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Rhodium-Catalyzed Formation of Stereocontrolled Trisubstituted Alkenes from Baylis–Hillman Adducts

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Abstract: We report here efficient and general conditions for the formation of stereodefined trisubstituted alkenes using the rhodium-catalyzed reaction of unactivated Baylis–Hillman adducts with either organoboronic acids and potassium trifluoro(organo)borates. The use of the [{Rh(cod)OH}$_2$] precursor gave very fast coupling reactions under low catalyst loading, very mild reaction conditions (from room temperature up to 50 °C) and without the need of additional phosphane ligands. Based on the new reaction conditions, the reaction, originally limited to Baylis–Hillman adducts derived from esters, could be extended to a large variety of Baylis–Hillman adducts, bearing either keto, cyano or amido functionalities. Moreover, the reaction of Baylis–Hillman adducts bearing esters functionality was improved and could be conducted at lower temperature using lower catalyst loading.

Keywords: alkenes · boron derivatives · conjugate addition · heterogeneous catalysis · rhodium

Introduction

The Baylis–Hillman reaction is a very useful and operationally simple reaction allowing carbon–carbon bond formation under mild conditions.[1,2] The reaction products, called Baylis–Hillman adducts, are highly functionalized substrates bearing both allyl alcohol and α,β-unsaturated ester moieties. Indeed, they have been further functionalized by palladium-catalyzed Heck reactions[3] or Friedel–Crafts reactions.[4] S_N2'[5,6] or π-allyl-[7] type reactions have also been described on Baylis–Hillman adducts, but the allyl alcohol moiety had to be further transformed to carbonate or acetate, which are better leaving groups. For example, Kabalka et al. reported palladium-catalyzed cross-coupling reactions of Baylis–Hillman acetates with bis(pinacolato)diboron[8] or potassium trifluoro(organo)borates,[9] allowing the formation of stereodefined alkenes via π-allylpalladium intermediates.[10] In terms of atom economy,[11] the use of unactivated Baylis–Hillman adducts, would be more desirable but they are generally less reactive in transition metal catalyzed reactions.

We recently reported that organoboronic acids[12] and potassium trifluoro(organo)borates[13,14] reacted with simple Baylis–Hillman adducts, derived from α,β-unsaturated esters in the presence of a rhodium complex, affording stereodefined trisubstituted (*E*)-alkenes[15] under mild conditions via an unusual mechanism. The initial reported catalyst, [{Rh(cod)Cl}$_2$], was active at 50 °C for boronic acids and 70 °C for potassium trifluoro(organo)borates.[12,13] Even if these conditions were rather mild, reactions with others Baylis–Hillman adducts, and particularly those derived from enones, gave lower yields and the formation of by-products was observed (see below). During the course of our studies, we found that even milder conditions could be achieved using another rhodium catalyst precursor, [{Rh(cod)OH}$_2$],[16] allowing not only to conduct many reactions under air at room temperature, but also to extend this reaction to other Baylis–Hillman adducts, and particularly those derived from enones. Herein, we want to report our results concerning the development of a very general reaction for the formation of functionalized stereodefined trisubstituted alkenes from readily available substrates.

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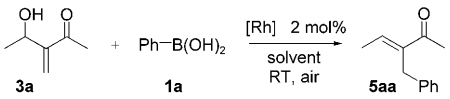
Results and Discussion

We have recently shown that, in the presence of commercially available [{Rh(cod)Cl}$_2$] catalyst precursor, boronic acids and potassium trifluoro(organo)borates added to the Baylis–Hillman substrates derived from α,β-unsaturated esters via 1,4-addition/β-hydroxyelimination process gave trisubstituted alkenes with high yields and stereoselectivities above 96:4 in favor of the *E* isomer.[12,13] However, when we wanted to extend these conditions to other Baylis–Hillman adducts, the results were disappointing. For example, reaction of phenylboronic acid (**1a**) with **3a** under previously described conditions[12] afforded only 50% yield of the expected alkene **5aa**, even if the conversion was quantitative (Table 1, entry 1); lower reaction temperatures did not increase the yields that much (entry 2). In order to achieve acceptable yields on the substrates, other reaction conditions were evaluated and particularly other rhodium catalyst precursors. We were pleased to find that a cationic rhodium (entry 3), and, even better, a hydroxy–rhodium (entry 4) were particularly suitable for this reaction, which was now fast even at room temperature. Most impressive, the reaction conducted with 1 mol% [{Rh(cod)OH}$_2$] was finished in less than five minutes and the expected alkene **5aa** was isolated in 88% yield (entry 5).

