Angewandte
International Edition Chemie

DOI: 10.1002/anie.201003348

Olefin Functionalization

Strategy Towards Olefin Carbohydroxylation: Transmetalation of 2-Rhodaoxetanes with Organoboron Nucleophiles**

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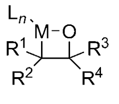
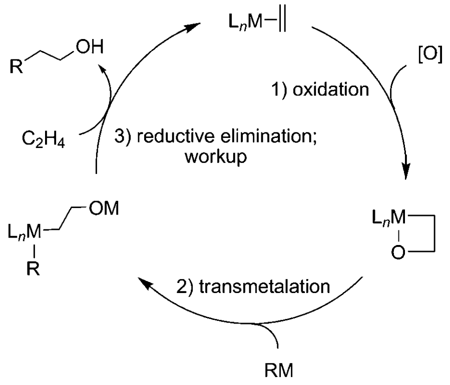
Catalytic olefin functionalization provides a means to convert readily available petrochemical feedstocks into valuable synthetic building blocks. A conventional method for converting olefins into functionalized alcohols involves sequential olefin epoxidation and nucleophilic ring opening. This strategy suffers from the requirement of harsh conditions for ring opening, which generally require strong nucleophiles. Moreover, conversion of terminal aliphatic olefins into chiral products is particularly problematic, owing to the low enantioselectivity of terminal aliphatic olefin epoxidation, despite recent progress.[1] Indeed, the typical strategy to obtain chiral, aliphatic epoxides derived from terminal olefins is by resolution of the enantiomeric mixture, which results in loss of half of the material. A second strategy involves dipolar cycloaddition of nitriles or nitrenes with subsequent N–O bond scission.[2] Alternatively, sequential Paterno–Büchi and oxetane hydrogenation provides the corresponding carboxydroxylated product.[3] Both of these procedures involve more than one step and have significant substrate limitations. In comparison, a one-step carbohydroxylation reaction would be more efficient. Nevertheless, only a few one-step protocols have been disclosed; these, too, suffer from inefficiency or limited scope.[4–8] Clearly, a need exists for more efficient carbohydroxylation strategies with broader substrate scope.[9] In response to this need, we propose that 2-metallaoxetanes can serve as reactive intermediates in a novel catalytic carbohydroxylation. Eventually, we anticipate that this methodology will be applicable to the enantioselective synthesis of functionalized alcohol building blocks from petrochemical feedstocks.



Scheme 1. Generic structure of metallaoxetanes.

2-Metallaoxetanes (Scheme 1) have been invoked as intermediates in various transformations, most prominently olefin oxidation reactions.[10] While their possible intermediacy triggered controversial debates at times,[11] recent experimental and theoretical data clearly establishes their involvement in selected epoxidations[12] and other olefin oxidation reactions[13] as well as some C–C bond-forming reactions as the Tebbe olefination or the nickel-catalyzed reductive coupling of alkynes and epoxides.[14] A number of different early,[15] mid,[16] and late[12,13,17] transition metallaoxetanes have been prepared and isolated; many of their structural features have been investigated.

We envisioned carbohydroxylation could involve the following steps: 1) oxidation of an olefin-coordinated metal complex to the 2-metallaoxetane; 2) transmetalation, resulting in ring opening of the metallaoxetane; 3) reductive elimination and subsequent olefin coordination to regenerate the catalyst (Scheme 2). Upon workup, a functionalized alcohol product would be produced. The proposed carbohydroxylation would constitute a mild, one-step equivalent to olefin epoxidation/nucleophilic ring opening, with different stereochemical implications. With substituted olefins, this method would provide complementary stereochemistry to simple expoxidation/ring-opening if reductive elimination proceeds with retention of configuration. The proposed catalytic process can also be considered the equivalent of olefin insertion into C–O bonds.



Scheme 2. Proposed catalytic cycle for carbohydroxylation of olefins.

