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Rh(III)-Catalyzed C−H Alkylation of Arenes Using Alkylboron Reagents

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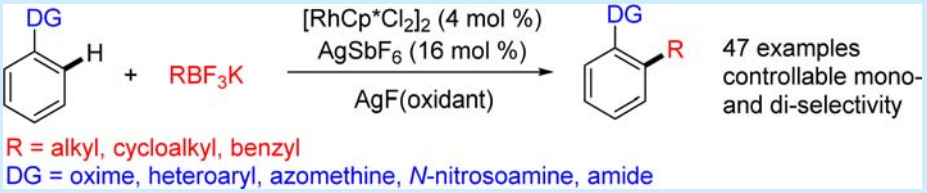
Supporting Information



ABSTRACT: Rhodium(III)-catalyzed direct alkylation of arenes using commercially available alkyltrifluoroborates is disclosed. Oximes, heteroarenes, azomethines, *N*-nitrosoamines, and amides are viable directing groups to entail this transformation. The alkyl group in the boron reagent can be extended to primary alkyls, benzyl, and cycloalkyls, and the reaction proceeded with controllable mono- and dialkylation selectivity when both *ortho* C−H sites are accessible.

Direct C−H bond functionalization has emerged as an increasingly valuable strategy for the construction of C−C bonds in organic synthesis.[1] In this regard, direct alkylation of the C−H bond of arenes remains a great challenge.[2] Palladium catalysis has been particularly well-studied for C−H alkylation.[3] Various other transition-metal catalysts have also been utilized to increase the catalytic efficiency, substrate scope, and functional group compatibility.[4] While alkylation of arenes was often performed using alkyl halides as the alkylating reagents,[3c,e,l,m,5] organo main group reagents such as organoborons[6] have been extensively employed in C−H alkylation[7] ever since the first report of palladium-catalyzed alkylation of arenes by the Yu group with these reagents in 2006.[3a]

Recently, Rh(III)-catalyzed C−H activation of arenes leading to efficient cross-couplings has attracted increasing attention.[8] Despite this attractive catalytic process, the coupling partners are mostly limited to unsaturated molecules such as alkenes,[9] alkynes,[10] ketones and aldehydes,[11] imines,[12] azides,[13] isocyanates,[14] azides,[15] and strained rings.[16] Although Rh(III)-catalyzed direct C−H arylation of arenes has been implemented using organoboron reagents[17] and aryl halides,[18] related alkylation reactions remain unexplored. This is likely associated with the low reactivity of rhodium(III) alkyl species toward $C(sp^2)-C(sp^3)$ reductive elimination. However, we reasoned that the competitive β-H elimination of Cp*Rh(DG-Ar)(alkyl) is suppressed due to the coordinative saturation enforced by the Cp* and the cyclometalated group. We now report Rh(III)-catalyzed oxidative C−H alkylation of diverse arenes bearing an *ortho*-directing group using potassium alkyltrifluoroborates.

We initiated our studies with the screening of the conditions for the coupling of methyl 4-(1-(methoxyimino)ethyl)benzoate with potassium *n*-butyltrifluoroborate (Table 1). Using $[RhCp^*Cl_2]_2$ (4.0 mol %) as a catalyst, a desired coupling occurred in the presence of $AgSbF_6$ (16 mol %) and AgF (3.0 equiv) in $ClCH_2CH_2Cl$ (entry 1), and the product **3hb** was isolated in 34% yield. In contrast, the reaction gave poor or no conversion when $AgSbF_6$ or $[RhCp^*Cl_2]_2$ was omitted (entries 3, 13). Screening of the oxidant indicated that the amount of AgF is crucial (entry 2), and coupling using other oxidants afforded inferior results (entries 4−8). Lowering the temperature to 80 °C resulted in diminished yield (entry 9). The use of 3 equiv of the boron reagent seems necessary because a slightly lower yield was isolated when the amount was reduced to 2 equiv (entry 10). The reaction proceeded with lower efficiency when the alkylating reagent was replaced by 2-butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane or butylboronic acid (entries 11, 12). Optimization of the solvent indicated that $ClCH_2CH_2Cl$ seems to be the optimal one (entries 14, 15).

