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Allylrhodium Isomerization

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The Isomerization of Allylrhodium Intermediates in the Rhodium-Catalyzed Nucleophilic Allylation of Cyclic Imines**

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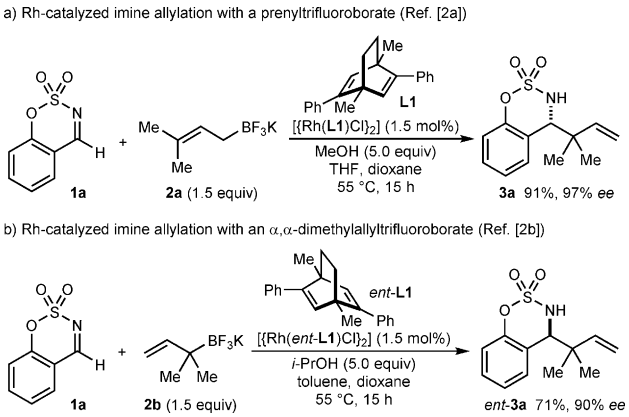
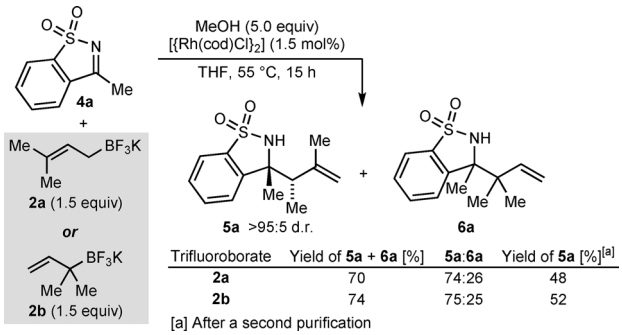
Abstract: *Allylrhodium species generated from potassium allyltrifluoroborates can undergo isomerization by 1,4-rhodium(I) migration to give more complex isomers, which then react with cyclic imines to provide products with up to three new stereochemical elements. High enantioselectivities are obtained using chiral diene–rhodium complexes.*

The catalytic enantioselective nucleophilic allylation of aldehydes and imines is a useful route to homoallylic alcohols and amine derivatives.[1] Recently, we described the enantioselective rhodium-catalyzed nucleophilic allylation[2] of cyclic imines[3,4] using the chiral dienes **L1**/*ent*-**L1**[5] which, to our knowledge, are the first examples of rhodium-catalyzed enantioselective additions of allylboron reagents to π-electrophiles.[6] These reactions enable the formation of products with up to two stereocenters with high diastereo- and enantioselectivities.[2] Herein, we report the discovery of an isomerization of allylrhodium intermediates, resulting in more complex allylrhodium species that would otherwise be difficult to access. This isomerization allows the formation of products containing up to three new stereochemical elements (two stereocenters and an alkene of defined geometry) with high diastereo- and enantiocontrol.

Previously, we demonstrated that the cyclic aldimine **1a** reacted with the prenyltrifluoroborate **2a** (Scheme 1a)[2a] or its isomer **2b** (Scheme 1b)[2b] to give the same reverse prenylation product **3a**, thus suggesting the involvement of a common allylrhodium intermediate. In further experiments, the racemic allylation of the saccharin-derived cyclic ketimine



Scheme 1. The enantioselective Rh-catalyzed allylation of cyclic imines.



Trifluoroborate	Yield of **5a** + **6a** [%]	**5a**:**6a**	Yield of **5a** [%][a]
2a	70	74:26	48
2b	74	75:25	52

[a] After a second purification

Scheme 2. The allylation of ketimine **4a** with **2a** or **2b**.

4a with the prenyltrifluoroborate **2a** was attempted (Scheme 2). Surprisingly, a 70% yield of a mixture of products was obtained, in which the expected reverse prenylation product **6a** was only the minor component (**5a**/**6a** = 74:26 by ^{1}H NMR analysis). The major product was the homoallylic sulfonamide **5a**, obtained in > 95:5 d.r.,[7] which presumably results from an isomerization of the allylrhodium intermediate. A second purification of this mixture led to the isolation of **5a** in 48% yield. Very similar results were obtained with the isomeric allyltrifluoroborate **2b**.