As a starting point, we sought to explore the reactivity of 2-metallaoxetanes with transmetalating reagents. Of particular interest was the report by de Bruin et al., demonstrating the conversion of a TPA-Rh^I-ethylene complex **2** (TPA = trispyridylmethylamine) into the corresponding rhodaoxetane **3** by aqueous hydrogen peroxide solution (Scheme 3).[17a] This would constitute the first step in a potential catalytic oxidative olefin functionalization reaction (Scheme 2). The mechanism of oxidation has been studied computationally.[18]

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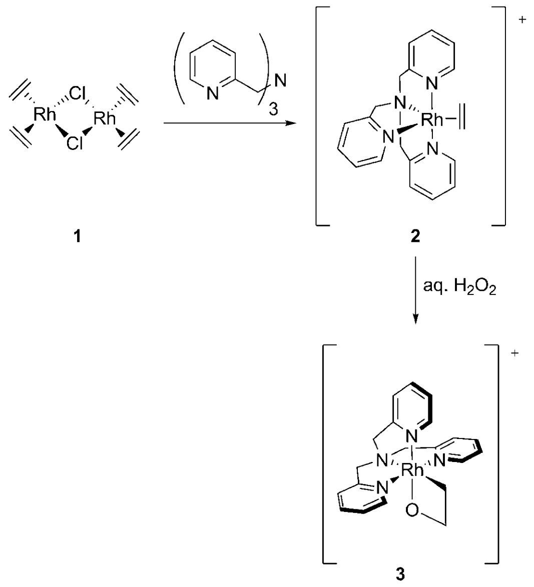
[**] We thank the following for support of this research: NSERC (Discovery Grant, Research Tools and Instrumentation Grants), University of British Columbia (UGF, Laird and 4YF to A.D.), and Mountain Equipment Coop (A.D.).

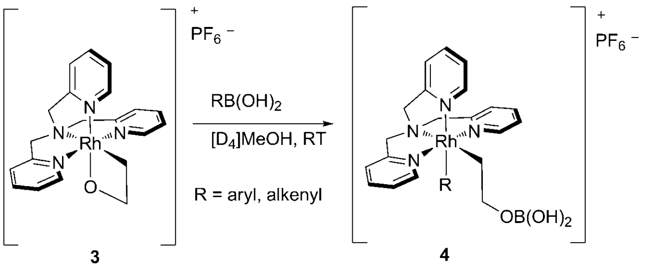
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201003348.



Scheme 3. Reported synthesis of 2-rhodaoxetane **3**.

Inspired by the elegant simplicity of this report, we decided to use rhodaoxetane **3** for preliminary stoichiometric investigations. De Bruin et al. had reported reactivity of the rhodaoxetane species with electrophiles, but nucleophiles were found to be ineffective.[17d] Nevertheless, we anticipated the transmetalation could be achieved under suitable conditions. Thus, our first objective was to explore the reactivity of rhodaoxetane **3** with various organometallic reagents.

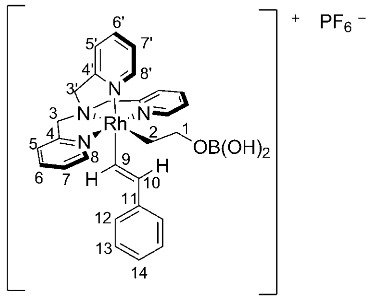
Gratifyingly, **3** reacted readily with various aryl- and alkenylboronic acids to generate **4**, without any evidence of β-hydride elimination (Scheme 4). It is noteworthy that **4** can be generated directly from the olefin complex **2** with H_2O_2 and arylboronic acid being added simultaneously.[19] Moreover, although Kuwano and co-workers recently proposed transmetalation of organoboron nucleophiles to a Rh^{III} center as a possible catalytic pathway,[20] to the best of our knowledge our work presents the first experimental evidence for transmetalation involving a Rh^{III}–O bond.



Scheme 4. Transmetalation of **3** with arylboronic acids.

For example, when rhodaoxetane **3** is treated with one equivalent of p-$BrC_6H_4B(OH)_2$ in methanol at room temperature over 8 h one new product (**4a**) is formed as indicated by ^{1}H NMR spectroscopy (Figure 1). Based on comparison to 1,3,5-trimethoxybenzene as an internal standard, **4a** is produced in 71 % yield. Upon isolation, a 42 % yield of **4a** is obtained.

