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DOI: 10.1039/C8CC03144D

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Directed *Ortho* C-H borylation catalyzed by Cp*Rh(III)-NHC complex

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

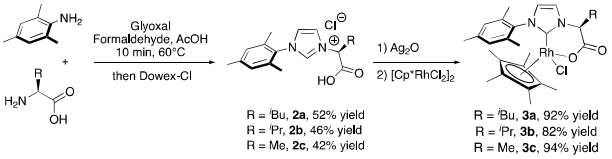
www.rsc.org/

Jompol Thongpaen,[a] Thibault Schmid,[a] Loic Toupet,[b] Vincent Dorcet,[c] Marc Mauduit[a] and Olivier Baslé*[a]

Cp*Rh(NHC) complexes with bulky chiral bidentate NHC-carboxylate ligands were efficiently synthesized and fully characterized including solid-state structures. These unprecedented rhodium (III) complexes demonstrated high selectivity in the pyridine-directed *ortho*-C-H borylation of arenes under mild conditions.

Transition metal-catalyzed direct C-H bond borylation is among the most important synthetic route to organoboron compounds that are versatile intermediates in medicinal chemistry and material science.[1] While the selectivity of the arene functionalization was mainly governed by steric hindrance for original catalytic systems,[2] considerable interest has been recently given to the development of efficient catalyst for the regioselective *ortho*-borylation assisted by directing-groups.[3] In this concern, high efficiency has been achieved with a variety of transition metals in association with various phosphine and nitrogen-based ligands.[4] On the other hand, and despite the tremendous success of *N*-heterocyclic carbene (NHC) ligands in homogeneous catalysis,[5] the use of NHC ligand in transition metal-catalyzed C-H bond borylation is scarce,[6] and reports involving regioselective *ortho*-borylation with NHC/metal catalyst are even more rare.[7] In the last decade, Rh(III)-catalyzed C-H functionalization of arene has attracted increasing attention, especially with the development of efficient Cp*Rh (pentamethylcyclopentadienyl rhodium)-based catalytic systems for regioselective C-C and C-heteroatom bond formation assisted by directing-group.[8] While Cp*Rh(III) complexes are recognized as the most active catalysts for the C-H borylation of alkanes,[9] including methane,[10] much less interest has been given to this family of complexes in the directed C-H borylation of arenes.[11] The present report describes the pyridine-directed regioselective *ortho*-C-H borylation of arenes catalyzed by newly developed (NHC)Cp*Rh(III) complexes under mild reaction conditions.

Recently, we described a practical multicomponent strategy that provides access to various unsymmetrical NHC ligands precursors, including carboxyalkyl-NHCs that are beyond reach otherwise.[12] NHC ligands containing an additional donor functionality have demonstrated significant benefit in stabilizing a variety of transition-metal complexes.[13] Therefore, we decided to evaluate our new chiral bidentate NHCs as ligands for the synthesis of stable Rh(III) complexes bearing the relatively electron rich and sterically demanding Cp* ligand.[14]



Scheme 1 Synthesis of Cp*Rh(NHC) complexes with bulky chiral bidentate NHC ligands.

NHC Ligands precursors were readily prepared by simply mixing mesitylamine, an amino-acid, formaldehyde and glyoxal in acetic acid for few minutes (Scheme 1).[12b] Starting from *L*-leucine (**1a**), *L*-valine (**1b**) and *L*-alanine (**1c**), we could obtain the corresponding unsymmetrical imidazolium salts (**2a**, **2b, 2c**) with good selectivity and satisfactory 52%, 46% and 42% yield, respectively. The chloride salts were subsequently reacted with Ag_2O to form the olig- or polymeric carbene silver intermediates that were subsequently engaged in a transmetallation reaction with $[Cp^*RhCl_2]_2$ affording the corresponding chelating (NHC)Cp*RhCl complexes (**3a**, **3b, 3c**) in excellent 92%, 82% and 94% yield, respectively. The ^{13}C NMR spectroscopy analyses evidenced doublet peaks at δ_C 170.7 ppm ($^1J_{Rh\text{-}C}$ = 54.7 Hz), δ_C 170.1 ppm ($^1J_{Rh\text{-}C}$ = 55.0 Hz) and δ_C 169.5 ppm ($^1J_{Rh\text{-}C}$ = 54.5 Hz) characteristic of the ^{103}Rh