Table 1. Optimization of the reaction conditions for the addition of **1a** to **3a**.[a]



Entry	[Rh]	Solvent	Conversion[b]	*t*
1	[{Rh(cod)Cl}$_2$]	MeOH	100[c] (50)	30 min
2	[{Rh(cod)Cl}$_2$]	MeOH	100 (60)	6 h
3	[Rh(cod)$_2$]PF$_6$	MeOH	100	30 min
4	[{Rh(cod)OH}$_2$]	MeOH	100 (89)	5 min
5	[{Rh(cod)OH}$_2$]	MeOH	100[d] (88)	5 min
6	[{Rh(cod)OH}$_2$]	isopropanol	83	30 min
7	[{Rh(cod)OH}$_2$]	toluene	72	30 min
8	[{Rh(cod)OH}$_2$]	dioxane	77	30 min
9	[{Rh(cod)OH}$_2$]	DMF	< 10	1 h
10	[{Rh(cod)OH}$_2$]	H_2O	0	4 h

[a] Reactions conducted by using 0.5 mmol Baylis–Hillman adduct **3a**, 1 mmol of **1a** with 2 mol% [Rh] at RT in 2 mL of solvent. [b] Conversion determined by GC. Isolated yields in brackets. The isomeric ratio was 99:1 in favor of the *E* isomer. [c] Reaction conducted at 50°C. [d] Reaction conducted with 1 mol% [Rh].

Other solvents were also evaluated using the hydroxy–rhodium catalyst precursor (entries 5–10) but no beneficial effect was observed in nonprotic solvents. Indeed, as shown before,[12] alcoholic solvents are also most suitable for the reaction of Baylis–Hillman adducts with boronic acids using [{Rh(cod)OH}$_2$]. Using the same catalyst precursor, and the previously optimized solvent system (toluene/MeOH 1:1),[13] the addition of potassium trifluoro(phenyl)borate (**1a′**) to **3a** also occurred at room temperature, but the reaction was slower (at least 24 h for complete conversion). Indeed, in order to shorten the reaction time, reactions with potassium aryltrifluoroborates were best conducted at 50°C; in all reactions examined, complete conversion was observed within hours.

A comparison of the reactivity of the two catalyst precursors, [{Rh(cod)OH}$_2$] and [{Rh(cod)Cl}$_2$], was evaluated in the reaction of Baylis–Hillman adduct **3a** with phenylboronic acid (**1a**) under optimized conditions (Figure 1). In the case of the hydroxy–rhodium precursor, the reaction was completed within a few minutes at room temperature, whereas more than 5 h were necessary with the chloride–rhodium precursor. More surprisingly, fast reaction was also observed using [{Rh(cod)OH}$_2$] when the reaction was conducted at 0°C (Figure 1). In view of the postulated reaction mechanism, where a hydroxy–rhodium species is generated after β-hydroxy elimination,[12,13] the result suggests that the chloride anion is not a spectator ligand in this reaction, because, on the contrary, similar reaction rates should be observed with this two catalyst precursors after an inductive period. Further studies are currently under way in our laboratory in order to investigate the exact role played by the rhodium counter-anion.