We next explored the scope and limitation of this reaction (Schemes 1 and 2). Oximes bearing different electron-donating (**3fa**) and -withdrawing (**3da**, **3ga**−**3ka**) groups at the *ortho* and *meta* positions of the phenyl ring all coupled smoothly with $MeBF_3K$ in high monoselectivity. In contrast, a mixture of mono- and dimethylated products was obtained for non- or *para*-substituted oximes. To our delight, lowering the amount of $MeBF_3K$ and AgF can greatly improve the monoselectivity such that only a trace of the dimethylated product could be detected (**3aa**, **3ea**−**3ka**). The oxime substrate is not restricted to those derived from acetophenones, and oximes with other ketone platforms also reacted smoothly in comparably high yield (**3la**−**3pa**). Moreover, product **3ha** was isolated in 70% yield in a gram-scale (5 mmol) synthesis using a reduced loading of the catalyst ($[RhCp^*Cl_2]_2$ (2.0 mol %) and $AgSbF_6$ (8 mol %)).

To define the scope of the directing group further, the alkylation of other arenes, especially those bearing a

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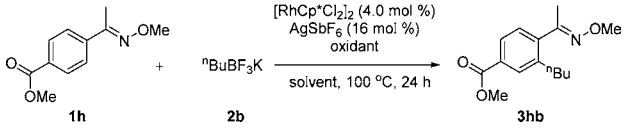
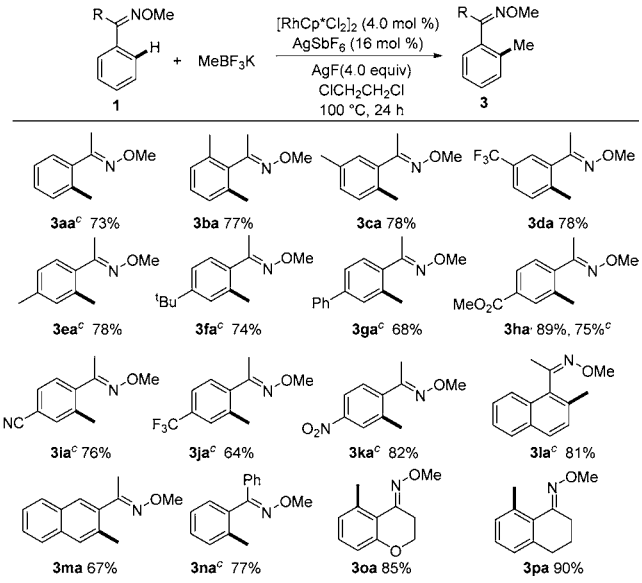
Table 1. Optimization Studies[a]



entry	oxidant (equiv)	solvent	yield[b]
1	AgF (3.0)	$ClCH_2CH_2Cl$	34%
2	AgF (4.0)	$ClCH_2CH_2Cl$	89%
3[c]	AgF (4.0)	$ClCH_2CH_2Cl$	28%
4	Ag_2O (4.0)	$ClCH_2CH_2Cl$	31%
5	AgOAc (4.0)	$ClCH_2CH_2Cl$	nd
6	Ag_2CO_3 (4.0)	$ClCH_2CH_2Cl$	44%
7	CuF_2 (4.0)	$ClCH_2CH_2Cl$	trace
8	AgF/Ag_2O (2.0/2.0)	$ClCH_2CH_2Cl$	47%
9[d]	AgF (4.0)	$ClCH_2CH_2Cl$	79%
10[e]	AgF (4.0)	$ClCH_2CH_2Cl$	80%
11[f]	AgF (4.0)	$ClCH_2CH_2Cl$	64%
12[g]	AgF (4.0)	$ClCH_2CH_2Cl$	25%
13[h]	AgF (4.0)	$ClCH_2CH_2Cl$	ND
14	AgF (4.0)	1,4-dioxane	25%
15	AgF (4.0)	toluene	18%