A mechanism that is consistent with these observations and also explains the stereochemical outcome is presented in Scheme 3. First, the transmetalation of the trifluoroborates **2a** or **2b** with rhodium is expected to result in the allylrhodium species **7**, as described previously.[2] With more reactive cyclic imines such as **1a** (Scheme 1), the reaction with the allylrhodium species **7** proceeds readily to provide the expected reverse prenylation products such as **3a**. However, the

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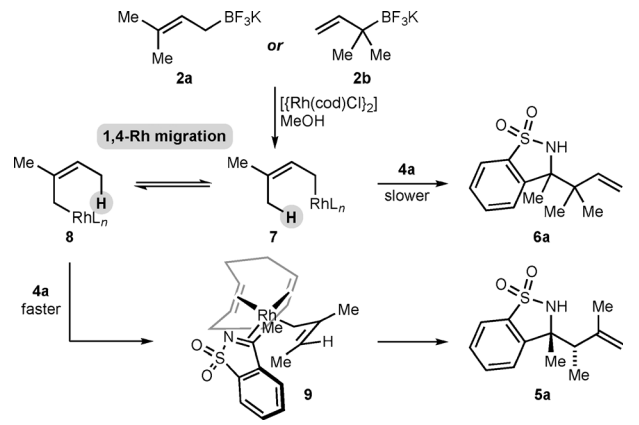
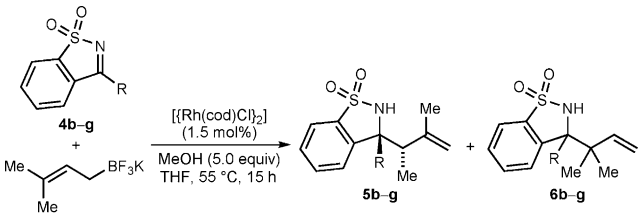


Scheme 3. The isomerization of the prenylrhodium species **7**.

saccharin-derived imine **4a** is considerably less reactive than the aldimine **1a**, and the formation of the sterically congested reverse prenylation product **6a** is less favored. Instead, we hypothesize that a reversible 1,4-rhodium migration[8–10] of **7**, involving the participation of a hydrogen atom on the *cis*-methyl group, occurs to give the *Z*-allylrhodium species **8**. Reaction of **8** with the imine **4a** then takes place through a cyclic six-membered transition state **9** to produce the less sterically hindered allylation product **5a**. To our knowledge, only a single example of this type of prenylrhodium isomerization has been reported previously, by the group of Yorimitsu and Oshima,[11] and the opportunities offered by this chemistry have not been explored further.

This isomerization–allylation using allyltrifluoroborate **2a** also occurred with other saccharin-derived imines (Table 1). In addition to **4a** (Scheme 2), the reaction was tolerant of imines containing ethyl (entry 1), *n*-butyl (entry 2), *n*-hexyl (entry 3), and 3-phenylpropyl groups (entry 4). In these cases,

Table 1: The allylation of imines **4a–g** with potassium allyltrifluoroborate **2a**.[a]



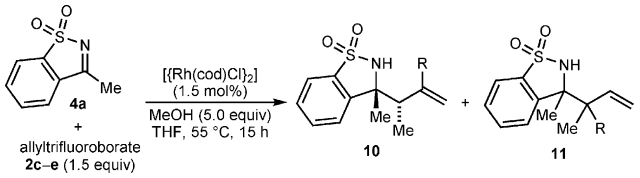
	Substrate	Yield of **5**+**6** [%][b]	**5**/**6**[c]	Yield of **5** [%][d]	d.r. of **5**[c]
1	**4b** R = Et	84	76:24	62	>95:5
2	**4c** R = *n*Bu	66	75:25	50	>95:5
3	**4d** R = *n*Hex	91	79:21	61	>95:5
4	**4e** R = $CH_2CH_2CH_2Ph$	69	76:24	47	>95:5
5	**4f** R = (*E*)-CH=CHPh	68	72:28	56	85:15
6	**4g** R = (*E*)-CH=CH(4-EtC_6H_4)	75	82:18	46	76:24