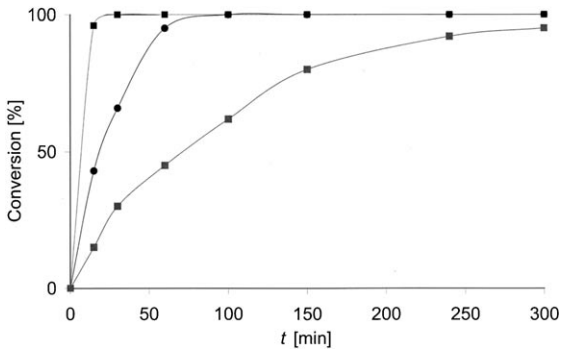


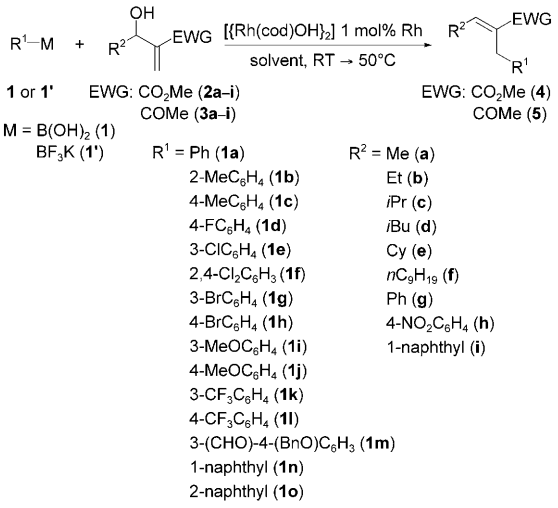
Figure 1. Compared reactivity of [{Rh(cod)OH}$_2$] and [{Rh(cod)Cl}$_2$] in the addition of **1a** to **3a** (0.5 mol% [{Rh(cod)OH}$_2$] at 20 (■) and at 0°C (●); 0.5 mol% [{Rh(cod)Cl}$_2$] at 20°C (■)).

The generality of the reaction conditions was evaluated on various Baylis–Hillman adduct with either boronic acids **1** or trifluoroborate species **1′** (Scheme 1). The new optimized experimental conditions were first re-evaluated on the reaction of Baylis–Hillman adducts **2** derived from ester (EWG = CO_2Me). In reactions with arylboronic acids, Baylis–Hillman adducts **3** afforded the expected trisubstituted alkenes in good yields and high stereoselectivity (Table 2). With all substrates examined, reactions were completed within a few minutes at room temperature using only 1 mol% of rhodium catalyst precursor. Moreover, faster reactions and generally higher yields of alkenes were observed compared with the reaction using previously published reaction conditions: [{Rh(cod)Cl}$_2$] at 50°C (entries 2, 4, 9, 14).[12] Once again, it appeared that either aromatic or aliphatic Baylis–Hillman adducts show similar reactivity.[17]

Table 2. Formation of trisubstituted alkenes from Baylis–Hillman adduct **2** derived from enoates.[a]

Entry	**1** or **1′**	**2**	Product **4**	Yield[b] with $R^1B(OH)_2$ [%]	Yield[c] with R^1BF_3K [%]	*E*/*Z*[d]
1	**1a**	**2a**	**4aa**	86	(86)[f]	99:1
2	**1b**	**2a**	**4ba**	98 (85)		>99:1
3	**1c**	**2a**	**4ca**	(95)		99:1
4	**1d**	**2a**	**4da**	87 (87)		99:1
5	**1g**	**2a**	**4ga**		54 (60)	99:1
6	**1h**	**2a**	**4ha**	89 (95)		98:2
7	**1i**	**2a**	**4ia**	(65)	74 (83)[f]	99:1
8	**1l**	**2a**	**4la**	82 (86)[e]	(63)[e]	99:1
9	**1o**	**2a**	**4oa**	73	(98)	98:2
10	**1a**	**2d**	**4ad**	93 (61)	(91)	96:4
11	**1d**	**2d**	**4dd**	82		94:6
12	**1n**	**2e**	**4ne**		95	88:12
13	**1a**	**2f**	**4af**	(75)	(70)[f]	96:4
14	**1e**	**2f**	**4ef**	(75)		97:3
15	**1a**	**2g**	**4ag**	99 (74)	(98)[f]	97:3
16	**1j**	**2g**	**4jg**	>99	45	96:4
17	**1o**	**2g**	**4og**		>99 (98)	97:3
18	**1a**	**2h**	**4ah**	72 (86)	(58)	96:4

