**Abstract:** Allylrhodium species derived from δ-trifluoroboryl β,γ-unsaturated esters undergo chain walking towards the ester moiety. The resulting allylrhodium species react with imines to give products containing two new stereocenters and a Z-alkene. By using a chiral diene ligand, products can be obtained with high enantiomeric selectivities, where a pronounced matched/mismatched effect with the chirality of the allyl trifluoroborate is evident.

**Scheme 1.** Discovery of allylrhodium chain walking.

**Table 1: Investigation of imine scope (a–d)**

| Entry | Product | R   | Yield [%] |
|-------|---------|-----|-----------|
| 1     | 3a      | Me  | 68        |
| 2     | 3b      | H   | 72        |
| 3     | 3c      | OMe| 65        |
| 4     | 3d      | Br  | 65        |
| 5     | 3e      |     | 65        |
| 6     | 3f      | Me  | 65        |
| 7     | 3g      | Et  | 53        |
| 8     | 3h      | nBu | 54       |
| 9     | 3i      | (CH$_2$)$_3$Ph | 55   |
| 10    | 3j      | iPr | <5        |

[a] Reactions were conducted using 0.30 mmol of 1. The diastereomeric ratios were confirmed by $^1$H NMR analysis of the unpurified reactions. [b] Yield of isolated products. [c] The regiosomer 4a was isolated in 6% yield (Scheme 1). [d] In the unpurified reaction, traces of a product derived from allylation without chain walking were detected. [e] Isolated as an 87:13 mixture of 3d with the regiosomeric product 4d. See Ref. [13].

**Communications**

**Chain Walking of Allylrhodium Species Towards Esters During Rhodium-Catalyzed Nucleophilic Allylations of Imines**

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The migration of metal centers along carbon chains occurs in several important reactions.[1–7] Many of these migrations take place by β-hydride elimination and hydrometalation sequences, in which the direction of travel is controlled by thermodynamics, a ligand, or a nearby functional group. With few exceptions,[8–10] these migrations involve simple alkylmetal species. The ability to chain walk a metal together with a second functional group has significant synthetic opportunities, but this mode of reactivity remains largely underdeveloped. Herein, we describe, to our knowledge, the first examples of allylrhodium chain walking, and its application in the preparation of enantioenriched products.

During our studies of enantioselective Rh-catalyzed nucleophilic allylations of imines,[5] the reaction of imine 1a with racemic allyltrifluoroborate 2a in the presence of [Rh(cod)Cl]$_2$ (1.5 mol%) and iPrOH (5.0 equiv) was conducted (Scheme 1). Surprisingly, allylation at the α- or γ-carbon atoms relative to the boron atom of 2a was not observed. Instead, this reaction gave homoallylic sulfamates 3a (68% yield) and 4a (6% yield), each in > 95:5 d.r. (Scheme 1).[10–12] This result suggests the reactive intermediates are allylrhodium species 5 and 6, formed from migration of the allylrhodium species generated initially from transmetalation of 2a with rhodium.

The scope of this unexpected reaction was extended to include aldimines bearing methyl, methoxy, bromo, or dioxazole groups, which gave products with high diastereoselectivities in 65–72% yield (Table 1, entries 1–5). Ketimines containing linear alky groups at the imine carbon were also effective (entries 6–9). However, an isopropyl-substituted imine was recovered unchanged (entry 10). With one exception (entry 3), no products of allylation at the α- or γ-carbons relative to the boron atom of 2a were obtained. Furthermore, except for the reactions producing 3a and 3d (entries 1 and
4), the alternative regioisomers were difficult to detect by \(^1\)H NMR spectroscopy.

Next, the potassium allyltrifluoroborate was varied (Table 2). As well as ethyl esters (Table 1) and benzyl esters (Table 2, entries 1–5, 7, and 8), a 2-naphthyl ester was accommodated (Table 2, entry 6). Regarding the substituent \(\alpha\) to the boron atom, alkyl (entries 1, 2, 7, and 8) and chloroalkyl groups (entry 3) were tolerated. Product \(3l\) was isolated along with a product of allylation without allylrhodium chain walking, in a 95:5 ratio (entry 2).

[13] Alkyl substituents containing phenyl or benzyloxy groups resulted in lower conversions and yields (entries 4 and 5).

The reaction of \(1b\) with allyltrifluoroborate \(2h\), in which boron is bonded to a primary rather than a secondary carbon, gave not only \(3s\), but also a significant quantity of product \(7\) in 80:20 d.r., derived from allylation without chain walking [Eq. (1)]. The reaction of \(1b\) with allyltrifluoroborate \(2h\), in which boron is bonded to a primary rather than a secondary carbon, gave not only \(3s\), but also a significant quantity of product \(7\) in 80:20 d.r., derived from allylation without chain walking [Eq. (1)].

Interestingly, the reaction of \(Z\)-allyltrifluoroborate \(8\) with aldime \(1b\) gave \(3b\) in 70% yield (Scheme 2, top), which is the same product obtained from the corresponding \(E\)-isomer \(2a\) (Table 1, entry 2). Furthermore, despite possessing a substitution pattern different to all allyltrifluoroborates employed until this point, allyltrifluoroborate \(9\) reacted in the same manner to give \(3t\) (Scheme 2, bottom). These results suggest that regardless of the geometrical or positional isomerism of the allyltrifluoroborate within the \(\beta\) to \(\delta\) carbons, the reactions proceed through common types of allylrhodium intermediates. However, homoallylic boron reagents were unreactive.