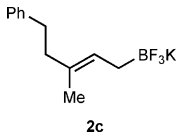
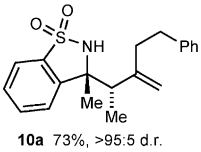
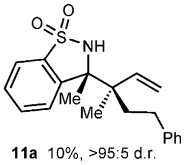
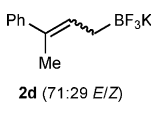
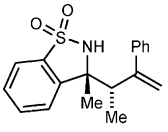
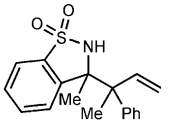
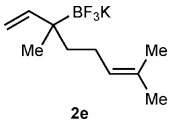
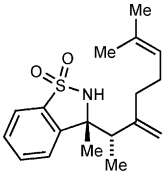
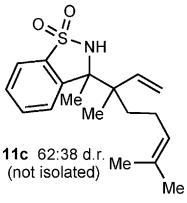
[a] Reactions were conducted with 0.30 mmol of **4a–g**. [b] Yield of an isolated, combined mixture of **5** and **6**. [c] Determined by ^{1}H NMR analysis. [d] Yield of an isolated, pure sample of **5** after a second purification.

the allylation products **5** resulting from the isomerization were formed as the major products in >95:5 d.r. α,β-Unsaturated imines were also tolerated, though the diastereoselectivities of these reactions were slightly lower than those of the previous examples (Table 1, entries 5 and 6).

Other potassium allyltrifluoroborates were also effective in this process. For example, allyltrifluoroborate **2c** reacted with **4a** to give the isomerization product **10a** in 73% yield and the "standard" product **11a** in 10% yield, both in >95:5 d.r. (Table 2, entry 1). In contrast, the allyltrifluoroborate **2d**,

Table 2: The allylation of **4a** with various potassium allyltrifluoroborates.[a]



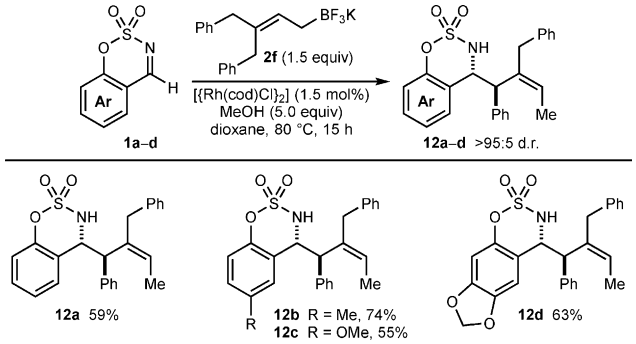
Entry	Allyltrifluoroborate	Product(s)	
1	 **2c**	 **10a** 73%, >95:5 d.r.	 **11a** 10%, >95:5 d.r.
2	 **2d** (71:29 *E*/*Z*)	 **10b** 78%, 76:24 d.r.	 **11b** (not detected)
3	 **2e**	 **10c** 48%[b], >95:5 d.r. Ratio of **10c**:**11c** = 69:31 Yield of **10c** + **11c** = 82%	 **11c** 62:38 d.r. (not isolated)

[a] Reactions were conducted with 0.30 mmol of **4a**. Yields are of isolated products. Ratios of isomerized to non-isomerized products, and diastereomeric ratios were determined by ^{1}H NMR analysis. [b] Yield of **10c** after a second purification.

which was prepared as a 71:29 mixture of *E*/*Z* isomers, reacted with **4a** to give only the isomerization product **10b**, albeit as an inseparable 76:24 diastereomeric mixture (entry 2). Since it was not possible to prepare **2d** in the geometrically pure form, it is difficult to assess the relative contributions of the *E*- and *Z*-isomers in the formation of **10b**. The absence of the "standard" product **11b** in this reaction is most likely due to the steric hindrance that would be encountered in forming such a crowded bond. The α,α-disubstituted allyltrifluoroborate **2e** also reacted with **4a** to give an 82% yield of a combined 69:31 mixture of the isomerized and non-isomerized products **10e** and **11e**, respectively (entry 3). These products were difficult to separate by column chroma-

