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Rhodium-Catalyzed Allylation of Benzyl Acetates with Allylsilanes

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Abstract: Benzyl acetate reacted with allyltrimethylsilane to give an allylation product in the presence of a catalytic amount of the (cyclooctadiene)rhodium(I) chloride dimer {[Rh(cod)Cl]$_2$}, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBARF), and triphenyl phosphite [P(OPh)$_3$] in refluxing 1,2-dichloroethane. Primary, secondary and tertiary benzyl acetates could be used for the reaction. Moreover, allylation of *gem*-benzyl acetate was possible with [Rh(cod)Cl]$_2$, NaBARF, and P(OPh)$_3$. Monoallylation and diallylation of *gem*-benzyl acetate could be controlled by altering the reaction conditions. Cationic rhodium species generated *in situ* act as a Lewis acid catalyst to give a benzyl carbocation by elimination of the acetoxy group from the benzylic carbon.

Keywords: allylation; allylsilane; benzyl acetate; rhodium; sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBARF)

Introduction

Lewis acid catalysis is essential for efficient carbon-carbon bond-forming reactions.[1] Typical Lewis acid-catalyzed or -mediated carbon-carbon bond-forming reactions include the Friedel–Crafts reaction,[2] Diels–Alder reaction,[3] Mukaiyama aldol reaction[4] and Sakurai–Hosomi allylation.[5] These reactions are useful for constructing complex molecular structures from readily available compounds under mild conditions. Representative Lewis acids for these reactions are boron,[6] aluminum,[7] tin[8] and titanium[9] compounds. To date, enantioselective Lewis acid catalysts for these reactions have been reported. In contrast to early transition metals such as titanium and zirconium, much less attention has been paid to late transition metals as Lewis acids because of their lower Lewis acidity.[10] Late transition metal complexes with a non-coordinated counteranion have been expected to act as potential Lewis acid catalysts because dissociation of the non-coordinated counteranion from the metal center generates a positive charge leading to a high electrophilicity. In the course of our study on iridium-catalyzed carbon-carbon bond-forming reactions,[11] we found that cationic iridium and rhodium complexes were new and efficient Lewis acid catalysts for the Mukaiyama aldol reaction and Mannich reaction.[11m] It is clear that these cationic complexes are sufficiently electrophilic to act as Lewis acids. These results prompted us to explore late transition metal Lewis acid-catalyzed carbon-carbon bond-forming reactions.

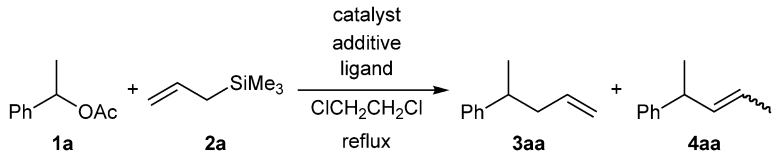
The Sakurai–Hosomi reaction is one of the most useful carbon-carbon bond-forming reactions.[5] Lewis acid-activated aldehydes, ketones, acetals, and ketals react with allylsilanes to give allylation products. In contrast, the reactions of benzylic electrophiles such as benzyl halides, benzyl alcohols and their derivatives with allylsilanes have been less developed than those of aldehydes and ketones.[12–15] Recently, the Lewis acid-mediated or -catalyzed allylation of benzylic electrophiles using allylsilanes has been reported. Boron,[12] indium,[13] and bismuth[14] compounds, montmorillonite,[15] and molecular iodine[16] have been used as Lewis acid catalysts for the reaction. No late transition metal catalysts have been reported to be used in this reaction. New Lewis acid catalysts are still needed to further expand the scope and selectivity of the reaction. In this article, we report the full de-

tails of the rhodium-catalyzed allylation of benzyl acetates using allylsilanes.

