Low-Valent Tungsten Catalysis Enables Site-Selective Isomerization–Hydroboration of Unactivated Alkenes

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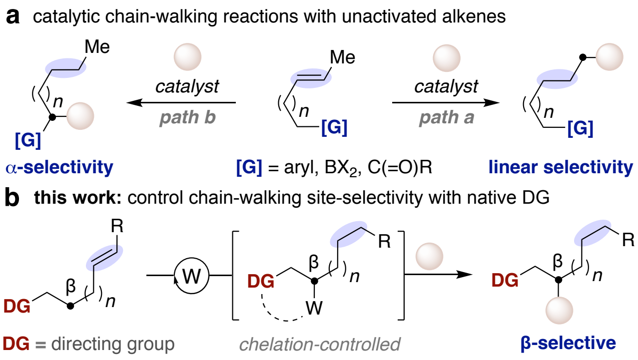
Supporting Information Placeholder

ABSTRACT: A tungsten-catalyzed hydroboration of unactivated alkenes at distal C*(sp^3)*–H bonds aided by native directing groups is described herein. The method is characterized by its simplicity, exquisite regio- and chemoselectivity and wide substrate scope, offering a complementary site-selectivity pattern to other metal-catalyzed borylation reactions and chain-walking protocols.

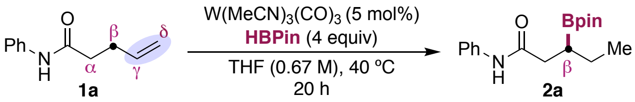
Chain-walking has emerged as a powerful strategy for forging C–C bonds at remote C(sp^3) sites by controlled migration of the metal catalyst through a hydrocarbon side chain.[1] At present, these protocols can promote functionalization at either the terminal position of the alkyl chain or adjacent to a stabilizing group (Scheme 1a, *paths a & b*). Despite recent advances, several challenges remain to be addressed. Among them, expanding the scope of chain-walking reactions beyond C–C bond-formation[2] and achieving tunable selectivity to target previously inaccessible C*(sp^3)*–H sites would be worthwhile endeavors for chemical innovation.

Scheme 1. Olefin Functionalization via Chain-Walking.



Elegant work by Chirik[3a-g] and others[3e-f] has shown the ability of Co catalysts to trigger chain-walking borylation of unactivated alkenes for forging C*(sp^3)*–B bonds at terminal primary sites or α- to arenes or alkyl boronates. Although Koh recently leveraged the stabilizing features of π-benzyl intermediates (*path b,* [G] = aryl) to promote a homobenzylic protoborylation,[5] the means to enable C–B bond-formation through alkylmetal stabilization at less-activated sp^3 sites via chain-walking still remains elusive. Based on recent findings by our group,[6] we wondered whether we could enable a W-catalyzed C*(sp^3)*–B bond-formation controlled by native directing groups at C*(sp^3)*–H sites that are beyond reach in conventional chain-walking events (Scheme 1b).[7]

Table 1. Optimization of the Reaction Conditions.[a]