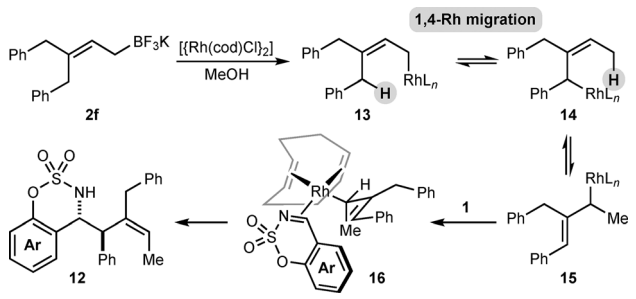
tography, but a further purification led to the isolation of **10c** in 48% yield.

To further investigate the scope of this process, the aldimines **1a–e** were examined (Scheme 4).[12] These substrates are considerably more reactive than the ketimines **4a–g** examined thus far, and imine **1a** has already been shown to provide only the reverse prenylation products with the prenyltrifluoroborate **2a** or its isomer **2b** (Scheme 1). The reactions of **1a** with allyltrifluoroborates **2c–e** also gave products resulting from an allylation without isomerization. We speculated that the use of even more sterically hindered allyltrifluoroborates would be required to disfavor the "standard" pathway, giving a better chance for the isomerization of the corresponding allylrhodium species to occur. Indeed, the reaction of **1a** with allyltrifluoroborate **2f** led to the product **12a**, resulting from allylrhodium isomerization, in 59% yield, with none of the "standard" allylation product observed (Scheme 4).[13] Notably, **12a** was formed as a single diastereomer with control over three stereochemical elements: two stereogenic centers in the *anti*-configuration, and a *Z*-alkene. Other cyclic aldimines **1b–d** also reacted smoothly with **2f** to give the products **12b–d** in 55–74% yield.



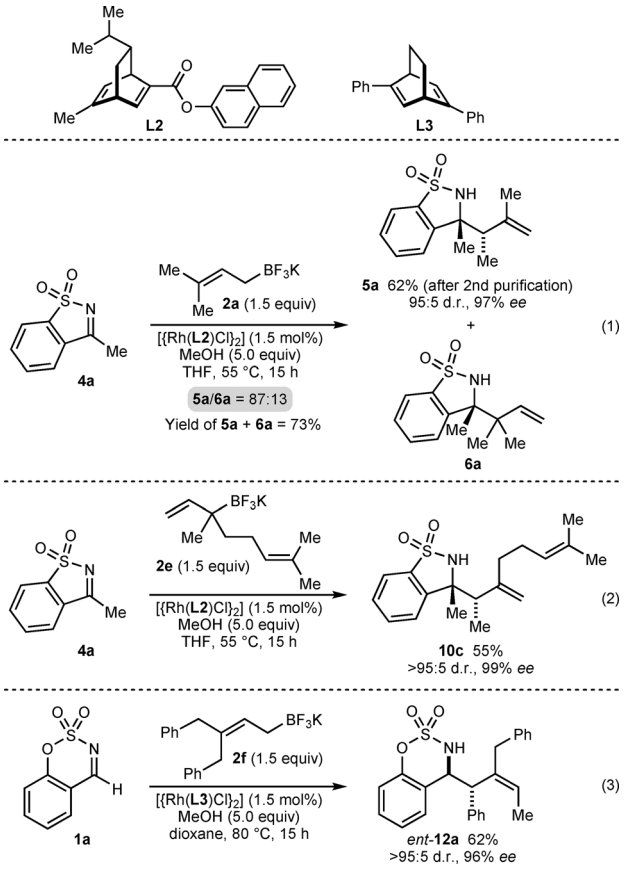
Scheme 4. The allylation of aldimines **1a–d** with allyltrifluoroborate **2f**. Reactions were conducted with 0.30 mmol of **1a–d**. Yields are of isolated products.

