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Synthesis of *Z*-(Pinacolato)allylboron and *Z*-(Pinacolato)alkenylboron Compounds through Stereoselective Catalytic Cross-Metathesis

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Abstract

The first examples of catalytic cross-metathesis (CM) reactions that furnish *Z*-(pinacolato)allylboron and *Z*-(pinacolato)alkenylboron compounds are disclosed. Products are generated with high *Z* selectivity by the use of a W-based mono-aryloxy pyrrolide (MAP) complex (up to 91% yield and >98:2 *Z:E*). The more sterically demanding *Z*-alkenylboron species are obtained in the presence of Mo-based MAP complexes in up to 93% yield and 97% *Z* selectivity. *Z*-selective CM with 1,3-dienes and aryl olefins are reported for the first time. The utility of the approach, in combination with catalytic cross coupling, is demonstrated by a concise and stereoselective synthesis of anti-cancer agent combretastatin A-4.

Organoboron compounds are vital to chemical synthesis, and among them, (pinacolato)allylboron [allyl-B(pin)] and (pinacolato)alkenylboron [vinyl-B(pin)] reagents hold a prominent position.¹ The former set is used in countless stereoselective additions² and the latter are partners in a myriad of catalytic cross couplings.³ Since the stereochemical outcome of transformations with such entities is contingent on whether a *Z*- or an *E*-organoboron is employed,^{4,5} of considerable value are methods for facile and efficient access to stereodefined acyclic allyl-B(pin) and alkenyl-B(pin) compounds. Contrary to the *E* isomers, however, protocols for selective synthesis of higher energy *Z*-allyl- or *Z*-alkenylboron species are uncommon, and especially scarce are related processes that are catalytic. Nicatalyzed hydroboration of dienes has been shown to afford *Z*-allyl-B(pin) products;⁶ Ir-, Rh-⁷ and, most recently, Ru-catalyzed⁸ methods for trans boron-hydride additions to terminal alkynes have been devised to furnish *Z*-alkenyl-B(pin) compounds. Such protocols were introduced as alternatives to non-catalytic procedures, which, while highly stereoselective, are multi-step and require strong base (e.g., *n*-BuK^{9a} or *n*-BuLi^{9b}) or acid (e.g., glacial acetic acid).¹⁰ Stereoselective cross-metathesis (CM)¹¹ of commercially available allyl- or alkenyl-B(pin) with terminal alkenes offers an attractive general strategy for synthesis of *Z*-allyl- or *Z*-alkenylboron entities (Scheme 1), one that is entirely distinct from catalytic alkyne hydroborations mentioned above; nonetheless, all existing CM protocols deliver the corresponding *E* isomers predominantly.¹² Herein, we demonstrate that catalytic CM can be used to access *Z*-allyl- or *Z*-alkenylboron compounds efficiently and

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Supporting Information Available: Experimental procedures and spectral, analytical data for all products (PDF). This material is available on the web: <http://www.pubs.acs.org>.

with high stereoselectivity.¹³ Transformations are promoted by W or Mo complexes, offering a generalizable, and at times unique, entry to stereoselective synthesis of a range of valuable organoboron reagents and intermediates.