Because these reactions provide chiral products from chiral substrates, we investigated whether enantioenriched allyltrifluoroborates would give enantioenriched products. However, attempts to purify \(3o\) by column chromatography were unsuccessful. A pure sample was obtained by preparative TLC.

Next, chiral rhodium complexes were investigated for their ability to provide enantioenriched products from racemic allyltrifluoroborates (Scheme 4).

Table 2: Investigation of allyltrifluoroborate scope.\(^[4]\)

\[
\begin{array}{ccc}
\text{Entry} & \text{Product} & \text{R} & \text{Yield [%]}\\
1 & 3k & \text{Me} & 69\\
2 & 3i & \text{Pr} & 70[4]\n\\
3 & 3m & (\text{CH}_2)_2\text{Cl} & 63\\
4[6] & 3n & \text{Ph} & 36 (59)[4]\n\\
5[6] & 3o & \text{OBn} & (53)[4]\n\\
6[6] & 3p & & 62\\
7 & 3q & \text{Me} & 67\\
8 & 3r & \text{Pr} & 58
\end{array}
\]

[a] Reactions were conducted using 0.30 mmol of \(1\). The diastereomeric ratios were confirmed by \(^1\)H NMR analysis of the unpurified reactions. [b] Yield of isolated products. [c] Isolated as a 95:5 mixture of \(3l\) and the product of allylation without allylrhodium chain walking. See Ref. [13]. [d] Using 2.5 mol% of \([\text{Rh}(\text{cod})\text{Cl}]_2\). [e] Yields in parentheses were determined by \(^1\)H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [f] Attempts to purify \(3o\) by column chromatography were unsuccessful. A pure sample was obtained by preparative TLC.

Scheme 2. Effect of geometrical and positional isomerism of the allyltrifluoroborate.
the yields of some of these reactions were low, and the scope is more limited than when using [[Rh(cod)Cl]_2]. For example, enantioselective additions to ketimines were unsuccessful. Interestingly, a pronounced matched/mismatched effect was observed with enantioenriched allyltrifluoroborates. The reaction of 1b with (R)-2a (94% ee) using chiral diene L1 gave (S,S)-3b with results identical to the reaction using racemic 2a (Scheme 5, top; compare with Scheme 4). However, the corresponding reaction with (S)-2a (94% ee) gave a complex mixture; although 3b was detected in small but unquantifiable amounts by 1H NMR analysis, it could not be isolated. Currently, it is unclear which steps of the proposed mechanism (see below) are rendered inefficient by the stereochemical mismatch of the ligand and the allyltrifluoroborate.

A proposed mechanism, using imine 1a and allyltrifluoroborate 2a as representative substrates, is shown in Scheme 6. The reaction of 2a with iPrOH can reversibly generate a mixed alkoxide/fluoride boron ate complex 11, which transmetalates with rhodium complex 10[14,15] to give interconverting allylrhodium species 12 and 13. β-Hydride elimination of 13 then gives a rhodium hydride species bound to ethyl sorbate (as in 14). [20,21] Hydrorhodation of the alkene distal to the ester then provides interconverting allylrhodium species 5 and 6. A possible driving force for this chain walking migration is the formation of a more stable, more conjugated
allylrhodium species \(5\). Nucleophilic alkylation of \(1\) by \(5\) through a chairlike conformation \(15\), in which the ethyl group is pseudoaxial to avoid unfavorable interactions with the cyclooctadiene ligand.\(^{[6e,22]}\) Finally, protonolysis of \(16\) with HX (X = Cl, F, or OTf) releases the product \(3\) and regenerates \(10\). The minor regioisomer \(4\) is the result of alkylation of \(1\) with allylrhodium species \(6\).

Support for this mechanism was provided by the reaction of aldimine \(1\), allyltrifluoroborate \(2\) (1.5 equiv), and allylsorbat (17, 1.5 equiv), using \([\text{Rh}(\text{C}_3\text{H}_5)_2\text{Cl}_2]\) as a precatalyst [Eq. (2)]. This reaction gave mostly unreacted \(1\) and 17, along with unidentified products resulting from decomposition of \(2\). However, by HPLC-MS, small quantities of the expected product \(3\) derived from allyltrifluoroborate \(2\) (0.4% yield), the crossover product \(3\) derived from ethyl sorbat (17; 3.4% yield), and \(\alpha,\beta,\gamma,\delta\)-unsaturated benzyl ester 18 (2.7% yield) were also detected.\(^{[13]}\)

![Scheme 6](image1)

Presumably, the initial catalytic species in this reaction is a complex of rhodium and ethyl sorbates (17), possibly the \(s\)-cis-\(\eta^1\) complex 19, which reacts with 2c according to the mechanism shown in Scheme 6 to give the rhodium hydride 20 (Scheme 7). Hydorohdration of the \(\alpha,\beta,\gamma,\delta\)-unsaturated benzyl ester would give allylrhodium species 21, which reacts with 1b to give the expected product 31. Alternatively, a structural reorganization of 20 could give 22, which can then undergo hydrorhodation of ethyl sorbate to give allylrhodium species 5 and the crossover product 3a.

In summary, we have reported the chain walking of allylrhodium species derived from \(\delta\)-trifluoroborol \(\beta,\gamma\)-unsaturated esters during the rhodium-catalyzed nucleophilic alkylation of imines, which gives products with two new stereocenters and a Z-alkene. Enantioselective catalysis is possible using a chiral diene ligand, where a strong matched/ mismatched effect was observed. Further exploration of this novel mode of reactivity is underway in our laboratories.

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