[a]Reactions were carried out using methyl 4-(1-(methoxyimino)ethyl)-benzoate (0.2 mmol), $^nBuBF_3K$ (0.6 mmol), $[RhCp^*Cl_2]_2$ (4.0 mol %), and $AgSbF_6$ (16 mol %) in a solvent (3 mL) under nitrogen at 100 °C for 24 h. [b]Isolated yield. [c]No $AgSbF_6$ was used. [d]Reaction was performed at 80 °C. [e]Reaction was performed using $^nBuBF_3K$ (2.0 equiv). [f]Reaction was performed using butylboronic acid (0.6 mmol). [g]Reaction was performed using 2-butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.6 mmol). [h]No catalyst was used.

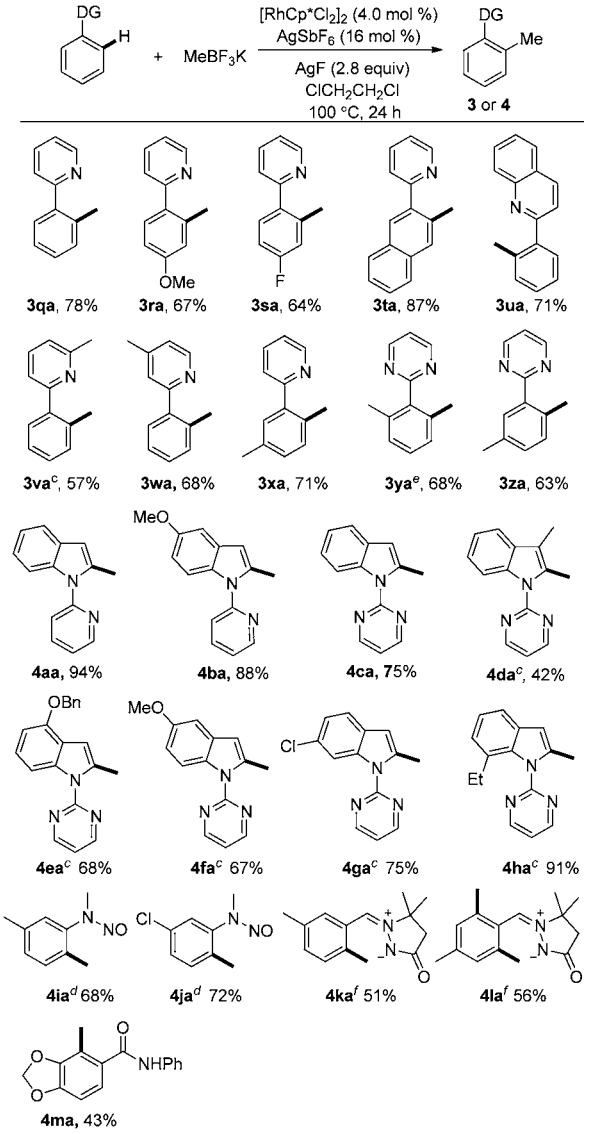
Scheme 1. Methylation of Oximes[a,b]



[a]Reaction conditions: oximes (0.2 mmol), $MeBF_3K$ (0.6 mmol), AgF (0.8 mmol), $[RhCp^*Cl_2]_2$ (0.008 mmol), $AgSbF_6$ (0.032 mmol), $ClCH_2CH_2Cl$ (3.0 mL), 100 °C, 24 h, sealed tube under nitrogen. [b]Isolated yield after column chromatography. [c]Reaction was performed using $MeBF_3K$ (0.5 mmol) and AgF (0.6 mmol).