Results and Discussion

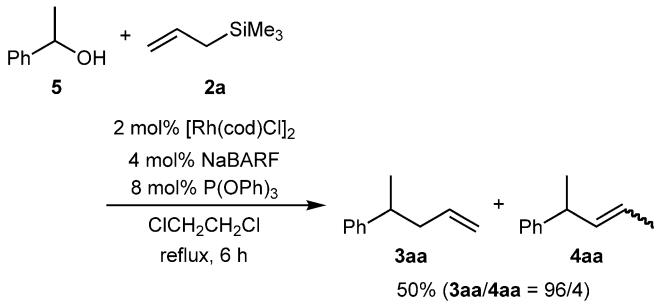
1-Phenylethyl acetate (**1a**) reacted with 3 equivalents of allyltrimethylsilane (**2a**) to give 4-phenyl-1-pentene (**3aa**) in the presence of a catalytic amount of the rhodium(I) complex $[Rh(cod)Cl]_2$ (cod = 1,5-cyclooctadiene), NaBARF {BARF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate}, and triphenyl phosphite $[P(OPh)_3]$ in refluxing 1,2-dichloroethane. It is well known that the reaction of a transition metal-Cl bond with NaBARF generates a cationic transition metal complex with the tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion. Catalyst screening was performed by reacting 1-phenylethyl acetate (**1a**) with allyltrimethylsilane (**2a**). The results are summarized in Table 1. In the absence of any ligand, the reaction did not occur (entry 1). The catalytic activity depended on the ligand used (entries 2–4). When PPh_3 and DPPE were used as ligands, the reaction did not occur (entries 2 and 3) and the starting material was recovered in quantitative yield. $P(OPh)_3$ was the most efficient ligand. When 8 mol% of $P(OPh)_3$ (P/Rh = 2) was used, the product **3aa** was obtained in 93% yield (entry 4). The electron-withdrawing property of $P(OPh)_3$ would enhance the Lewis acidity of cationic rhodium species generated *in situ*, whereas the electron-donating property of PPh_3 and DPPE would reduce the Lewis acidity of cationic rhodium species to inhibit the reaction. An increase in the amount of NaBARF from 4 mol% to 8 mol% increased the yield of product and shortened the reaction time. An excess amount of NaBARF relative to the Rh–Cl bond is needed to generate a sufficient amount of cationic rhodium species. When 8 mol% of NaBARF (NaBARF/Rh = 2) was used, the reaction was completed in 1 h and gave **3aa** in 99% yield (entry 6). The solvent affected the reaction. 1,2-Dichloroethane gave the best result (entry 6). Benzene, ethyl acetate and THF were less effective (entries 7–9). The concentration did not affect the reaction (entries 6,10 and 11). $[Rh(cod)Cl]_2$ alone did not have any catalytic activity for the reaction (entry 12). NaBARF alone also did not have any catalytic activity (entry 13). The cationic rhodium complex $[Rh(cod)_2]SbF_6$ had a lower catalyt-

Table 1. Reaction of benzyl acetate **1a** with allylsilane **2a**.[a]



Entry	Catalyst (mol%)	Additive (mol%)	Ligand (mol%)	Time [h]	Yield [%][b]	**3aa**/**4aa**[c]
1	$[Rh(cod)Cl]_2$ (2)	NaBARF (2)	none	24	0	–
2	$[Rh(cod)Cl]_2$ (2)	NaBARF (4)	PPh_3 (8)	24	0	–
3	$[Rh(cod)Cl]_2$ (2)	NaBARF (4)	DPPE (4)	24	0	–
4	$[Rh(cod)Cl]_2$ (2)	NaBARF (4)	$P(OPh)_3$ (8)	15	93	99/1
5	$[Rh(cod)Cl]_2$ (2)	NaBARF (6)	$P(OPh)_3$ (8)	6	85	99/1
6	$[Rh(cod)Cl]_2$ (2)	NaBARF (8)	$P(OPh)_3$ (8)	1	99	99/1
7[d]	$[Rh(cod)Cl]_2$ (2)	NaBARF (8)	$P(OPh)_3$ (8)	24	46	99/1
8[e]	$[Rh(cod)Cl]_2$ (2)	NaBARF (8)	$P(OPh)_3$ (8)	24	0	–
9[f]	$[Rh(cod)Cl]_2$ (2)	NaBARF (8)	$P(OPh)_3$ (8)	24	0	–
10[g]	$[Rh(cod)Cl]_2$ (2)	NaBARF (8)	$P(OPh)_3$ (8)	1	99	99/1
11[h]	$[Rh(cod)Cl]_2$ (2)	NaBARF (8)	$P(OPh)_3$ (8)	1	87	99/1
12	$[Rh(cod)Cl]_2$ (2)	none	$P(OPh)_3$ (8)	24	0	–
13	none	NaBARF (4)	$P(OPh)_3$ (8)	24	0	–
14	$[Rh(cod)_2]SbF_6$ (4)	none	$P(OPh)_3$ (8)	24	54	98/2
15	$[Ir(cod)Cl]_2$ (2)	NaBARF (4)	$P(OPh)_3$ (8)	15	83	49/51