We began by examining reactions with allyl-B(pin) **4**. A challenge in promoting this class of transformations does not lie as much in attaining high efficiency but rather in whether erosion of kinetic stereoselectivity due to post-CM isomerization can be avoided as the reaction progresses towards high conversion.^{13a} Thus, although we had determined earlier that *Z*-selective homocoupling of allyl-B(pin) can be promoted efficiently with Mo-based mono-aryloxy pyrrolide (MAP) complexes,¹⁴ access to the less hindered disubstituted alkenes would require identifying a catalyst that strikes the desired balance between reactivity and selectivity. As the screening data in entries 1–4 of Table 1 indicate, when Mo-based MAP complexes **1a–b** or **2a–b** are used, CM of allyl-B(pin) **4** and 1-decene proceeds readily to 50–75% conversion, but *Z* selectivity is moderate (69:31–87:13 *Z:E*). Control experiments indicate stereoselectivity is diminished as the reactions proceed further; this is especially true when the more reactive adamantylimido alkylidenes derived from **1a** are involved (63% conv and ~1:1 *Z:E* after 24 h), although such complexes likely deliver high kinetic *Z* selectivity consistent with the previously suggested stereochemical model (large size difference between the adamantyl and aryloxy ligands).^{13a,c} With the more hindered Mo arylimido systems, there is less post-CM isomerization (vs **1a–b**), but kinetic selectivity is probably also lower based on the above rationale. In the presence of the less active but more stereodifferentiating W alkylidene **3** (increased size differential between imido and aryloxy groups),^{13a,c} **6a** is isolated with 95:5 *Z:E* selectivity (entry 5, Table 1);¹⁵ oxidative workup delivers *Z*-allylic alcohol **6a** in 65% overall yield. To the best of our knowledge, this is the first report of a W-catalyzed *Z*-selective CM. Reactions with commonly used and moderately *E*-selective Ru-based carbenes require 12 hours at 40 °C (e.g., Grubbs second-generation: 18% yield of **6a**, 73% *E*, in 2.0 h at 22 °C);^{12a} when Mo(CHCMe₂Ph)(N(2,6-*i*-Pr)₂C₆H₃)(OCMe(CF₃)₂)₂ (**7**) is used, **6a** is obtained in 54% yield and with moderate *E* selectivity (76:24 *E:Z*).¹⁶

Various terminal alkenes undergo *Z*-selective CM with allyl-B(pin) **4** within two hours at ambient temperature (Scheme 2). The *Z*-disubstituted allyl-B(pin) compounds, sensitive to purification and isolation, were directly treated with benzaldehyde to afford the derived homoallylic alcohols; the diastereoselectivity levels with which **8a–8f** and **10** are obtained serve as an indicator of the isomeric purity of the corresponding allyl-B(pin) intermediate.¹² Disubstituted allylboron compounds are formed in 91:9 to >98:2 *Z:E* selectivity (based on dr) and the unsaturated alcohols are isolated in 68–91% yield. In one instance (**8e**), the use of Mo complex **2a** is required, since the sizeable silyl ether likely causes the W alkylidenes derived from **3** to be less efficient (30% conv, 23% yield). Furthermore, the disubstituted alkene in **5e** is relatively hindered and *Z*-to-*E* interconversion by post-CM isomerization with the more active Mo catalyst is less of a factor (vs a more accessible alkene such as **5a**). Another notable finding in Scheme 2 relates to the first instance of a *Z*-selective CM reaction with a 1,3-diene,¹⁷ affording **10** in 72% yield and 95:5 dr; such products were not reported in connection to the aforementioned Ni-catalyzed protocol.⁶

Next, we probed the possibility of *Z*-selective CM with vinyl-B(pin) **11**. This class of transformations, Mo- or W-catalyzed variants of which are unknown, poses several distinct challenges. In contrast to formerly reported processes^{13a} as well as those mentioned above, the p orbital at the boron center of a B(pin)-substituted alkylidene can stabilize electron density at the alkylidene carbon to diminish catalyst activity. Furthermore, vinylboron **11** is more sterically demanding than the cross partners examined thus far (including allyl-B(pin) **4**).^{13a}

Catalyst screening was performed with **11** and β -branched terminal alkene **12** (Table 2); there is appreciable conversion to **13a** (50–95% conv) and 86:14 *Z:E* selectivity under conditions where, unlike reactions with **4**, vinyl-B(pin) **11** is present in excess. In additional contrast to syntheses of the more exposed alkenes of *Z*-allyl-B(pin)s **5a–f** (Table 1), it is Mo complexes **2a–b** that provide the highest efficiency and stereoselectivity: **13a** is obtained in ~68% yield and 93:7 *Z* selectivity (entries 3–4, Table 2). CM is highly *Z*-selective with the less sterically demanding **1a**, but CM proceeds to only 56% conv (entry 1, Table 2); this is likely due to lower stability of the derived alkylidenes, including the methyldiene generated from ethylene formed as the byproduct (ambient pressure used). As expected, reaction with W-based **3** proceeds less readily than with most Mo variants, but, surprisingly, and for reasons that are unclear, it is less stereoselective (entry 5; 86:14 *Z:E*). We elected to use complex **2a** for further studies (vs **2b**), for its relative ease of preparation.