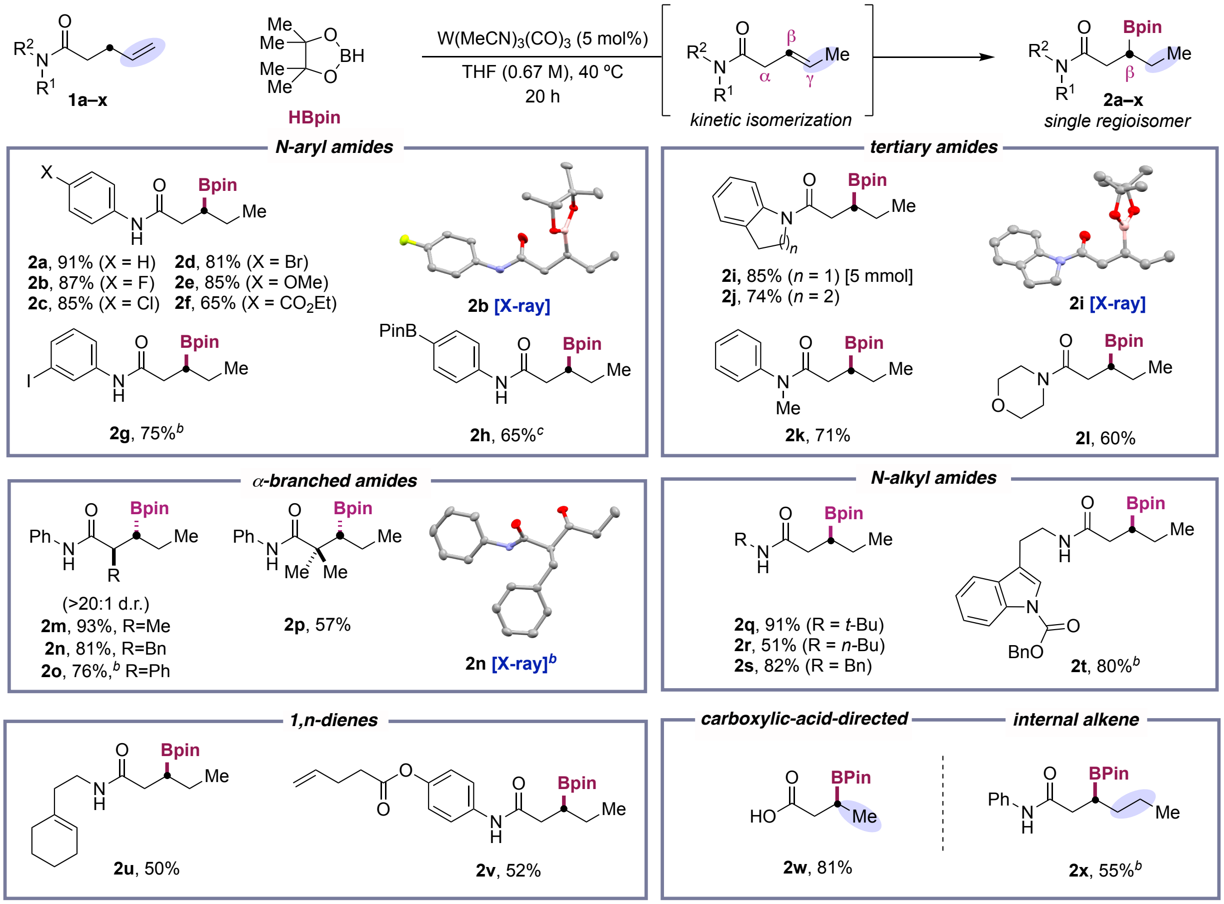
entry	deviation from standard conditions	**2a** (%)[b]	**2a** (r.r.)[d]
1	none	93 (91)[c]	>50:1
2	$W(CO)_6$ or $W(\eta^6\text{-mes})(CO)_3$ (5 mol%)	<5	—
3	PCy_3 (5 mol%)	<5	—
4	IPr•HCl and KO*t*-Bu (5 mol%)	<5	—
5	HBpin (2 equiv)	46	>50:1
6	2-MeTHF as solvent	62	>50:1
7	1,4-dioxane as solvent	65	40:1
8	Et_2O as solvent	68	>50:1
9	PhMe as solvent	25	>50:1
10	THF (0.10 M)	62	>50:1
11	450-Watt UV lamp at rt	<5	—

[a] **1a** (0.20 mmol), $W(MeCN)_3(CO)_3$ (5 mol%), HBPin (0.80 mmol), THF (0.67 M), 40 ºC, 20 h. [b] Yields determined by GC using decane as internal standard. [c] Isolated yield. [d] Regioisomeric ratio (r.r.) calculated by LCMS or GCMS between β and γ/δ.

Specifically, we believed that the ability of low-valent W catalysts to adopt multiple coordination geometries[6,8-9] combined with their high Lewis acidity when compared to later transition metals, would be particularly critical for success. We anticipated that such a technology would not only expand the boundaries of chain-walking reactions by offering a complementary site-selectivity profile, but also stimulate the adoption of low-valent W catalysts in alkene functionalization.[6,7a-c] As part of our interest in alkene functionalization and chain-walking reactions,[10] we describe the successful implementation of this goal, culminating in the development of the first W-catalyzed hydroboration of alkenes.[11]

We began our work by evaluating the catalytic borylation of **1a** (Table 1). After some experimentation,[12] a protocol employing commercially available W(MeCN)$_3$(CO)$_3$ and HBpin provided the best results, delivering **2a** as a single β-regioisomer in 91% isolated yield. As expected, the nature of the catalyst and lability of the ligands had a non-negligible impact on reactivity. Indeed, only traces of **2a** were observed when changing the three weakly coordinating MeCN ligands to strongly binding CO or η^6-mesitylene (entry 2). Similarly, the inclusion of phosphine ligands (entry 3) or the *N*-heterocyclic carbenes (entry 4) resulted in low conversions to **2a**, likely due to the formation of a catalytically inactive, more electron-rich metal center. Solvents other than THF had a deleterious impact on both yield and regioselectivity (entries 6–10). Tentatively, these observations suggest that THF might be serving as a ligand for tungsten, and/or facilitating the formation of a Lewis pair with HBpin to modulate its reactivity. As shown in entry 11, exposure of **1a** under UV irradiation resulted in negligible formation of **2a**. Importantly, control experiments with β,γ- or α,β-unsaturated amides clearly show that isomerization stops at the β,γ-position and that hydroboration is exclusively catalyzed by tungsten.[13]