[a] Reactions conducted by using 0.5 mmol Baylis–Hillman adduct **2** and 1 mmol of RBF_3K or $RB(OH)_2$. [b] Yields obtained by conducting the reaction in MeOH at RT with 0.5 mol% [{Rh(cod)OH}$_2$]. Between parenthesis, yields obtained by using the previous system: MeOH, 50°C with 0.5 mol% [{Rh(cod)Cl}$_2$]. [c] Yields obtained by conducting the reaction in Tol/MeOH 1:1 at 50°C with 0.5 mol% [{Rh(cod)OH}$_2$]. Between parenthesis, yields obtained by using the previous system: Tol/MeOH, 70°C with 1.5 mol% [{Rh(cod)Cl}$_2$]. [d] Determined by GC–MS and ^{1}H NMR spectroscopy. [e] From ref. [12]. [f] From ref. [13].



Scheme 1. Rhodium-catalyzed formation of stereodefined trisubstituted alkenes.

Concerning the isomeric *E*/*Z* ratio, they are uniformly high for aliphatic substituted Baylis–Hillman adducts (99:1, entries 1–11), but they are slightly decreased when the steric hindrance of the substituent is increased: from 96:4 for aromatic substituents (entries 15–18) to 88:12 for cyclohexyl substituents (entry 12). In reactions with potassium trifluoro(organo)borates, good yields and selectivities were also achieved for those Baylis–Hillman adducts. However, compared with the reaction with boronic acids, these new conditions did not result in increased yields. Identical levels of isomeric purities were observed in the reactions involving potassium trifluoro(organo)borates compared with those involving boronic acids. Importantly the yields and isomeric purities of the trisubstituted alkenes **4** are not influenced by the electronic properties (electron-withdrawing or -releasing substituents) of the arylboron derivative. Overall these new reaction conditions compare favorably to the previous reported for the reactions of Baylis–Hillman adducts derived from α,β-unsaturated esters: lower reaction temperature, comparable yields and selectivities, lower catalyst loading for the reactions involving potassium trifluoro(organo)borates (1 mol% compared with 3 mol% previously used).[13]

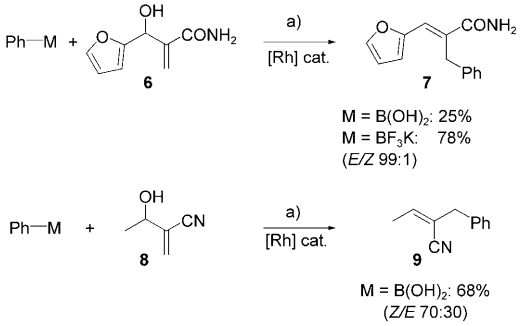
Under these optimized conditions, we also evaluated the generality of the reaction of Baylis–Hillman adducts **3** derived from enones. As mentioned before, under our previous conditions using [{Rh(cod)Cl}$_2$], low yields were observed despite quantitative conversion. These low yields were attributed to the decomposition of the Baylis–Hillman adduct, which are prone to polymerization under slow reaction conditions (low catalytic activity). However, when using the highly efficient hydroxy–rhodium precursor, we were pleased to find that these sensitive substrates do participate to the reaction, affording, once again, stereodefined trisubstituted alkenes in good yields and selectivities (Scheme 1, Table 3). Very high yields were generally achieved independently to the electronic nature of aryltrifluoroborates or arylboronic acids and, to a given Baylis–Hillman adduct, isomeric ratios were constant. From the results it also appears, as observed for Baylis–Hillman adduct derived from α,β-unsaturated esters, that increasing steric hindrance on the aliphatic R^2 moiety resulted in a slight decrease of the isomeric ratio: from more than 99:1 (entries 1–23) to merely 97:3 for isopropyl substituted Baylis–Hillman adduct **3c** (entries 24–26), still in favor of the *E* isomer. Notably higher yields, but comparable *E*/*Z* ratios, were generally observed using potassium trifluoro(organo)borates compared with boronic acids (entries 1–4, 12, 18): for example, in the addition to Baylis–Hillman substrate **3a**, alkene **5aa** was obtained in 89% yield using phenylboronic acid (**1a**), whereas the yield was improved to 99% using potassium trifluoro(phenyl)borate (**1a′**, entry 1). Indeed, this reaction affords a straightforward access to highly useful enones, which are susceptible to further functionalization by Michael-type addition reactions.[18]