Characterization of the product was conducted as follows. The rhodaoxetane moiety of **3** has two signals ($\delta = 4.99$ ppm, t, $^3J(H,H) = 7.5$ Hz, $O\text{-}CH_2\text{-}CH_2$ and 2.40 ppm, dt, $^3J(H,H) = 7.6$ Hz, $^2J(Rh,H) = 2.5$ Hz, $CH_2\text{-}CH_2\text{-}Rh$) that disappear during the course of the reaction while the new product shows two new signals (H1 = 3.92 ppm, dd, $^3J(H,H) = 5.5$ Hz, $J = 5.3$ Hz and H2 = 3.55–3.47 ppm, m). Likewise, the signals for the protons in the methylene bridges of the TPA ligand are shifted to lower field ($\delta = 5.37$ ppm, d[AB], $^2J(H,H) = 15.3$ Hz in **3**; 5.91 ppm, d[AB], $^2J(H,H) = 15.1$ Hz, H3 in **4a**). Finally, the signals ascribed to the protons *ortho* to the pyridine N atom also shift. Rhodaoxetane **3** has signals at $\delta = 9.04$ ppm, d, $^3J(H,H) = 5.3$ Hz and $\delta = 8.71$ ppm, d, $^3J(H,H) = 6.1$ Hz, whereas **4a** has signals at 8.67, $^3J(H,H) = 5.5$ Hz (H8) and $\delta = 8.85$ ppm, d, $^3J(H,H) = 5.9$ Hz (H8′). Two additional new signals can be observed in the aromatic region of the ^{1}H NMR spectrum: Two [AB] type doublets arise at $\delta = 7.52$ ppm and 7.25 ppm both integrating to 2H. Their correlation is affirmed through the clear roofing effect as well as cross-peaks observed in the COSY spectrum of the compound. Similar results were obtained with (*E*)-styrylboronic acid as a substrate which gave rise to compound **4b** (Scheme 5).



4b

Scheme 5. Reaction product with (*E*)-styrylboronic acid.

The chemical shifts are consistent with the observations of de Bruin et al. regarding acid-mediated rhodaoxetane ring opening. The smaller ^3J coupling constants for the signal at $\delta = 3.92$ ppm (H1) of 5.5 Hz and 5.3 Hz could also indicate a ring expansion through transesterification of the organoboronic acid to a six-membered oxametallacycle rather than ring opening[17d] to give a compound of the general structure of **5** (Scheme 6). Low-resolution ESI mass spectra of the reaction products show a single signal at M^+ reduced by 18 mass units. This can be best explained by dehydration of the boronic acid moiety of the transmetalated products in the spectrometer. It should be noted that the MS results are also consistent with transesterification of the boronic acid. High resolution mass spectra confirm the empirical formula.

To differentiate between these options and in the absence of X-ray quality crystals, we performed further spectroscopic

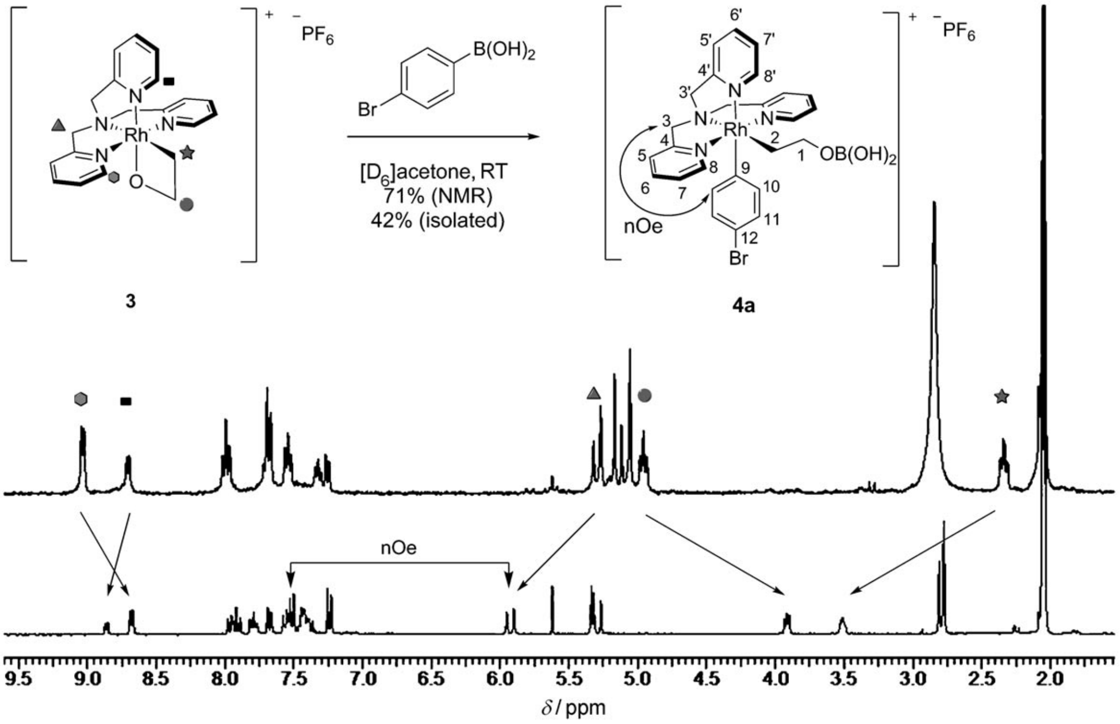
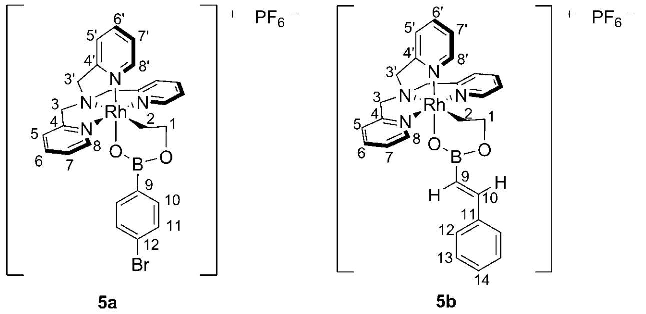