Table 2. Site-Selective *sp*^{3} C–H Borylation of Unactivated Alkenes Aided by Native Directing Groups.[a]

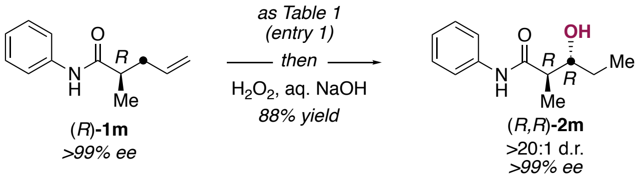


[a] Reaction conditions as in Table 1, entry 1; Isolated yields. [b] Isolated as the aliphatic alcohol following treatment with H$_2$O$_2$, aq. NaOH. [c] HBpin (5 equiv). All depicted X-ray structures have hydrogen atoms omitted for clarity.

Next, we turned our attention to exploring the generality of our protocol. As shown in Table 2, a variety of *N*-aryl secondary amides could be employed as substrates, and the C(*sp*^{3})–H borylation could be conducted in the presence of aryl fluorides, chlorides, bromides, and iodides (**2b–d, 2g**). Importantly, no borylation or reduction at the C(*sp*^{2})–halide bond was detected in the crude reaction mixtures. This finding is particularly important, showing a complementary selectivity pattern to that observed for other low-valent transition metals that would otherwise result in functionalization at the C(*sp*^{2}) site. Likewise, functional groups prone to reduction, such as esters (**2f**,

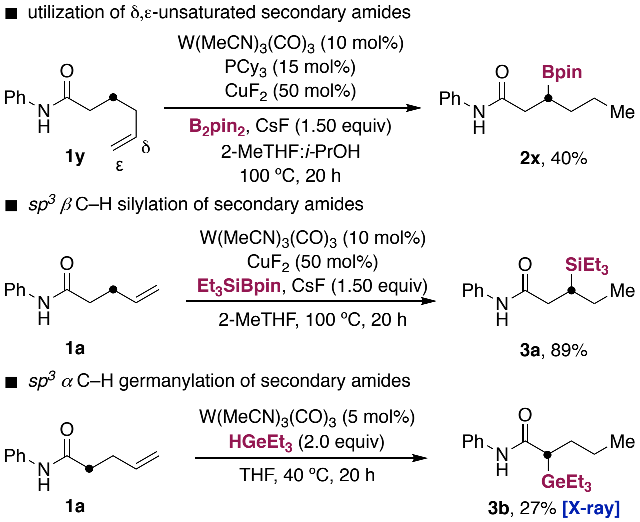
2t and **2v**), or the presence of an arylboronate (**2h**) did not interfere with the efficacy of the sp^3 β-borylation event. The reaction could be extended to tertiary amides (**2i–l**) and *N*-alkyl secondary amides (**2q–t**). The former observation is particularly interesting, as it does not only expand the range of amides that can be utilized,[14] but also suggests that binding of the substrate to the tungsten catalyst does not require the presence of a (deprotonatable) N–H bond. In addition, it is worth noting the reaction en route to **2i** could be easily scaled up to 5 mmol scale without an erosion in yield. The preparation of **2i–j, 2l** and **2t** illustrates that substrates containing *N*-heterocycles—particularly prevalent motifs in natural products and advanced synthetic intermediates—can easily be accessed under our protocol. The chemoselectivity of our reaction is further illustrated by the successful preparation of **2u** and **2v** possessing additional alkenes on the side chain. Under the limits of detection, diene substrates (**2u, 2v**) underwent monofunctionalization without additional borylation or competitive isomerization occurring at the second alkene. As shown for **2w**, the reaction could be similarly applied to internal alkenes, albeit in moderate yields. Although esters (**2v**) or ketones were not competent as directing groups, a free carboxylic acid delivered **2w** as single regioisomer. Particularly noteworthy is the ability to easily access α-branched products **2m–p** in good yields and excellent diastereoselectivities (>20:1).

Scheme 2. Preservation of an α-Stereocenter.