functionalizable[19] directing group, was performed under the optimized reaction conditions (Scheme 2). The coupling of 2-phenylpyridines bearing different EDG, methyl, and halogen groups at the *ortho*, *meta*, and *para* positions all proceeded well (**3qa**−**3za**). This methylation reaction was fully applicable to

Scheme 2. Scope of Chelation-Assisted C−H Methylation[a,b]



[a]Reaction conditions: arene (0.20 mmol), $MeBF_3K$ (0.60 mmol), AgF (0.56 mmol), $[RhCp^*Cl_2]_2$ (0.008 mmol), $AgSbF_6$ (0.032 mmol), $ClCH_2CH_2Cl$ (3.0 mL), 100 °C, 24 h, sealed tube under nitrogen. [b]Isolated yield after column chromatography. [c]Reaction was performed using $MeBF_3K$ (0.6 mmol), AgF (0.6 mmol). [d]Reaction was performed using $MeBF_3K$ (0.4 mmol), AgF (0.6 mmol). [e]Reaction was performed using $MeBF_3K$ (0.7 mmol), AgF (0.6 mmol). [f]Reaction was performed using $MeBF_3K$ (0.8 mmol), AgF (0.6 mmol).

N-(2-pyridine)indoles and *N*-(2-pyrimidyl)indoles (**4aa**−**4ha**, 42−94% yields). The arene substrate can be further extended to *N*-nitrosoanilines,[20] and products **4ia** and **4ja** were isolated in good yield, where the introduction of a *meta*-methyl or -chloro blocking group ensured monoselectivity. Using azomethine imine as a directing group, the *meta* methyl substituted substrate coupled in moderate yield with mono-selectivity (**4ka**). However, the *para* methyl substituted azomethine substrate reacted in dimethylation selectivity (**4la**) in the presence of an excess of $MeBF_3K$ and AgF. Interestingly, *N*-phenylbenzo[*d*][1,3]dioxole-5-carboxamide is also a viable arene source, and the reaction proceeded at the more sterically hindered *ortho* position (**4ma**) in moderate yield.

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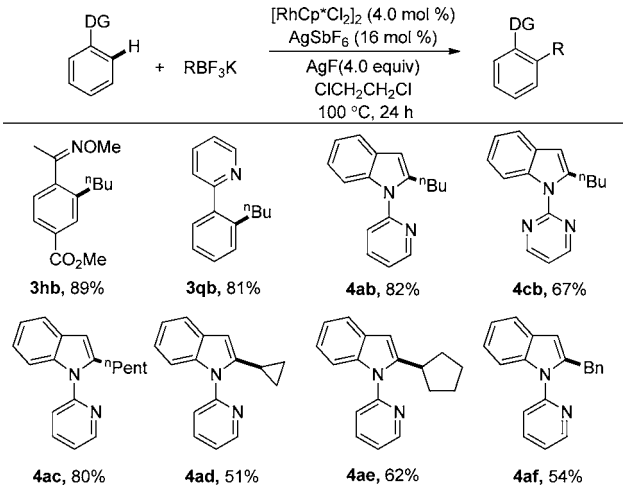
We next examined the scope of the boron reagent under the optimized reaction conditions (Scheme 3). Our results revealed

Scheme 3. Scope of Other Alkylating Reagents[a,b]