Figure 1. ^{1}H NMR spectrum comparing 3 (top) to 4a (bottom).



Scheme 6. Possible alternative structures.

investigations. The multiplicity of the ^{13}C signal of C9 should elucidate this issue. A doublet would appear in the case of coupling to Rh ($I = 1/2$) while a quartet should indicate connectivity to boron ($I = 3/2$). ^{13}C NMR data of the isolated product complexes was inconclusive as the quarternary signal of interest (C9) could not be detected directly. Literature precedents exist for both cases—non-observable C–B[22] as well as C–Rh[23] signals.

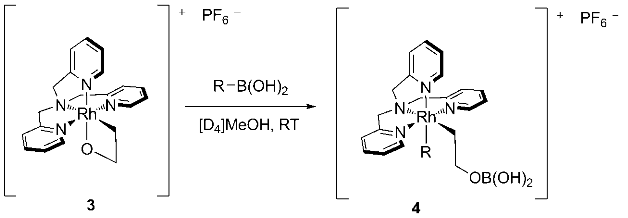
In **4a** indirect detection of the quarternary carbon atom through HMBC (heteronuclear multiple bond coherence) contacts to H10 and H11 was possible, and in compound **4b** an HSQC (heteronuclear single quantum coherence) experiment allowed for indirect detection of C9. The shape of the HSQC signal indicates the multiplicity of a doublet for the carbon signal with a coupling constant ^2J of ca. 6 Hz. Although the digital resolution of the experiment (7.4 Hz) is on the same scale as the observed coupling constant, the offset of the HSQC signal was reproducible and it was not detected in any of the other signals in the spectrum which suggests that the observation is valid.[24]

In addition, the 2D NOESY spectrum of **4a** shows a clear NOE contact between the axial TPA–methylene bridge proton signal at $\delta = 5.91$ ppm (H3) and the H10 signal at $\delta = 7.52$ ppm (Figure 1). In the *(E)*-styrylboronic acid product **4b** a similar contact is observed between H10 and H3 (axial). There are also contacts between H9 and H3 (axial) as well as H10 and H1. It is questionable whether these correlations would be possible in the six-membered ring structures **5a** or **5b**.

When rhodaoxetane **3** was exposed to alkylboronic acids under standard conditions no conversion of starting material could be detected (Table 1, entries 13–15). This can be interpreted as a greater reluctance of sp^3-hybridized carbon centers to perform transmetalation which is commonly observed. In comparison, we would expect that alkylboronic acids should undergo the ring expansion (transesterification) in the same manner as their aryl and alkenyl counterparts.

Furthermore, organoboronic esters reacted successfully and the expected products were formed in comparable yields. Yet, the reaction times were notably longer when compared to their parent boronic acid (compare Table 1, entry 4 and Table 2 entries 4 and 5). Employment of the sterically more demanding pinacol ester led to a greater increase in reaction time. The spectra of **4a**, **4s**, and **4t**, referenced to an internal standard, show different chemical shifts for most signals which would not be expected in the case of transesterification as the same product should be formed. These results are consistent with transmetalation (which would form a different product in each case), rather than transesterification of the

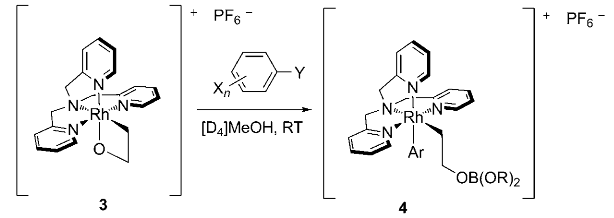
Table 1: Scope of transmetalation.



