonyl compounds from these calculations would be caused by the steric factor, which is highly disadvantageous to the four-membered transition state.

In summary, reductive C−O bond cleavage of allylic ethers with $Cp^*_2Sm(thf)_n$ provides a convenient method for the selective generation of substituted allylic samarium complexes. Since this reaction takes place cleanly, structure of the complexes is easily confirmed by NMR. The complexes thus generated react with various electrophiles in good yields. However, their regiochemistry has been proved to be opposite to that previously reported and dependent on the kind of electrophile: the most substituted (blanched) homoallylic alcohols with carbonyl compounds and the least substituted (linear) allylsilanes with silyl chlorides are obtained selectively. Anti diastereoselectivity is observed in the former reaction. These results can be explained by six- and four-membered transition states, respectively.

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded at 270 and 67 MHz, respectively. IR spectra were taken on a FT-IR spectrophotometer. Mass spectra were obtained at 70 eV on a GC−MS apparatus. Microanalyses were performed at our analytical laboratory. All reactions were carried out under argon using standard Schlenk and vacuum line techniques. All solvents (THF, cyclohexane, benzene, and toluene) were distilled from sodium benzophenone ketyl, stored over sodium metal, and degassed by trap-to-trap distillation just before use. Other materials were also degassed and stored under argon after purification. $(C_5Me_5)_2Sm(thf)_2$ (**1**)[22] and $(C_5Me_5)_2Sm$ (**2**)[23] were synthesized by the reported methods. Allylic benzyl ethers **3** were prepared from the corresponding sodium or lithium allylic alkoxides and benzyl bromide.

Reaction of Allyl Benzyl Ether (3a) with 1. The ether **3a** (52 mg, 0.35 mmol) was added to a solution of **1** (392 mg, 0.69 mmol) in cyclohexane (4 mL). The mixture was stirred for 1 h at room temperature and quenched with 2 M HCl (0.5 mL). Propene was identified in the gas phase of the reaction vessel by GC analyses using authentic gas samples. The liquid phase was extracted with ether, washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Benzyl alcohol (83% yield), **3a** (10%), and Cp*H (>99%) were detected by GC in the crude mixture.

NMR Tube Reaction of Allylic Benzyl Ethers 3 with $Cp^*_2Sm(thf)_2$ (1) and Cp^*_2Sm (2). The samarocene **1** or **2** (2.0 equiv) was placed in an NMR tube and dissolved in cyclohexane-d_{12} or benzene-d_6 (0.2 M). Then, the ether **3** was added to the solution by microsyringe. After the mixture was cooled to −78 °C, the sample tube was sealed under argon. The reaction was monitored by ^{1}H NMR at room temperature, and the result measured after 1 h is shown in Table 1, unless otherwise noted. Yield was determined by integration ratio of the product **4** to the substrate **3** remained.

$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$ (4a)[8] from 1: ^{1}H NMR(C_6D_{12}) δ 1.16 (30H, s), 5.70 (4H, br s), 15.19 (1H, br s); ^{13}C NMR(C_6D_{12}) δ 16.6 (C_5Me_5), 20.9 (CH_2), 116.2 (C_5Me_5), 178.0 (CH). **4a from 2:** ^{1}H NMR(C_6D_6) δ 1.04 (15H, s), 1.24 (15H, s), 3.65 (2H, br s), 7.09 (2H, br s), 15.57 (1H, br s); ^{13}C NMR(C_6D_6) δ 15.8 (C_5Me_5), 16.1 (C_5Me_5), 20.1 (CH_2), 114.7 (C_5Me_5), 116.6 (C_5Me_5), 176.6 (CH).

(20) Although static allylsamariums **4**, generated with **2**, have not been used in the trapping reactions with carbonyl compounds, they would provide similar results as fluxional complexes, since they can change readily to η^1-complexes **B** by coordination of the electrophiles.

(21) Koga, N. 13th Annual Meeting of the Rare Earth Society of Japan, Kyoto, May 23−24, 1996, Abstract 23.

(22) Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941−946.

(23) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4270−4272.