The formation of products **12** can be rationalized by the pathway shown in Scheme 5. After formation of the allylrhodium species **13**, the imine allylation is disfavored due to the high steric congestion at the γ-carbon. Therefore, 1,4-Rh^{I} migration of **13** occurs to form the benzylrhodium species **14**. Although the imine can react with **14** at this stage, the observed product is consistent with an allylation by the allylrhodium species **15**, formed from **14** by 1,3-allylic transposition of rhodium (through σ–π–σ interconversion). Interestingly, if a cyclic six-membered transition state is operative, the *Z*-geometry of the alkene in **12** must arise from the methyl group occupying a pseudoaxial position (as in **16**), which avoids an unfavorable steric interaction with the cyclooctadiene ligand.

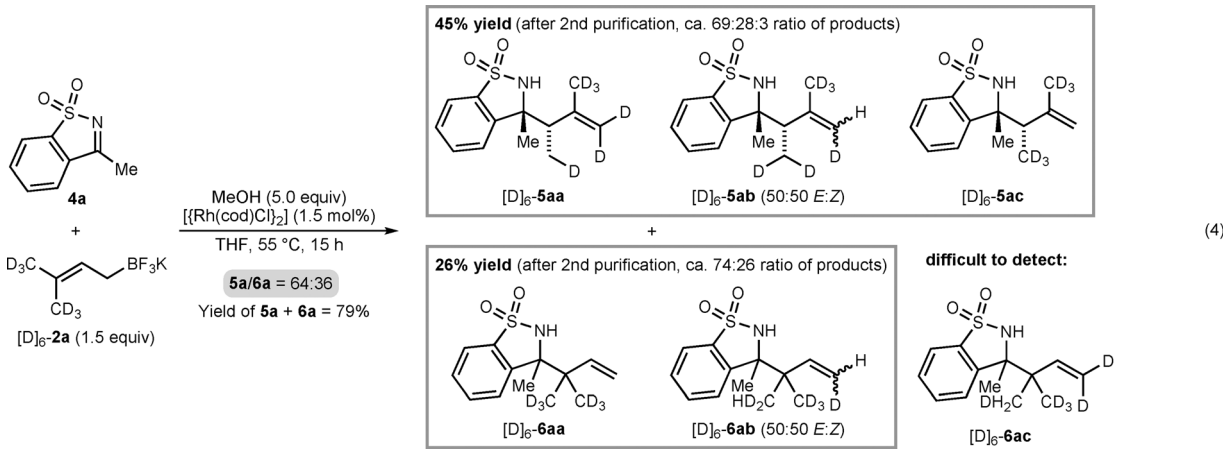


Scheme 5. The isomerization of the allylrhodium species **13**.

Enantioselective variants of these reactions were also investigated using chiral diene ligands[14] (Scheme 6). The reaction of imine **4a** with prenyltrifluoroborate **2a** proceeded best[15] using the α-phellandrene-derived chiral diene **L2**,[16] which gave **5a** as the major product (**5a**/**6a** = 87:13) in 62% yield, >95:5 d.r., and 97% *ee* [Eq. (1)].[17] High diastereo- and enantioselectivities were also observed in the reaction of **4a** with the α,α-disubstituted allyltrifluoroborate **2c** using **L2** [Eq. (2)]. In contrast to the corresponding reaction using [{Rh(cod)Cl}$_2$] as the precatalyst (Table 2, entry 3), this reaction led to none of the "standard" allylation product **11c**. This observation may be a result of the more sterically hindered nature of **L2** compared with cyclooctadiene. Finally, the reaction of **1a** with allyltrifluoroborate **2f** was unsuccessful when **L2** was employed, but the use of diene **L3**[18] gave *ent*-**12a** in 62% yield, >95:5 d.r., and 96% *ee* [Eq. (3)].



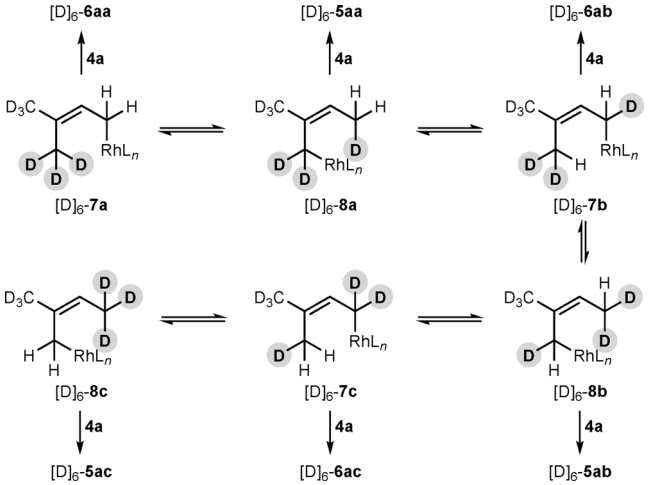
Scheme 6. Enantioselective allylations. Reactions were conducted with 0.30 mmol of imine. Yields are of isolated products. Enantiomeric excesses were determined by HPLC analysis on a chiral stationary phase.