Entry[a]	R	X	Product	*t*	Yield[b]
1	4-X-C_6H_4	Br	**4a**	280 min	71% (42%)
2	*(E)*-styryl		**4b**	420 min	63% (56%)
3	4-X-C_6H_4	Cl	**4c**	250 min	71%
4		F	**4d**	200 min	92%
5		H	**4e**	560 min	94% (75%)
6		CH_3	**4f**	490 min	69%
7		Ph	**4g**	270 min	42%
8		OCH_3	**4h**	600 min	87% (48%)
9		OH	**4i**	n/a	0%
10		$N(CH_3)_2$	**4j**	380 min	73%
11		$C(O)CH_3$	**4k**	180 min	77%
12		SCH_3	**4l**	400 min	53%
13[c]	CH_3		**4m**	14 days	0%
14[c]	CH_3CH_2		**4n**	14 days	0%
15[c]	$CH_3(CH_2)_3$		**4o**	14 days	0%

[a] Reaction conditions: 5 mg **3** (0.1 mL of a 0.086 M standard solution), 10 equiv boronic acid, 0.6 mL CD_3OD, RT. [b] NMR yield referenced to an internal standard of 1,3,5-trimethoxybenzene; isolated yield after purification in parentheses. [c] No conversion of starting material was observed after 14 days.

Table 2: Product-based mechanistic studies.



Entry[a]	X	Y	Product	*t*	Yield[b]
1	2-Br	$B(OH)_2$	**4p**	270 min	75%
2	3-Br	$B(OH)_2$	**4q**	300 min	71%
3	2,6-$(CH_3)_2$	$B(OH)_2$	**4r**	14 days	31%
4	4-Br	pinacol ester	**4s**	440 min	62%
5	4-Br	neopentyl ester	**4t**	350 min	68%
6	4-Br	BF_3K	**4u**	21 days	0%

[a] Reaction conditions: 5 mg **3** (0.1 mL of a 0.086 M standard solution), 10 equiv boronic acid, 0.6 mL CD_3OD, RT. [b] NMR spectroscopic yield referenced to an internal standard of 1,3,5-trimethoxybenzene.

aryl boronic acid or esters, which would show the same product in each case.

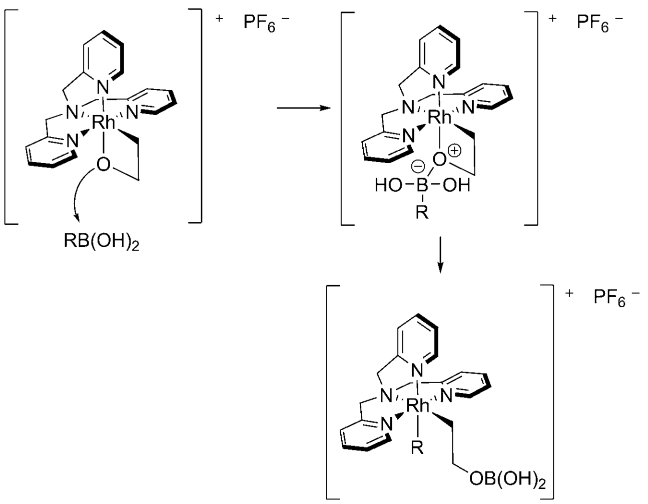
Overall, this data is more supportive of transmetalation of 4-bromophenylboronic acid than transesterification/ring expansion. Having established that transmetalation was feasible, we sought to explore the reactivity of a series of *para*-substituted arylboronic acids (Table 1, entries 1 and 3–11). In most cases, the yields reported are based on ^1H NMR spectroscopy, using 1,3,5-trimethoxybenzene as an internal standard. In some cases, the product was isolated; yields are given in parentheses. ^1H NMR spectra, as well as HRMS, have been obtained for all products, ^{13}C NMR spectra could be acquired for the isolated products. The transmetalation reaction can also be carried out successfully in acetone or dichloromethane although limited solubility of the boronic acids in the latter requires slightly longer reaction times.