The reaction conditions are not limited to Baylis–Hillman adducts derived from α,β-unsaturated esters and ketones. For example, reaction of Baylis–Hillman adduct **6** (Scheme 2), derived from α,β-unsaturated amide also underwent the coupling reaction to afford functionalized amide **7** with high stereoselectivity (*E*/*Z* 99:1). A moderate yield was achieved using phenylboronic acid as coupling partner, whereas the use of potassium trifluoro(phenyl)borate (**1a′**) allowed the formation of trisubstituted alkene **7** in a 78% yield. The lower yield observed in the reaction with boronic

Table 3. Formation of trisubstituted alkenes from Baylis–Hillman adduct **3** derived from enones.[a]

Entry	**1** or **1′**	**3**	Product **5**	Yield[b] with $R^1B(OH)_2$ [%]	Yield[c] with R^1BF_3K [%]	*E*/*Z*[d]
1	**1a**	**3a**	**5aa**	89	99	>99:1
2	**1b**	**3a**	**5ba**	71	54	>99:1
3	**1d**	**3a**	**5da**	80	88	>99:1
4	**1e**	**3a**	**5ea**	44	76	>99:1
5	**1f**	**3a**	**5fa**	72		>99:1
6	**1g**	**3a**	**5ga**	43		99:1
7	**1i**	**3a**	**5ia**	40	36	>99:1
8	**1j**	**3a**	**5ja**	85		>99:1
9	**1k**	**3a**	**5ka**	80		>99:1
10	**1l**	**3a**	**5la**	73		>99:1
11	**1n**	**3a**	**5na**	82		99:1
12	**1o**	**3a**	**5oa**	79	81	>99:1
13	**1a**	**3b**	**5ab**	73		>99:1
14	**1b**	**3b**	**5bb**	80		>99:1
15	**1d**	**3b**	**5db**	89		99:1
16	**1e**	**3b**	**5eb**	89		99:1
17	**1g**	**3b**	**5gb**		52	>99:1
18	**1i**	**3b**	**5ib**	50	59	99:1
19	**1j**	**3b**	**5jb**	70		>99:1
20	**1l**	**3b**	**5lb**	95		>99:1
21	**1m**	**3b**	**5mb**		48	
22	**1n**	**3b**	**5nb**	68		>99:1
23	**1o**	**3b**	**5ob**		70	>99:1
24	**1b**	**3c**	**5bc**	56		96:4
25	**1j**	**3c**	**5jc**	83		97:3
26	**1k**	**3c**	**5kc**	50		>99:1

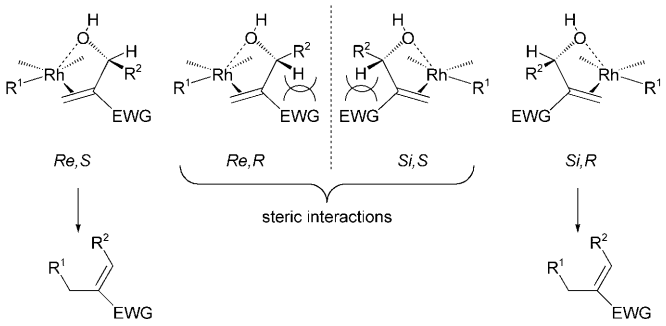
[a] Reactions conducted by using 0.5 mmol Baylis–Hillman adduct **3** and 1 mmol of RBF_3K or $RB(OH)_2$ in the presence of 0.5 mol% [{Rh(cod)OH}$_2$]. [b] Yields obtained by conducting the reaction in MeOH at RT. [c] Yields obtained by conducting the reaction in Tol/MeOH 1:1 at 50°C. [d] Determined by GC–MS and ^{1}H NMR spectroscopy.