(4)

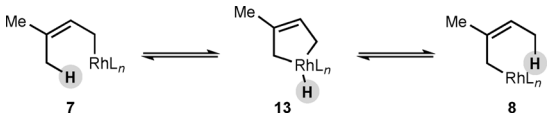
To gain further insight into this process, the reaction of imine **4a** with the hexadeuterated prenyltrifluoroborate [D]$_6$-**2a** was conducted [Eq. (4)]. Purification of the reaction mixture gave two fractions. The first fraction was an inseparable mixture (45% yield) of the isomerized products [D]$_6$-**5aa**, [D]$_6$-**5ab** (a 50:50 *E*/*Z*-mixture), and [D]$_6$-**5ac**, in an approximate ratio of 69:28:3, respectively. The second fraction was an inseparable mixture (26% yield) of the reverse prenylation products [D]$_6$-**6aa** and [D]$_6$-**6ab** (a 50:50 *E*/*Z* mixture) in an approximate ratio of 74:26, respectively. It was difficult to detect the presence of [D]$_6$-**6ac**.

This experiment provides the following information: First, the presence of several products differing in their levels of deuteration at the alkene and one of the methyl groups demonstrates that the isomerization of the intermediate allylrhodium species is reversible, which leads to deuterium–hydrogen exchange (Scheme 7). Second, no deuterium



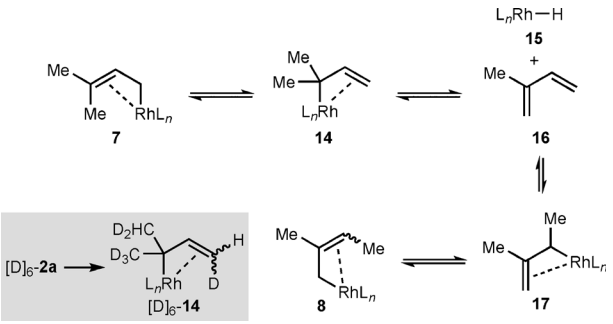
Scheme 7. Deuterium–hydrogen exchange through the reversible 1,4-Rh^{I} migration of allylrhodium species [D]$_6$-**7** and [D]$_6$-**8**.

depletion was detected in the CD_3 group attached to the alkene in the isomerized products [D]$_6$-**5aa**, [D]$_6$-**5ab**, and [D]$_6$-**5ac**, which suggests that the 1,4-Rh^{I} migration occurs only between the *cis*-substituents of the allylrhodium species, and that *E*/*Z* isomerization does not take place to any considerable extent. We therefore assume that the 1,4-Rh^{I} migration occurs by a C–H oxidative addition–reductive elimination sequence through intermediate **13** (Scheme 8), which is consistent with mechanisms suggested for other types of 1,4-Rh^{I} migration reported previously.[8a,10q]



Scheme 8. The proposed mechanism of the 1,4-Rh^{I} migration.

An alternative mechanism for the isomerization of a prenylrhodium species has been proposed by others.[11] This mechanism (Scheme 9), which involves enyl ($\sigma+\pi$)



Scheme 9. An alternative mechanism for the isomerization of the prenylrhodium species **7** (Ref. [11]).

organorhodium species,[19] starts with the 1,3-allylic transposition of rhodium from **7** to form **14**, followed by β-hydride elimination to form a rhodium hydride **15** and isoprene (**16**). Hydrorhodation of **16** with **15** gives **17**, which then isomerizes to **8**. According to this mechanism, the hexadeuterated prenyltrifluoroborate [D]$_6$-**2a** would lead to the intermediate [D]$_6$-**14**. β-Hydride elimination from [D]$_6$-**14** would likely

result in deuterium–hydrogen exchange from both methyl groups, which is not observed in the experiment shown in Equation (4). Therefore, at present, we tentatively favor the isomerization mechanism shown in Scheme 8.