[a] *Reaction conditions:* **1a** (1 mmol) and **2a** (3 mmol) in the presence of catalyst, additive, and ligand in 1,2-dichloroethane (5 mL).
[b] Isolated yield (combined yield of **3aa** and **4aa**).
[c] Determined by ^1H NMR.
[d] Benzene was used as solvent.
[e] Ethyl acetate was used as solvent.
[f] THF was used as solvent.
[g] 10 mL of 1,2-dichloroethane were used as solvent.
[h] 2 mL of 1,2-dichloroethane were used as solvent.



Scheme 1. Allylation of benzyl alcohol **5**.

ic activity than the combination of $[Rh(cod)Cl]_2$ and NaBARF, and the product **3aa** was obtained in 54% yield (entry 14). The reaction catalyzed by $[Ir(cod)Cl]_2$ instead of $[Rh(cod)Cl]_2$ gave a mixture of **3aa** and **4aa** in 83% yield (entry 15). In the iridium-catalyzed reaction, the allylated product **3aa** was isomerized to the internal alkene **4aa**. Isomerization from **3aa** to **4aa** was not observed under rhodium catalysis. This result showed that a rhodium catalyst was more suitable for the reaction than an iridium catalyst.

The direct substitution of a hydroxy group by a nucleophile is an important process in organic synthesis. The direct substitution of a hydroxy group with allylsilanes mediated by a catalytic amount of Lewis acid has been reported.[12a,13a–d,14,15] The reaction is more direct if benzyl alcohol can be used as a substrate. We tried the catalytic substitution of a hydroxy group with allylsilane. The reaction of 1-phenyl-1-ethanol (**5**) with allylsilane **2a** under the same optimized reaction conditions as above gave the products in 50% yield (Scheme 1). Unfortunately, direct substitution of alcohol **5** did not give a satisfactory result. Acetate **1a** was more suitable for this transformation than alcohol **5**.

To examine the scope and limitation of the reaction, a series of acetates **1** was subjected to the reaction with allylsilane **2a** under the optimized conditions. The results are summarized in Table 2. The electronic property of the substituent on the phenyl ring affected the reaction. Substrates bearing electron-donating substituents such as methyl, methoxy and chloro groups (**1b–d**) smoothly reacted with allylsilane **2a** to give the corresponding products in yields of 91–99% (entries 1–3). Acetate **1e** bearing a methoxycarbonyl group needed a longer reaction time to complete the reaction than **1b–d**. Product **3ea** was obtained in lower yield than products **3aa–ca** (entry 4). Nitro and cyano groups on the phenyl ring strongly disturbed the reaction to give no allylated products (entries 5 and 6). The starting materials were recovered in quantitative yield after refluxing in 1,2-dichloroethane for 24 h. 1-(1-Naphthyl)ethyl acetate **1h** and 1-(2-naphthyl)ethyl acetate **1i** smoothly under-

Table 2. Reaction of various acetates **1** with allylsilane **2a**.[a]

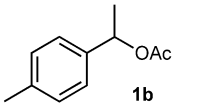
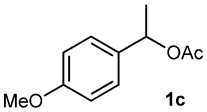
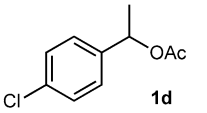
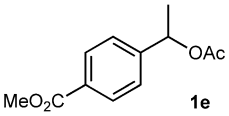
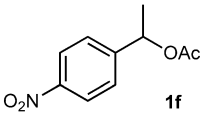
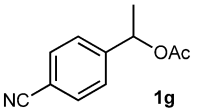
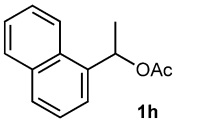
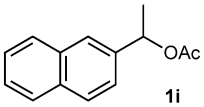
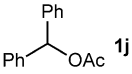
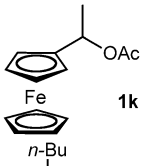
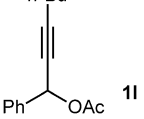
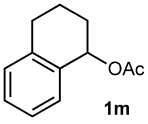
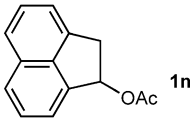
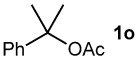
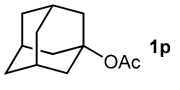
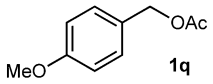
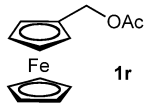
Entry	**1**	Product	Time [h]	Yield [%][b]
1	 **1b**	**3ba**	3	94
2	 **1c**	**3ca**	0.5	91
3	 **1d**	**3da**	1	99
4	 **1e**	**3ea**	24	75
5	 **1f**	**3fa**	24	0
6	 **1g**	**3ga**	24	0
7	 **1h**	**3ha**	1	98
8	 **1i**	**3ia**	1	97
9	 **1j**	**3ja**	1	98
10	 **1k**	**3ka**	1	96
11	 **1l**	**3la**	1	89
12	 **1m**	**3ma**	1	97
13	 **1n**	**3na**	6	39[c]
14	 **1o**	**3oa**	1	96
15	 **1p**	**3pa**	9	83[d]