Scheme 2. Extension to other Baylis–Hillman adducts.

acid **1a** can be attributed to the lower reaction temperature, as well as the lower reactivity of such a Baylis–Hillman adduct. Similarly, cyano derivative Baylis–Hillman adduct **8** also participated in the reaction. The coupling with phenylboronic acid afforded the cyano-alkene **9** in 68% yield. Interestingly, and as observed in Friedel–Crafts reactions with such adducts,[19] reversed, although moderate, selectivity was observed and the *Z* isomer was the major isomer formed. Although we don't have any supported explanation to account for the observed stereoselectivities, it is surprising that the stereoselectivities observed in this rhodium-catalyzed reaction are very similar to Lewis acid catalyzed Friedel–Crafts reaction[20] or uncatalyzed addition of organometallics[5] to acetates of Baylis–Hillman adducts. In our proposed reaction mechanism,[12,13] which was partially validated by deuterium labeling studies, after transmetalation of the arylborane moiety insertion of the alkene in the aryl–rhodium bond occurs, which affords an alkyl–rhodium species bearing an hydroxy substituent in the β-position of the rhodium center. Subsequently, β-hydroxy elimination occurs to afford the trisubstituted alkene and an active hydroxy–rhodium species.

Indeed, the stereoselectivity observed for the obtained trisubstituted alkenes originates from the complexation of the starting Baylis–Hillman adduct to the rhodium center, that is, before the irreversible C–C bond formation.[16a,21] Moreover, the stereoselectivity observed is independent of the configuration of the hydroxyl group (a racemic mixture is used as starting material). Once transmetalation has occurred, four different complexes can be formed upon complexation of the starting Baylis–Hillman adduct, depending on the configuration of the hydroxyl substituent and the face of complexation (Scheme 3), assuming that the hydroxy

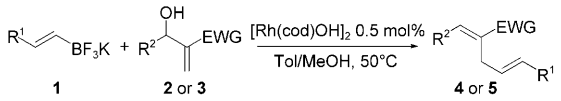


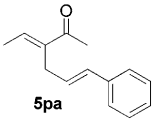
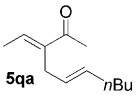
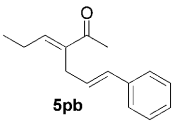
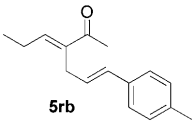
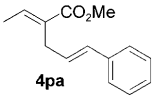
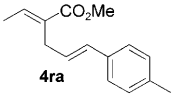
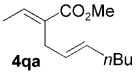
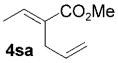
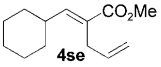
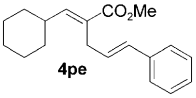
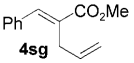
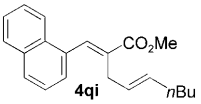
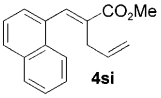
Scheme 3. Tentative explanation of the observed stereoselectivities.

substituent is also partially complexed to the rhodium(I) center. We believe that steric interaction between R^2 and EWG substituents is responsible of the lowest stability of complexes *Re*,*R* and *Si*,*S*, which should have resulted in the formation of (*Z*)-trisubstituted alkenes. Indeed, depending on the configuration of the hydroxy substituent of the starting Baylis–Hillman adduct, two equivalent complexes *Re*,*S* or *Si*,*R* can be formed, which leads to the formation to the (*E*)-trisubstituted alkenes. The lowest and slightly reversed stereoselectivities obtained with cyano Baylis–Hillman derivatives can be explained by lowest interaction between R^2 and EWG, resulting in the formation of the different rhodium isomers in variable proportions. Further studies, and particularly DFT studies, are currently conducted in our laboratory.