In summary, allylrhodium intermediates generated from γ,γ- or α,α-disubstituted potassium allyltrifluoroborates can undergo isomerization into more complex allylrhodium species, which then react with cyclic imines in highly diastereoselective allylations to give products containing up to three new stereochemical elements. The isomerization is proposed to occur by a 1,4-Rh^{I} migration, and products resulting from this process are favored when the combination of the steric hindrance of the initially formed allylrhodium species and the reactivity of the imine is such that allylation is disfavored. Finally, the use of chiral diene–rhodium complexes confers high enantioselectivities onto the reactions. This work demonstrates the power of rhodium catalysis to generate stereochemically complex products from simple starting materials through isomerization processes. Further applications of 1,4-Rh^{I} migrations involving allylrhodium species are underway in our group.

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[7] The stereochemistries of products **5b**, **5e**, **11a**, **12c**, and **12d** were confirmed by X-ray crystallography. See the Supporting Information for details. The stereochemistries of the remaining products were assigned by analogy. CCDC 1013875 (**5b**), 1013876 (**5e**), 1013877 (**12c**), 1013878 (**12d**), and 1019074 (**11a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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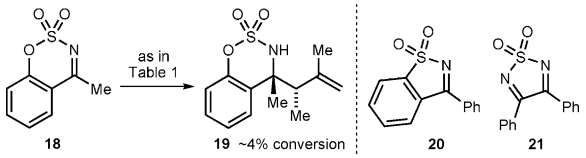
[11] a) Y. Takada, S. Hayashi, K. Hirano, H. Yorimitsu, K. Oshima, *Org. Lett.* **2006**, *8*, 2515 – 2517; b) Y. Sumida, Y. Takada, S. Hayashi, K. Hirano, H. Yorimitsu, K. Oshima, *Chem. Asian J.* **2008**, *3*, 119 – 125.

[12] Other cyclic imines **18**, **20**, and **21** were not suitable substrates in these reactions. Imine **18** reacted with prenyltrifluoroborate **2a** under the conditions shown in Table 1 to provide what appeared to be **19** in only ≈4% conversion, with the remaining mass balance being unreacted **18**. Imines **20** and **21** were completely unreactive.



[13] Attempted reactions of **2f** with imine **4a** led to no traces of any allylation products.

[14] Reviews of chiral dienes: a) C.-G. Feng, M.-H. Xu, G.-Q. Lin, *Synlett* **2011**, 1345 – 1356; b) R. Shintani, T. Hayashi, *Aldrichimica Acta* **2009**, *42*, 31 – 38; c) J. B. Johnson, T. Rovis, *Angew. Chem. Int. Ed.* **2008**, *47*, 840 – 871; *Angew. Chem.* **2008**, *120*, 852 – 884; d) C. Defieber, H. Grutzmacher, E. M. Carreira, *Angew. Chem. Int. Ed.* **2008**, *47*, 4482 – 4502; *Angew. Chem.* **2008**, *120*, 4558 – 4579.

[15] Diene *ent*-**L1** (see Scheme 1a) gave a 71:29 mixture of *ent*-**5a** and *ent*-**6a**, and *ent*-**5a** was formed in 98% *ee*. However, the conversion of this reaction was only 65%. Diene **L3** (Ref. [18]) gave a 36:64 mixture of *ent*-**5a** and *ent*-**6a** in 85% conversion (*ee* values not determined).

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[17] The absolute configurations of the products in Scheme 6 were assigned by analogy with the stereochemical outcomes obtained in previous studies (see Ref. [2]).

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[19] The enyl ($\sigma+\pi$) character of the allylrhodium(I) species could also be invoked in our reactions described herein. For evidence of the enyl ($\sigma+\pi$) character of the allylrhodium(III) species, see: P. A. Evans, J. D. Nelson, *J. Am. Chem. Soc.* **1998**, *120*, 5581 – 5582.