Table 2. (Continued)

Entry	1	Product	Time [h]	Yield [%][b]
16	 1q	**3qa**	1	95
17	 1r	**3ra**	1	96

[a] *Reaction conditions:* **1** (1 mmol) and **2a** (3 mmol) in the presence of $[Rh(cod)Cl]_2$ (0.02 mmol), NaBARF (0.08 mmol), and $P(OPh)_3$ (0.08 mmol) in refluxing 1,2-dichloroethane (5 mL).

[b] Isolated yield.

[c] 2% yield of **4na** was obtained as an unseparable by-product.

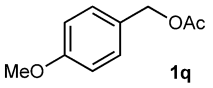
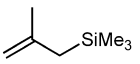
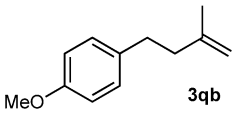
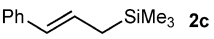
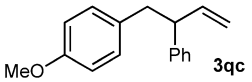
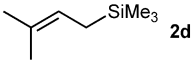
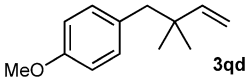
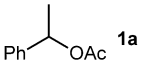
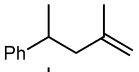
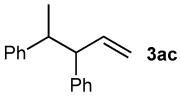
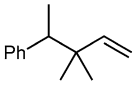
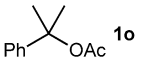
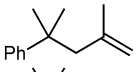
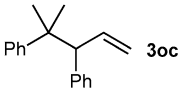
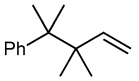
[d] 10% yield of **4pa** was obtained as an unseparable by-product.

went the reaction with **2a** to give the corresponding products (**3ha** and **3ia**) in nearly quantitative yields (entries 7 and 8). Acetates that are more hindered than **1a** such as diphenylmethyl acetate (**1j**) and 1-ferrocenylethyl acetate (**1k**) smoothly reacted with **2a** to give the allylated products in excellent yields (entries 9 and 10). Propargylic substitution with a carbon nucleophile is an attractive approach for obtaining useful building blocks as product.[17,18] Previous studies revealed that the substitution product was allene[19] or alkyne.[17,18] The selectivity of the product depends on the substrates and catalyst. Under our reaction conditions, propargylic acetate **1l** reacted with allylsilane **2a** to give the alkyne product **3la** in 89% yield (entry 11). The propargylic position was substituted with an allyl moiety. The carbon-carbon triple bond in the substrate was inert during the reaction. No allene product was obtained. The reaction of 1,2,3,4-tetrahydronaphthalen-1-yl acetate (**1m**) gave **3ma** in 97% yield, while the reaction of 1-acenaphthenyl acetate (**1n**) gave **3na** in a lower yield of 39% (entries 12 and 13). Tertiary acetate **1o** smoothly reacted with **2a** to give product **3oa** in quantitative yield (entry 14). Adamantyl acetate **1p** was transformed to the allylated product in high yield, but it needed a longer reaction time to complete than **1o** (entry 15). Products **3oa** and **3pa** have all-carbon-substituted quaternary carbon centers.[20] Notably, our reaction represents a novel catalytic method for the construction of an all-carbon-substituted quaternary carbon center. Our reaction could be applied to primary acetates. Acetate **1q** substituted with a methoxy group smoothly reacted with **2a** to give product **3qa** in 95% yield. On the other hand, benzyl acetate did not react with **2a** under the same reaction conditions, and the starting material was recovered. An electron-donating group on a phenyl ring is necessary for the reaction of primary benzyl acetate. The reaction of acetate **1f** bearing a ferrocenyl moiety gave **3ra** in 96% yield (entry 17).