Due to their ready availability and higher stability compared with trivalent organoboron derivatives, the reactivity of potassium alken-1-yltrifluoroborates[14] was also evaluated under these reaction conditions, using either Baylis–Hillman adducts bearing ketone (Table 4, entries 1–4) or ester functionalities (entries 5–13). Indeed, in the presence of

Table 4. Rhodium-catalyzed formation of 1,4-dienes.[a]



Entry	Product	Yield [%]	*E*/*Z*[b]
1	 **5pa**	70	99:1
2	 **5qa**	80[c]	99:1
3	 **5pb**	86	97:3
4	 **5rb**	93 (84)	99:1
5	 **4pa**	(84)[d]	98:2
6	 **4ra**	93 (91)[d]	98:2
7	 **4qa**	93	99:1
8	 **4sa**	75[c]	98:2
9	 **4se**	80	90:10
10	 **4pe**	95	92:8
11	 **4sg**	97	99:1
12	 **4qi**	43	96:4
13	 **4si**	57 (44)[d]	96/4

[a] Reactions conducted by using 0.5 mmol Baylis–Hillman adduct **2** or **3** and 1 mmol of RBF_3K in the presence of 0.5 mol% [{Rh(cod)OH}$_2$] in Tol/MeOH 1:1 at 50°C. [b] Determined by GC–MS and ^{1}H NMR spectroscopy. [c] Reaction conducted at 80°C. [d] From ref. [13].

0.5 mol% [{Rh(cod)OH}$_2$], potassium alkenyltrifluoroborates added smoothly to Baylis–Hillman adducts affording useful 1,4-dienes in high yields and high stereoselectivities on both double bonds: (*E*)-alkene from the α,β-unsaturated moiety while maintaining the geometry of the incoming organometallic partner. Compared with previous reaction conditions, similar or slightly higher yields were obtained, while using lower catalytic loading (three times less). More particularly, useful potassium vinyltrifluoroborate[22,14] also participated in this reaction, which afforded the expected 1,4-dienes in good yields (entries 8–9, 11,13). Once again lower stereoselectivities were observed when the steric hindrance on the R^2 substituent was increased (entries 9–10). Thus, using this efficient catalytic reaction, highly functionalized 1,4-dienes were easily accessible from readily available reagents: an aldehyde, a Michael acceptor (the Baylis–Hillman reagent) and potassium alkenyltrifluoroborate.

Conclusion

We have described and extended an highly efficient reaction to access stereodefined trisubstituted alkenes from the coupling of readily available Baylis–Hillman adducts with either organoboronic acids or potassium trifluoro(organo)borates. Compared with their trivalent congeners, trifluoroborate derivatives show several advantages in terms of stability and ease of preparation and purification.[14] High yields were generally achieved using a large variety of Baylis–Hillman adducts derived from α,β-unsaturated esters, ketones, amides and cyano derivatives. This reaction, involving a 1,4-addition/β-hydroxy elimination mechanism, presents several attractive features, not only because of the simple reaction conditions (low temperature, aerobic conditions) but also by the use of easily accessible Baylis–Hillman adducts as starting materials. We hope that this methodology will provide new opportunities in organic synthesis due to its high versatility and the ready availability of the reagents.

Experimental Section

Typical procedure for the reaction of organoboronic acids or potassium trifluoro(organo)borates with Baylis–Hillman adducts: A mixture of the Baylis–Hillman adduct (0.5 mmol), potassium trifluoro(organo)borate or organoboronic acids (2 equivalents), [{Rh(cod)OH}$_2$] (2.2 mg, 0.5 mol%) were placed in a flask and then a toluene/methanol mixture (1 mL, for RBF_3K) or methanol (1 mL, for $RB(OH)_2$) were added at room temperature. The flask was closed and the reaction mixture was stirred at the indicated temperature until completion of the reaction (followed by GC analysis). Purification by silica gel chromatography afforded analytically pure products.

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