$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHMe)$ (4b)[8] from 1: ^{1}H NMR (C_6D_{12}) δ −4.61 (3H, br s), 1.14 (30H, s), 6.08 (1H, br s), 9.16 (2H, br s), 14.61 (1H, br s). **4b from 2:** ^{1}H NMR(C_6D_6) δ −4.60 (3H, br s), 1.15 (15H, s), 1.24 (15H, s), 6.12 (1H, br s), 7.07 (1H, br s), 10.75 (1H, br s), 14.66 (1H, br s).

$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHPh)$ (4d)[8] from 1: ^{1}H NMR (C_6D_{12}) δ 1.05 (30H, s), 3.72 (2H, d, J = 7.3 Hz), 5.59 (2H, t, J = 7.6 Hz), 6.25 (1H, br s), 6.30 (1H, t, J = 7.3 Hz), 7.96 (2H, br s), 15.08 (1H, br s). **4d from 2:** ^{1}H NMR(C_6D_6) δ 0.76 (15H, s), 1.26 (15H, s), 3.99 (2H, d, J = 7.3 Hz), 5.39 (1H, br s), 5.76 (2H, t, J = 7.6 Hz), 6.48 (1H, t, J = 7.3 Hz), 6.61 (1H, br s), 10.10 (1H, br s), 15.52 (1H, br s).

$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CMeCH_2)$ (4e) from 1: ^{1}H NMR(C_6D_6) δ 1.12 (30H, s), 5.07 (3H, s), 5.19 (4H, br s). **4e from 2:** ^{1}H NMR(C_6D_6) δ 1.13 (15H, s), 1.21 (15H, s), 3.67 (2H, br s), 5.23 (3H, s), 6.75 (2H, br s).

$(C_5Me_5)_2Sm(CH_2CHCMe_2)$ (4f) from 1: ^{1}H NMR(C_6D_6) δ 0.12 (3H, s), 0.31 (3H, s), 1.50 (30H, s), 8.01 (1H, br s), 9.32 (2H, br s).

$(C_5Me_5)_2Sm(\eta^3\text{-}MeCHCHCHMe)$ (4g) from 1 and 2: ^{1}H NMR (C_6D_{12}) δ −3.10 (6H, br s), 1.12 (15H, s), 1.15 (15H, s), 9.16 (2H, br s), 15.14 (1H, br s).

$(C_5Me_5)_2Sm(\eta^3\text{-}MeCHCHCHPh$ (4h) from 1: ^{1}H NMR (C_6D_6) δ −3.54 (3H, br s), 0.79 (15H, s), 1.15 (15H, s), 5.04 (2H, d, J = 7.3 Hz), 6.14 (2H, t, J = 7.3 Hz), 6.83 (1H, t, J = 7.3 Hz), 9.00 (1H, br s), 10.05 (1H, br s), 15.42 (1H, br s).

$(C_5Me_5)_2Sm$(cyclohexenyl) (4i) from 1: ^{1}H NMR(C_6D_6) δ 1.41 (15H, s), 1.86 (15H, s), 5.73 (2H, br s), 10.51 (1H, br s). Other methylene protons could not be assigned.

$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CMeCHMe)$ (4j) from 1: ^{1}H NMR (C_6D_6) δ −4.09 (3H, br s), 1.12 (30H, s), 5.26 (3H, s), 7.35 (1H, br s), 8.95 (2H, br s).

$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH^iPr)$ (4k) from 1: ^{1}H NMR(C_6D_6) δ −3.34 (6H, br s), 0.04 (1H, br s), 1.23 (30H, s), 5.40 (1H, br s), 9.10 (2H, br s), 15.07 (1H, br s).

Competitive Reaction of Benzyl *trans*-Cinnamyl Ether (3d) and Benzyl 3-Phenyl-2-propynyl Ether (6) with 1. A mixture of the ethers **3d** (200 mg, 0.89 mmol) and **6** (198 mg, 0.89 mmol) in toluene (2 mL) was added to a solution of **1** (983 mg, 1.74 mmol) in toluene (7 mL), and stirring was continued for 1 h at room temperature. Then cyclohexanone (177 mg, 1.80 mmol) was added to the mixture. After being stirred for 3 h at room temperature, the reaction was quenched with water (2 mL) and 2 M HCl (2 mL), and tetradecane was added to the mixture as an internal standard. The reaction mixture was extracted with ether, washed with aqueous Na_2CO_3 and brine, dried over $MgSO_4$, and concentrated in vacuo. 1-(1-Hydroxycyclohexyl)-1-phenylpropadiene (**8**) and 3-(1-hydoxycyclohexyl)-3-phenyl-1-propene (**9d**) were detected in 43% and 45% yields, respectively, by GC analyses.