Two additional points regarding CM with **11** merit note: (1) Unlike reactions with excess amounts of unhindered terminal alkenes, including allyl-B(pin) **4**, stereoselectivities do not improve under vacuum. This might arise from competitive formation of the relatively stable B(pin)-substituted alkylidene, preventing the availability of methyldiene complexes, which are more reactive and thus capable of promoting isomerization.¹⁸ Moreover, use of excess vinyl-B(pin) **11** reduces the concentration of alkyl-substituted alkylidenes, species that are better capable of causing loss of stereoselectivity (vs B(pin)-substituted alkylidenes).¹⁹ (2) Reactions with 5.0 mol % second-generation Grubbs catalyst or the corresponding phosphine-free variant are efficient, but afford **13a** in ~90:10 *E:Z* selectivity (~70% yield).¹⁶ When Mo bis-alkoxide **7** is used, there is only 33% conversion of **12** after 10 min (no further conv after 24 h), and **13a** is isolated in 15% yield and 68:32 *Z:E*.^{16,20} The latter inefficiency might be attributed to the low stability of the highly Lewis acidic bis(hexafluoro)-alkoxide Mo alkylidene, rendered more electron-deficient by its B(pin) substituent. The significantly higher conversion values furnished by the more robust MAP complexes (Table 2) are therefore noteworthy.²¹

An assortment of *Z*-alkenyl-B(pin) compounds can be obtained in 51–92% yield after purification, in contrast to allylboron compounds, and 90:10–97:3 *Z:E* (Scheme 3). Reactions with a sizeable cyclohexyl (**13d**) or silyl ether (**13e**) substituent or an electron-deficient allylic amide (**13f**) proceed to 78–94% conv, affording the *Z*-alkenyl-B(pin) products in 51–71% yield and 93:7–96:4 *Z:E* ratio. Stereoselective synthesis of *Z,E*-diene **13g** (72% yield, 93% *Z*) provides another example of CM involving an acyclic 1,3-diene. Enol ether **13h** is formed in 93:7 *Z:E* selectivity and isolated as the pure *Z* isomer (>98%) in 80% yield. Allyl-B(pin) **13i**, obtained in 60% yield²² and 97:3 *Z:E*, belongs to a class of reagents with demonstrated utility in stereoselective synthesis;²³ the CM strategy can allow access to related entities that bear differentiated boryl units. *Z*-Alkenyl-B(pin) entities represented by **13g–i** were not prepared through the aforementioned Ir-, Rh- or Ru-catalyzed alkyne hydroborations.^{7–8}

We then turned to reactions involving the most sterically demanding combination of substrates thus far: CM between vinyl-B(pin) and styrenes; in the context of *Z*-selective transformations, aryl olefins have only been used in ring-opening/CM processes.^{13c} CM of **11** and styrene proceeds with maximum *Z* selectivity when the more stereodifferentiating adamantylimido Mo MAP complex **1a** is employed; **14a** is isolated in 66% yield and 95:5 *Z:E* ratio.²⁴ Reactions with electron-rich methoxy-substituted styrenes proceed with similarly high *Z* selectivity (**14b–c** in 69% yield and 93:7–95:5 *Z:E*). CM with *p*-(trifluoromethyl)styrene is highly efficient, proceeding to 97% conversion to afford **14d** in 93% yield and 95:5 *Z:E*. In general, higher efficiencies are observed with excess styrene (vs **11**); this might be attributed to the more reactive benzyldienes being better capable of undergoing CM with **11** vs an electronically stabilized B(pin)-substituted alkylidene (from

initial reaction with **11**) reacting with an aryl olefin. Furthermore, electron-rich styrenes (cf. **14c** and **14e**) are less prone to homodimerization (reaction with another electron-rich olefin) than CM with electron deficient **11**, and can therefore be employed in relatively slight excess (1.5 equiv). Finally, in contrast to transformations with alkyl olefins (Scheme 3), reduced pressure (100 torr) leads to improved selectivity probably because the methylenide derived from adamantylimido **1a** is more reactive and readily subject to decomposition (e.g., **14a** formed in 60:40 *Z:E* at ambient pressure).^{13a}