On the basis of these results, we turned our attention to the scope of allylsilanes. Methallyltrimethylsilane **2b**, cinnamyltrimethylsilane **2c** and prenyltrimethylsilane **2d** were chosen as allylsilane components because they have different substitution structures of the carbon-carbon double bond. They were allowed to react with primary acetate **1q**, secondary acetate **1a** or tertiary acetate **1o**. The results are summarized in Table 3. Primary acetate **1q** was reacted with methallyltrimethylsilane (**2b**), cinnamyltrimethylsilane (**2c**), and prenyltrimethylsilane (**2d**) to give the respective allylated products **3qb**, **3qc**, and **3qd** in high yields (entries 1–3). As in the Lewis acid-mediated or -catalyzed reaction of aldehydes with allylsilanes **2c** and **2d**, the carbon-carbon bond-forming reaction was regiospecific to occur at the γ-position of allylsilanes. The reaction of secondary acetate **1a** with allylsilanes **2b–d** gave the corresponding products (**3ab**, **3ac**, and **3ad**) in yields of 83–98% (entries 4–6). The allylated product **3ac** was obtained as a 54/46 mixture of diastereomers. Contiguous tertiary and quaternary carbons were constructed in high yield. With a tertiary acetate, the yield depended on the allylsilane used. The tertiary acetate **1o** reacted with methallyltrimethylsilane (**2b**) to give the allylated product **3ob** in high yield, while the reaction of **1o** with γ-substituted allylsilanes **2c** and **2d** gave the products **3oc** and **3od** in lower yields (entries 7–9). Two contiguous quaternary carbons were constructed by the reaction.

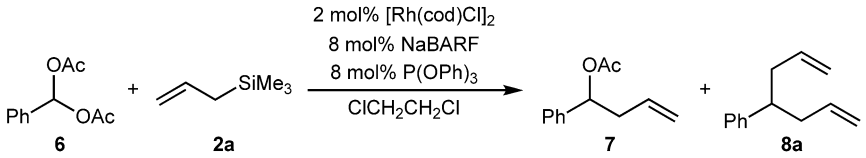
An allyl group is introduced at a benzylic position by substitution of an acetoxy group. We can extend this chemistry to a *gem*-diacetate,[21] which is easily prepared by the reaction of aldehydes with acetic anhydride.[22] The results are summarized in Table 4. The molar ratio of allylsilane **2** to **6** was important. *gem*-Diacetate **6** reacted with 1.5 equivalents of allylsilane **2a** in refluxing 1,2-dichloroethane for 24 h to give **7** in 23% yield (entry 1). Decomposition of **6** to benzaldehyde occurred as a competitive reaction to allylation. To increase the yield of allylation product **7** and **8a**, the allylation must be faster than the decomposition of **6** to benzaldehyde. An increase in the amount of allylsilane **2a** may promote allylation. We tried the reaction with 3 equivalents of allylsilane **2a**, but the results were unsatisfactory: product **7** was obtained in 41% yield and diallylation product **8a** was not obtained at all (entry 2). The reaction with 6 equivalents of allylsilane **2a** exclusively gave diallylation product **8a** in 43% yield (entry 3). To obtain monoallylation product **7** in high yield, the reaction temperature was important. The reaction with 6 equivalents of allylsilane **2a** at room temperature gave monoallylation product **7** in 90% yield (entry 4). A decrease in the amount of **2a** from 6 equivalents to

Table 3. Reaction of benzylic acetate **1** with allylsilane **2**.[a]

Entry	1	2	Product	Time [h]	Yield [%][b]
1	 **1q**	 **2b**	 **3qb**	5	99
2	**1q**	 **2c**	 **3qc**	2	99
3	**1q**	 **2d**	 **3qd**	6	92
4	 **1a**	**2b**	 **3ab**	1	83
5	**1a**	**2c**	 **3ac**	5	95[c]
6	**1a**	**2d**	 **3ad**	9	98
7	 **1o**	**2b**	 **3ob**	6	88
8	**1o**	**2c**	 **3oc**	4	54
9	**1o**	**2d**	 **3od**	3	79