One equivalent of boronic acid was sufficient to completely consume the starting rhodaoxetane and obtain moderate to excellent yields. As expected, reaction rates increased with an increase of concentration of the organoboron nucleophiles. It is noteworthy that up to an excess of 150 equivalents, the reaction rate still seemed to be dependent on the concentration of the boronic acid and no saturation was reached. While the reaction of **3** with 1 equivalent of 4-bromophenylboronic acid took just over 7 h to come to completion at room temperature, the employment of 10 equivalents reduced the reaction time to 280 min and upon use of 100 equivalents the reaction was completed after 90 min (reaction times monitored by ^1H NMR spectroscopy in 10–30 min intervals).

Overall, the reaction showed excellent functional-group compatibility. While an unprotected alcohol functionality is not tolerated by the protocol (Table 1, entry 8), arylboronic acids with halide (Table 1, entries 1–3), ether (Table 1, entry 7), tertiary amine (Table 1, entry 9), ketone (Table 1, entry 10), and thioether (Table 1, entry 11) substituents readily generated the corresponding ring-opened products in 42–94% NMR yields. In addition, the reaction yield is remarkably insensitive to electronic effects, as arylboronic acids with electron-withdrawing, electron-donating, and neutral substituents reacted cleanly.

De Bruin et al. suggested a mechanism for acid-mediated ring opening of rhodaoxetane **3**; protonation of the rhodaoxetane oxygen atom activates the structure which then opens under Rh−O bond cleavage in the presence of a coordinating ligand.[17d] In transmetalation, coordination of the rhodaoxetane oxygen would generate an -ate complex. In the present studies, no intermediates were observed spectroscopically ([D$_4$]methanol, RT). The data in Table 1 show that arylboronic acids bearing electron-withdrawing groups reacted the fastest, although there is no apparent linear correlation. Typically, formation of borate complexes during transmetalation is rate limiting and sensitive to electronic effects,[21] which is consistent with both of our observations. Accordingly, we propose the following mechanism for transmetalation: In a first step the rhodaoxetane oxygen coordinates to the boron center to give the -ate complex. This activates both, the oxetane and the boronic acid for the next step, the actual transmetalation from boron to rhodium (Scheme 7).

To further test our mechanistic hypothesis, we examined other organoboron nucleophiles. Increased steric bulk around the boron center (as with *ortho* substitution or boronic esters) should impede coordination of the oxetane and thus slow the reaction. In addition, if an -ate complex is indeed formed, trifluoroborates—in which the boron center is already tetravalent—should react slowly, if at all. If no pre-coordination of the oxetane is necessary, trifluoroborates should be reactive.



Scheme 7. Proposed mechanism for transmetalation.

As evident in Table 2, *ortho* or *meta* monosubstituted boronic acids did not affect the reaction rate or the yield significantly (Table 2, entries 1 and 2). In the case of two *ortho* substituents (Table 2, entry 3) though, both reaction rate and yield are decreased substantially. The reactivity of aryl boronic esters and lack of reactivity of aryl trifluoroborates supports the postulated mechanism of involving pre-coordination of boron to the rhodaoxetane oxygen, although other possibilities cannot be rigorously excluded at present. Further mechanistic studies are in progress.

In summary, we have reported the transmetalation of a wide variety of organoboron nucleophiles to rhodaoxetane **3** as a key step towards a novel carbohydroxylation protocol. This report presents the first experimental evidence for transmetalation from boronic acids to a Rh^{III} center, as well as the first transmetalation in general involving a Rh^{III}–O bond. Preliminary mechanistic studies suggest an interesting double-activation of the employed reagents through oxetane oxygen–boron pre-coordination. Investigations regarding reductive elimination from this species are ongoing and will be reported in due course.

Received: June 2, 2010
Revised: September 7, 2010
Published online: October 22, 2010

Keywords: boronic acid · olefin functionalization · rhodaoxetane · rhodium · transmetalation

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[19] Both the desired transmetalation product **4** and the phenolic by-product from H_2O_2 oxidation of the arylboronic acid are formed; this result demonstrates that sequential ethylene oxidation and transmetalation is competitive with aryl boronic acid decomposition, which bodes well for eventual development of a catalytic process. We are also assessing oxidants other than H_2O_2

to get maximum compatibility with the boron nucleophiles employed.

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[24] For a more detailed discussion of this investigation including all experimental parameters and sample spectra see the supporting information.