It is significant that the catalytic protocol is effective for synthesis of trimethoxyaryl-substituted vinyl-B(pin) **14e** (73% yield, 96:4 *Z:E*; Scheme 4); Pd-catalyzed cross coupling with the appropriate aryl bromide affords combretastatin A-4, a member of a class of anti-tumor agents. Stereoselective synthesis of the medicinal agent, 10 000 times more active than its *E* isomer,²⁵ demonstrates the power of combining catalytic CM and Suzuki-Miyaura-type processes to obtain congested *Z*-alkenes by an approach that is more concise than those adopted formerly.^{25,26}

The studies described above put forth several key additions to a limited repertoire of efficient *Z*-selective CM reactions.^{13,27} A W- and two Mo-based alkylidenes have emerged as optimal catalysts, underscoring the importance of the structural and chemical diversity of high oxidation-state alkylidenes to the development of methods that bear substantial scope. Equally notable is the facility with which the reactions of sterically demanding substrates proceed; this is in contrast to the activity levels exhibited thus far by *Z*-selective Ru-based carbenes.²⁷ Development of additional catalysts and methods for stereoselective olefin metathesis reactions are in progress.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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- (19). Vinyl-B(pin) **11** undergoes relatively facile, and likely not readily reversible, homocoupling to generate ethylene, providing another rationale for the higher conv observed when it is used in excess
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Scheme 1.

Scheme 2. Z-Selective Catalytic CM with Allyl-B(pin) **4**^a

^aReactions were performed in C₆H₆ at 22 °C with 5.0 equiv of cross partner. All yields are overall for two steps. Synthesis of **8e** involved the use of Mo complex **2a** under otherwise identical conditions, and formation of **8f** involved treatment with NaOH. See the Supporting Information (SI) for details.

Scheme 3. Z-Selective Catalytic CM with Vinyl-B(pin) 11: Generality^a

^aReactions were performed in C₆H₆ at 22 °C with 5.0 equiv **11**; yields are of Z/E mixtures, except for **13h** (>98% Z). See the SI for details.

Scheme 4. Z-Selective CM with Vinyl-B(pin) 11 and Styrenes^a

^aReactions were performed in C₆H₆ at 22 °C with 5.0 equiv styrene under N₂ atm., except for **14c** and **14e** where 1.5 equiv was used; yields are of Z/E mixtures. See the SI for details.

Table 1*Z*-Selective CM with Allyl-B(pin) 4: Catalyst Screening^a

entry	complex; mol %	time (h)	conv (%) ^b	yield of 6a (%) ^c	<i>Z:E</i> ^b
1	1a; 3.0	4.0	50	nd	87:13
2	1b; 3.0	24	66	nd	81:19
3	2a; 5.0	5.0	75	nd	78:22
4	2b; 5.0	4.0	52	nd	69:31
5	3; 5.0	2.0	78	65	95:5

nd = not determined.

^aReactions performed in C₆H₆ under N₂ atm with 5.0 equiv 1-decene; oxidative workup: H₂O₂, NaOH, 22 °C, 2.0 h.^bDetermined by analysis of ¹H MMR spectra of unpurified mixtures (of 5a for conv and of 6a for *Z:E*) and refer to consumption of the limiting substrate (±2%). See the Supporting Information for details.^cYield of isolated and purified 6a (isomeric mixture).

Table 2*Z*-Selective CM with Vinyl-B(pin) **11**: Catalyst Screening^a

entry	complex; mol %	conv (%) ^b	yield (%) ^c	<i>Z:E</i> ^b
1	1a ; 3.0	56	nd	96:4
2	1b ; 3.0	50	nd	93:7
3	2a ; 5.0	95	68	93:7
4	2b ; 5.0	98	69	93:7
5	3 ; 5.0	66	nd	86:14

^a Performed under N₂ atm. with 5.0 equiv **11**.^{b-c} See Table 1.