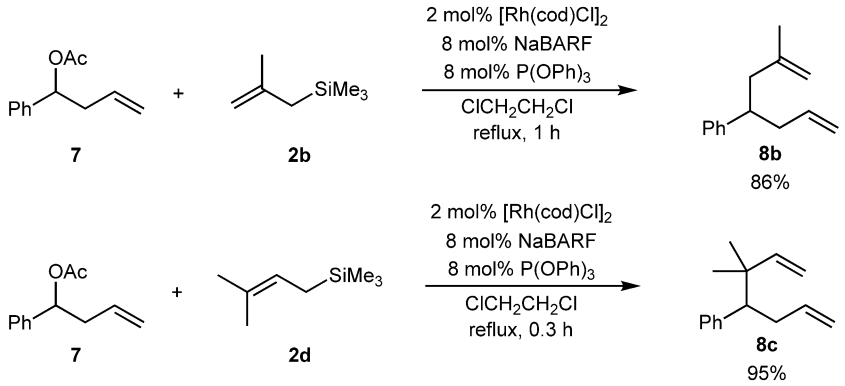
[a] *Reaction conditions:* **1** (1 mmol) and **2** (3 mmol) in the presence of $[Rh(cod)Cl]_2$ (0.02 mmol), NaBARF (0.08 mmol), and $P(OPh)_3$ (0.08 mmol) in refluxing 1,2-dichloroethane (5 mL).
[b] Isolated yield.
[c] Product **3ac** was obtained as an unseparable diastereomers in 54/46 ratio determined by ^1H NMR.

Table 4. Reaction of *gem*-diacetate **6** with allylsilane **2a**.[a]



Entry	Equiv. of **2a**	Temperature	Time [h]	Yield of **7** [%][b]	Yield of **8a** [%][b]
1	1.5	reflux	24	23	0
2	3	reflux	24	41	0
3	6	reflux	5	0	43[c]
4	6	reflux	24	0	29[d]
5	6	r.t.	0.5	90	0
6	5	r.t.	0.5	72	0

[a] *Reaction conditions:* **6** (1 mmol) and **2a** in the presence of $[Rh(cod)Cl]_2$ (0.02 mmol), NaBARF (0.08 mmol), and $P(OPh)_3$ (0.08 mmol) in 1,2-dichloroethane (5 mL).
[b] Isolated yield.
[c] A 12% yield of (*E*)-4-phenyl-1,5-heptadiene and a 7% yield of (*E*)-1-phenyl-1,3-butadiene were obtained as unseparable by-products.
[d] A 22% yield of (*E*)-4-phenyl-1,5-heptadiene and a 5% yield of (*E*)-1-phenyl-1,3-butadiene were obtained as unseparable by-products.

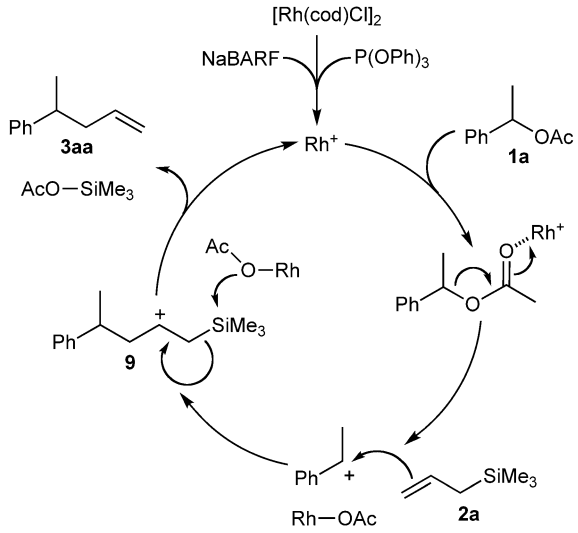


Scheme 2. Allylation of benzyl acetate **7**.

5 equivalents decreased the yield. The reaction of **1a** with 5 equivalents of **2a** gave **7** in 72% yield (entry 6). We could obtain both monoallylation product **7** and diallylation product **8a** in moderate to high yield by choosing suitable reaction conditions.