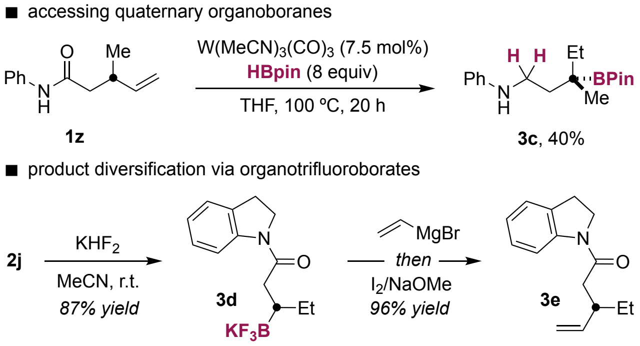
The *anti*-stereochemistry of substrates containing an α-substituent was unequivocally confirmed by X-ray crystallography of the aliphatic alcohol derived from the stereoretentive oxidation of **2n**. More importantly, **2m** could be obtained in high yield as a single enantiomer and diastereoisomer when starting from enantiopure **1m** (>99% ee) (Scheme 2). This finding has important mechanistic implications. Specifically, it suggests that alkene isomerization stops at the β,γ-position, as formation of a conjugated α,β-unsaturated amide would ablate the α-stereocenter in **2m**. This observation was further corroborated by the successful preparation of α,α-*gem*-dimethyl substituted **2p** in good yield and as single regioisomer despite the proximal steric hindrance.

Scheme 3. Expansion of the Coupling Partner Scope.



While aliphatic amides possessing a pendant alkene at the δ,ε-position resulted in trace amounts of the targeted sp^3 β-borylation under the optimized reaction conditions, a protocol based on CuF_2 and B_2pin_2 delivered **2x** in moderate yield, but as a single regioisomer (Scheme 3).[15] In line with these results, we wondered whether our protocol could be extended to other C–heteroatom bond-forming reactions. Gratifyingly, this was indeed the case, and an analogous silylation event could be conducted under otherwise identical reaction conditions (**3a**). Intriguingly, a hydrogermanylation could also be implemented in an unoptimized 27% yield. This reaction gave rise to **3b** with an unexpected α-selectivity pattern, the identity of which was unambiguously determined by X-ray diffraction. While the origin of such regioselectivity remains unclear, it suggests that boranes may react differently with low-valent tungsten catalyst when compared to other main group metal hydrides,[8a-c] thus setting the basis for enabling future catalytic endeavours.

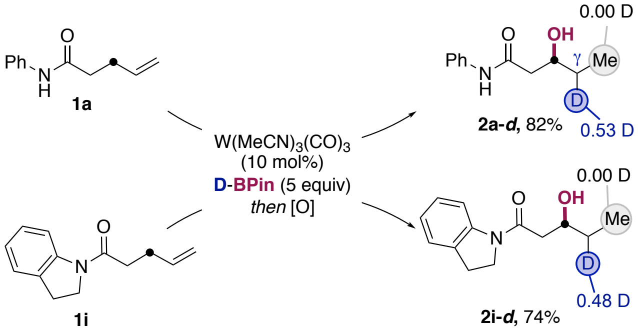
Scheme 4. Expansion of the Coupling Partner Scope.



Although β-branched γ,δ-unsaturated secondary amides showed poor yields under our optimized reaction conditions, an increase in the amount of HBpin at elevated temperatures enabled the formation of quaternary organoboranes (Scheme 4). Interestingly, a close inspection of the

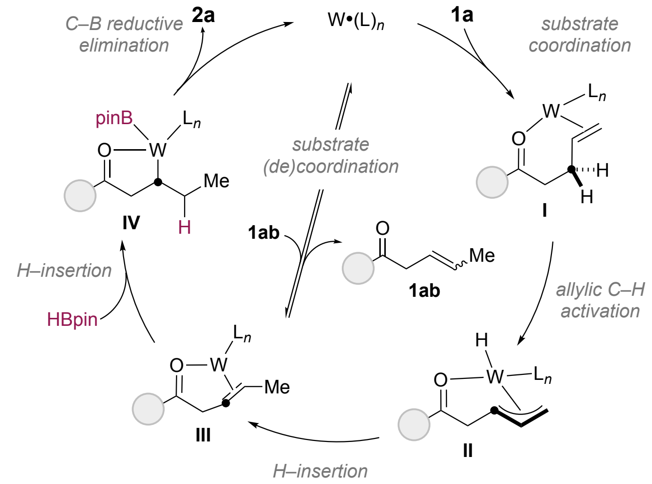
NMR data revealed *in situ* reduction of the carbonyl group under the reaction conditions, with **3c** being produced in modest 40% yield. Notably, **2j** can readily be converted to **3d** by reaction with KHF_2, providing an additional handle for further manipulation via cross-coupling reactions. **3d** could then be further derivatized via 1,2-boronate rearrangement, affording **3e** in 96% yield without competitive addition of the Grignard reagent to the carbonyl.