Competitive C−O Cleavage of *trans*-Cinnamyl 3-Phenyl-2-propynyl Ether (7) with 1. The ether **7** (164 mg, 0.66 mmol) was treated with **1** (761 mg, 1.35 mmol) in toluene (7 mL) at room temperature for 1 h. Then cyclohexanone (137 mg, 1.40 mmol) was added to the solution, and the mixture was stirred for 3 h at room temperature. After similar workup as above, the mixture was analyzed by GC to indicate the formation of **8** and **9d** in 77% and 17% yields, respectively. Column chromatography of the crude mixture on silica gel using hexanes−ethyl acetate eluent (10/1) gave pure **8** (107 mg, 76% yield) and **9d** (18 mg, 13% yield).

Reaction of Allylic Samariums 4 with Cyclohexanone. $Cp^*_2Sm(thf)_2$ (**1**) (2.0 equiv) was placed in a Schlenk tube and dissolved in toluene (ca. 0.2 M). Allylic ether **3** was syringed to the solution, and stirring was continued for 1 h at room temperature to generate allylic samarium **4**. The ethers **3f**,**i**,**j** were treated for 20 h at room temperature. In the case of **3k**, the reaction was carried out at 80 °C for 5 h. Then cyclohexanone (2.0 equiv) was added to the resulting solution of **4** at room temperature, and the mixture was stirred for 3−20 h. After addition of water and then 2 M HCl, the mixture was extracted with ether, washed with brine, dried over $MgSO_4$, and concentrated in vacuo. GC analyses of the crude reaction mixture indicated exclusive formation of the homoallylic alcohol **9**, which was isolated by column chromatography on silica gel using hexanes−ethyl acetate eluent. When 1.0 equiv of cyclohexanone was used, the yields of **9b** and **9d** decreased to 72% and 54% yields, respectively. In the reaction of **4i**−**k**, the starting ethers **3i**, **3j**, (Z-isomer), and **3k** were recovered in 51%, 55%, and 64% yields, respectively.

Reaction of Allylic Samariums 4 with Dimethylphenylsilyl and Trimethylsilyl Chlorides. Allylic samarium **4** was generated from **3** and **1** (2.0 equiv) in toluene by a similar procedure to the above. Then silyl chloride (4.0 equiv) was added to the solution of **4**, and the mixture was stirred at room temperature for 20 h. The reaction was quenched with water and 2 M HCl and worked up similarly. Ratios of the regio- and stereoisomers were determined by GC analyses and ^{1}H and ^{13}C NMR spectra of the crude reaction mixture. Allylic silanes **11** and **12** were isolated by column chromatography on silica gel or alumina using hexanes−ethyl acetate eluent.

Reaction of Allylic Samariums 4 with Acetophenone and Pivalaldehyde. Acetophenone or pivalaldehyde (2.0 equiv) was added to a solution of **4** in toluene, generated from **3** and **1** (2.0 equiv) in situ as above, and the mixture was stirred at room temperature for 6 or 3 h, respectively. After usual workup, the crude mixture was chromatographed on silica gel using hexanes−ethyl acetate eluent to give a mixture of two diastereomers **13** or **14**, whose ratio was determined by NMR. Stereochemistry of **13g** and **14b** was determined by comparison of their ^{1}H and ^{13}C NMR spectra with those of literature.[24,25] The structures of other products **13** and **14** were assigned by analogy.

Supporting Information Available: Complete characterization data (IR, MS, ^{1}H and ^{13}C NMR spectra, and elemental analyses) for compounds **8**, **9b**−**k**, **11d′**−**h**, **12b**−**h**, **13b**−**h′**, and **14b**−**d** (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9723016

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