The reaction of *gem*-diacetates with allylsilanes will be a new route to 1,6-heptadienes, which are good substrates for cycloisomerization. Much attention has been paid to the cycloisomerization of α,ω-dienes catalyzed by transition metal complexes,[23] since this can be used to construct cyclic compounds in a single step without any wasteful by-products. Our catalytic reaction would be more valuable if two different allyl groups could be introduced at the benzylic carbon. Based on the results described above, we tried a sequential substitution of a *gem*-diacetate. The results are shown in Scheme 2. The reaction of **7** with 3 equivalents of methallyltrimethylsilane **2b** at room temperature for 1 h gave **8b** in 86% yield. Prenyltrimethylsilane **2d** could be used for the sequential substitution. The reaction of **7** with 3 equivalents of **2d** at room temperature for 0.3 h gave **8c** in 95% yield. Contiguous tertiary and quaternary carbons were constructed in high yields.

We considered that this allylation reaction proceeds *via* a carbocation intermediate. First, the cationic rhodium species is formed by the reaction of $[Rh(cod)Cl]_2$ with NaBARF.[24] The coordination of carbonyl oxygen atom to cationic rhodium species promoted dissociation of the acetoxy group to generate a benzyl carbocation intermediate. Nucleophilic attack of allylsilane **2** at the γ-position of the silicon atom to a benzyl carbocation intermediate gives intermediate **9**, where a positive charge is generated at the β-position of the silicon atom. Nucleophilic attack of an acetoxy anion to silicon atom induces the elimination of trimethylsilyl acetate to give the allylated product **3** (Scheme 3). To obtain evidence of the formation of a benzyl carbocation intermediate, we examined the reaction of (*R*)-1-phenylethyl acetate [(*R*)-**1a**] with allyltrimethylsilane (**2a**). Product **3aa**



Scheme 3. Plausible reaction pathway.

was obtained in 80% yield as a racemic mixture.[25] The optical purity of the starting material was completely lost in the product. Elimination of an acetoxy group gives a planar achiral benzyl carbocation intermediate. Nucleophilic attack of allylsilane **2** occurs on both sides of the benzyl carbocation plane to give a racemic mixture of **3aa**. The results strongly support the formation of a benzyl carbocation intermediate by the elimination of an acetoxy group. The reaction of 2-octyl acetate with allyltrimethylsilane in refluxing 1,2-dichloroethane for 24 h gave no product, and the starting material was recovered quantitatively. Elimination of an acetoxy group from an aliphatic carbon did not occur under the optimized conditions, since an aliphatic secondary carbocation is less stable than a benzyl carbocation.

We tried the enantioselective allylation of **1a** with **2a** using chiral phosphoramidite ligands (*aS*,*R*,*R*)-**L1** and (*aS*,*S*,*S*)-**L2** (Figure 1) which were expected to be effective for the reaction due to an electronic-withdrawing property similar to that of $P(OPh)_3$.[26] Un-

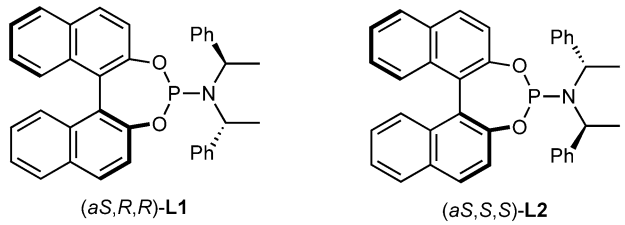


Figure 1. Chiral phosphoramidite ligands.

fortunately, the reaction of **1a** with **2a** under refluxing 1,2-dichloroethane for 24 h did not occur. The starting material remained in quantitative yield.

Conclusions

We have identified a novel Lewis acid catalysis of cationic rhodium complex generated *in situ*. Benzyl acetates react with allylsilanes to give allylated products in high yields. Primary, secondary and tertiary acetates could be allylated efficiently. Benzyl *gem*-diacetate could be used for the allylation. 1,6-Heptadienes were obtained as the product. Further development of the Lewis acid catalysis of a cationic rhodium complex is underway in our laboratory.

Experimental Section

Representative Procedure for the Allylation of Acetates (1 and 7) with Allylsilanes (2)

A flask was charged with $[Rh(cod)Cl]_2$ (10.0 mg, 0.02 mmol) and NaBARF (71.0 mg, 0.08 mmol). The flask was evacuated and filled with argon. To the flask were added 1,2-dichloroethane (5 mL) and $P(OPh)_3$ (24.4 mg, 0.08 mmol). Acetate **1a** (175 mg, 1.1 mmol) and allylsilane **2a** (343 mg, 3.0 mmol) were added to the reaction mixture. The mixture was stirred under reflux for 1 h. The progress of the reaction was monitored by GLC. After the reaction was complete, the solvent was evaporated under vacuum. Column chromatography (*n*-hexane) of the residue gave **3aa**; yield: 155 mg (1.1 mmol, 99%).