Scheme 5. Deuterium Labelling Studies.



Next, we turned our attention to studying the mechanism of our C(sp^3) β-borylation. *A priori*, one might expect that both 1,2- and 1,3-hydride shift might come into play for the initial alkene isomerization.[1,16] To this end, we conducted the borylation of **1a** and **1i** with DBpin. Deuterium incorporation at the γ-position was anticipated for a pathway consisting of 1,3-hydride shift; on the contrary, labelling at the terminal δ sp^3 site would indicate a mechanism via 1,2-hydride shift. As shown in Scheme 5, exclusive deuterium incorporation into the γ-position was observed in **2a-*d*** and **2i-*d***, thus strongly supporting the notion that alkene isomerization proceeds via 1,3-hydride shift. Conducting the reaction without HBpin corroborated previous findings[16] that showed the ability of W(0) to promote isomerization via 1,3-H shift without external hydride sources.[12] In addition, the lack of deuterium incorporation at the β-C(sp^3) site argues against a 1,1-hydroboration of a Fischer-type W-carbene. Although other scenarios might be conceivable,[17-18] we currently propose a pathway consisting of coordination of W(0) to both carbonyl group and the alkene (**I**) followed by allylic sp^3 C–H oxidative addition (**II**). Re-insertion of the metal hydride to the π-allyl moiety would formally result in an olefin isomerization, thus setting the stage for an oxidative addition of H–Bpin to W(0) intermediate **III** (Scheme 6). Subsequently, *exo*-hydride insertion to the β,γ-alkene might form **IV** which ultimately undergoes C–B reductive elimination to afford the final sp^3 β-borylation while regenerating the propagating W(0) catalyst.[18] From intermediate **III**, the isomerized alkene **1ab** is able to reversibly dissociate, as free **1ab** can be detected by *in situ* ^{1}H NMR.[12,19]

Scheme 6. Proposed Mechanism.



In conclusion, we have developed a protocol that illustrates the unique properties of the W(0)/W(II) redox cycle to address site-selectivity issues that have remained challenging for other transition metals in the chain-walking arena. Our sp^3 *β*-borylation is distinguished by its simplicity, mild conditions, and broad scope. This includes challenging functional group combinations, while exhibiting an exquisite chemo-, regio- and diastereoselectivity profile, thus offering a complementary technique in our synthetic repertoire for forging sp^3 C–B linkages.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website. Experimental procedures, spectral and crystallographic data (PDF)

Crystallographic data for **2b** (.cif)
Crystallographic data for **2j** (.cif)
Crystallographic data for **2u** (.cif)
Crystallographic data for **3b** (.cif)

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Author Contributions

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Note

The authors declare no competing financial interest.

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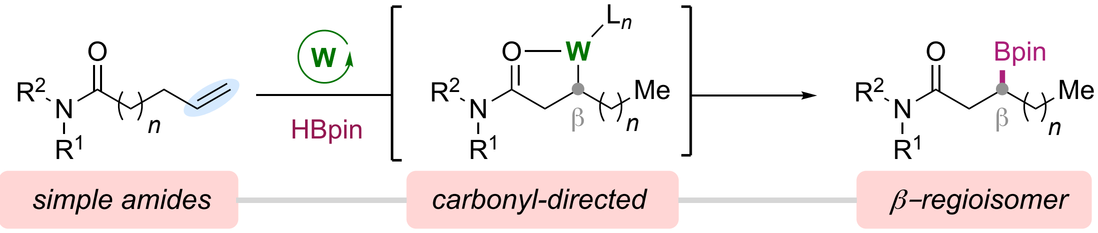
19. Computational work has shown that H–X (X = Si, Sn, Ge) oxidative addition to W(0) is slightly endergonic but kinetically accessible (ref. 7a), which is consistent with our inability to detect W–hydrides by ^{1}H NMR spectroscopy either under our optimized reaction conditions or by reacting $W(MeCN)_3(CO)_3$ with large excess of HBpin.



remote hydroboration • W redox catalysis • unique regioselectivity • distinct chemoselectivity