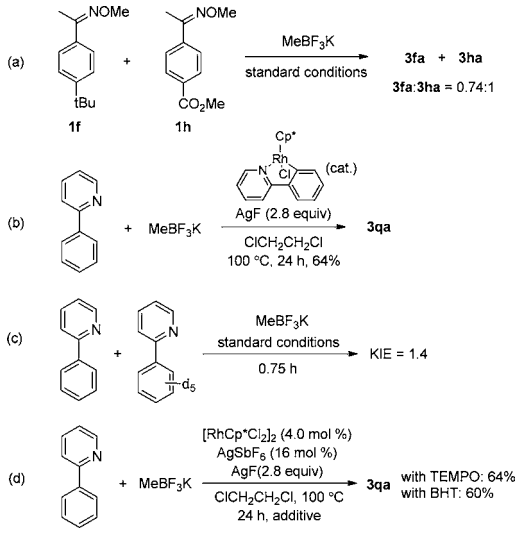


[a]Reaction conditions: arene (0.2 mmol), RBF_3K (0.6 mmol), AgF (0.8 mmol), $[RhCp^*Cl_2]_2$ (0.008 mmol), $AgSbF_6$ (0.032 mmol), $ClCH_2CH_2Cl$ (3.0 mL), 100 °C, 24 h, sealed tube under nitrogen. [b]Isolated yield after column chromatography.

that the coupling yield (67−82%) is not adversely affected in the butylation of oximes, 2-phenylpyridines, *N*-(2-pyridine)-indole, and *N*-(2-pyrimidyl)indole (**3hb**−**4cb**). Other functionalization such as pentylation (**4ac**), cycloalkylation (**4ad**, **4ae**), and benzylation (**4af**) has also been readily realized in moderate to good yields.

Several experiments have been performed to explore the reaction mechanism (Scheme 4). To probe the electronic

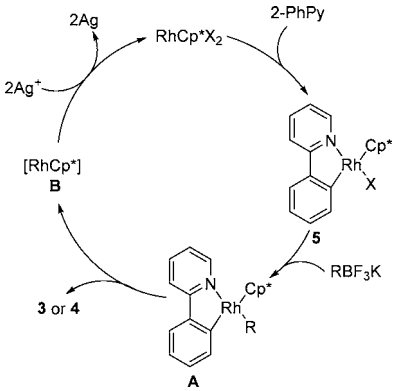
Scheme 4. Mechanistic Studies



preference of the oxime substrate, an intermolecular competition experiment has been carried out using an equimolar mixture of oximes that differ in electronic effects at the 4-position (Scheme 4a). ^1H NMR analysis of the product mixture indicated that the 4-CO_2Me substrate showed only slightly higher reactivity.

To probe the relevancy of C−H activation, rhodacyclic complex **5** was applied as a catalyst (8 mol %) for coupling of 2-PhPy with $MeBF_3K$, and product **3qa** was isolated in 64% yield, suggesting the relevancy of C−H activation (Scheme 4b). The kinetic isotope effect (KIE) was thus measured to gain mechanistic details. An intermolecular competition using 2-PhPy and 2-PhPy-d_5 with $MeBF_3K$ has been performed at low conversion, and a small value of KIE = 1.4 was obtained on the basis of ^1H NMR analysis (Scheme 4c), indicating that C−H bond cleavage is likely not involved in the rate-limiting step. In addition, the coupling of 2-PhPy with $MeBF_3K$ was performed in the presence of typical radical inhibitors such as TEMPO and BHT (Scheme 4d). The fact that the yield of product **3qa** was only slightly affected by both reagents (64% and 60%) suggests the irrelevancy of organic radical species. Thus, the coupling most likely involves transmetalation between the boron reagent and a rhodacyclic intermediate, followed by C−C reductive elimination (Scheme 5). The active Rh(III) catalyst is regenerated when the Rh(I) is reoxidized by Ag(I).

Scheme 5. Proposed Catalytic Cycle



In summary, we have developed the first rhodium-catalyzed direct alkylation of arenes using alkyltrifluoroborates. Both mono- and dialkylation have been achieved when both *ortho* C−H sites are accessible, and this selectivity is controllable by control of the reaction stoichiometry. Introduction of *ortho* and *meta* blocking groups ensured exclusive monoselectivity. This Rh(III)-catalyzed alkylation reaction expands the arsenal of coupling partners. With functionalizable directing groups installed, further useful chemical transformations of the coupled products can be expected. Future studies on Rh(III)-catalyzed C−H activation of other types of C−H bonds are underway in our laboratories.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, analytical data, and copies of NMR spectra of the products. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01232.

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Notes

The authors declare no competing financial interest.

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