4-Phenyl-1-pentene (3aa): ^{1}H NMR (500 MHz, in $CDCl_3$, TMS): $\delta = 1.25$ (d, $J = 6.9$ Hz, 3H), 2.28 (dddt, $J = 6.9$, 6.9, 13.8, and 1.4 Hz, 1H), 2.38 (dddt, $J = 6.9$, 6.9, 13.8, and 1.4 Hz, 1H), 2.78 (tq, $J = 6.9$ and 6.9 Hz, 1H), 4.95 (ddt, $J =$ 10.1, 2.5, and 1.4 Hz, 1H), 4.99 (ddt, $J = 17.0$, 2.5, and 1.4 Hz, 1H), 5.71 (ddt, $J = 17.0$, 10.1, and 6.9 Hz, 1H), 7.16–7.20 (m, 3H), 7.29 (t, $J = 7.8$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.5$, 39.8, 42.7, 115.9, 125.9, 127.0, 128.3, 137.2, 147.0; HR-MS (FAB): $m/z = 145.1016$, calcd. for $C_{11}H_{13}$ $[M-H]^+$: 145.1017.

Procedure for the Allylation of (*R*)-1-Phenylethyl Acetate [(*R*)-1a] with Allyltrimethylsilane (2a)

A flask was charged with $[Rh(cod)Cl]_2$ (10.4 mg, 0.02 mmol) and NaBARF (71.6 mg, 0.08 mmol). The flask was evacuated and filled with argon. To the flask were added 1,2-dichloroethane (5 mL) and $P(OPh)_3$ (24.4 mg, 0.08 mmol). Acetate (*R*)-**1a** (164 mg, 1.0 mmol) and allylsilane **2a** (346 mg, 3.0 mmol) were added to the reaction mixture. The mixture was stirred under reflux for 3 h. The progress of the reaction was monitored by GLC. After the reaction was complete, the solvent was evaporated under vacuum. Column chromatography (*n*-hexane) of the residue gave **3aa**; yield: 117 mg (0.80 mmol, 80%). The optical rotation was measured: $[\alpha]_D^{27}$: +0.08 (*c* 0.75, $CHCl_3$).

Procedure for the Allylation of *gem*-Diacetate (6) with Allyltrimethylsilane (2a).

A flask was charged with $[Rh(cod)Cl]_2$ (10.9 mg, 0.02 mmol) and NaBARF (82.9 mg, 0.09 mmol). The flask was evacuated and filled with argon. To the flask were added 1,2-dichloroethane (5 mL) and $P(OPh)_3$ (24.1 mg, 0.08 mmol). Allylsilane **2a** (667 mg, 5.8 mmol) and *gem*-diacetate **6** (208 mg, 1.0 mmol) were added to the reaction mixture. The mixture was stirred at room temperature for 0.5 h. The progress of the reaction was monitored by GLC. After the reaction was complete, the solvent was evaporated under vacuum. Column chromatography (*n*-hexane/AcOEt = 90/10) of the residue gave **7**; yield: 171 mg (0.90 mmol, 90%).

1-Phenyl-3-butenyl acetate (7): ^{1}H NMR (500 MHz, in $CDCl_3$, TMS): $\delta = 2.06$ (s, 3H), 2.55 (ddd, $J = 14.2$, 6.9, and 6.0 Hz, 1H), 2.65 (ddd, $J = 14.2$, 7.8, and 6.9 Hz, 1H), 5.05 (dm, $J = 10.1$ Hz, 1H), 5.07 (dm, $J = 17.0$ Hz, 1H), 5.70 (ddt, $J = 17.0$, 10.1, and 6.9 Hz, 1H), 5.81 (dd, $J = 7.8$ and 6.0 Hz, 1H), 7.26–7.34 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 21.2, 40.7, 75.1, 118.0, 126.5, 127.9, 128.4, 133.3, 140.0, 170.2; HR-MS (FAB): m/z 191.1077, calcd. for $C_{12}H_{15}O_2$ $[M+H]^+$: 191.1072.

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