[a] Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR - UMR 6226, F-35000 Rennes, France.
[b] Univ Rennes, CNRS, IPR - UMR 6251, F-35000 Rennes, France.
[c] Univ Rennes, CNRS, ISCR - UMR 6226, F-35000 Rennes, France.
E-mail: Olivier.basle@ensc-rennes.fr

† Electronic Supplementary Information (ESI) available: NMR spectra. CCDC 1405507 and 1818181. For ESI and crystallographic data see DOI: 10.1039/x0xx00000x

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DOI: 10.1039/C8CC03144D

coupling with the carbenic carbon of **3a**, **3b** and **3c**, respectively.[14] According to ^{1}H NMR analysis, complexes **3a** and **3b** were formed in two inseparable diastereomers (d.r. = 9:1); and only the solid-state structure of the $(S)_C(S)_{Rh}$ isomers were determined by X-ray crystallography analyses (Figure 1). According to the crystal structure, these rhodium complexes exhibit a three-legged piano-stool-typed geometry, which is commonly observed in half-sandwich complex,[15] and the bond length between Rh and NHC was measured to be 2.067 Å in **3a** and 2.056 Å in **3b**. On the other hand, a decrease of the diastereoselectivity was observed in the synthesis of complex **3c** (d.r. = 75:25) that is attributed to the reduced chiral information of the alanine based NHC ligand **2c**.

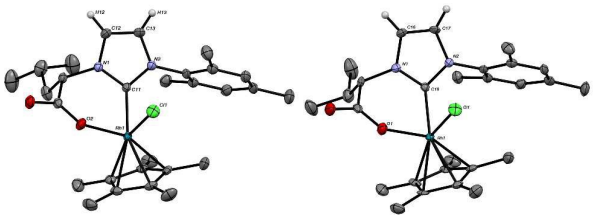
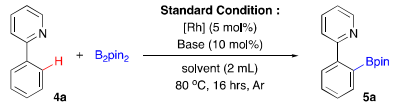


Figure 1 X-ray crystal structure of **3a** (left) and **3b** (right). Hydrogen atoms are omitted for clarity.

With those new complexes in hand, we decided to evaluate their potential as catalysts in the C-H bond borylation of 2-phenylpyridine using B_2pin_2 [bis(pinacolato)diboron] as borylating reagent (Table 1). First, the base screening was performed in toluene at 80 °C in the presence of complex **3a** as catalyst. While no reaction was observed with potassium acetate, the desired product could be formed in modest yields in the presence of potassium carbonate and sodium *tert*-butoxide (entries 1-3). To our delight, a decrease of the bulkiness of the alkoxide base resulted in an increase of the catalytic activities to afford the borylated product in up to 71% NMR yield when using sodium methoxide (entry 5). Then, lower catalytic activities were observed when toluene was replaced by tetrahydrofuran or *n*-octane (entries 6 and 7). The optimized reaction conditions were found using benzene as solvent at 80 °C with 10 mol% of NaOMe, affording the borylated product in 86% yield (entry 8). In fact, a decrease of the reaction temperature to 70°C has halved the yield (entry 9), and no reaction was observed at room temperature (entry 10). When pinacolborane (HBpin) was used instead of B_2pin_2, the desired product could only be obtained in modest 20% yield (entry 11). It is also important to note that under the optimal reaction conditions, complex **3b** could catalyzed with similar efficiency the borylation reaction (entry 12), while a noticeable decrease of catalytic activity was observed with the aniline based complex **3c** (entry 13). On the other hand, $[Cp^*RhCl_2]_2$ exhibited only poor activity to afford product **5a** in 20% yield (entry 15). Moreover, the use of the monodentate IMes NHC had no beneficial effect on the reaction (entry 14), further highlighting the importance of the chelating NHC ligand for the catalyst activity. Finally, control experiments confirmed that the borylation reaction did not occur in the absence of base or rhodium complex (entry 16-17).

Table 1 Optimization of Reaction Condition[a]



Entry	Cat.	Base	Solvent	Temp.	Yield (%)[b]
1	**3a**	KOAc	toluene	80	0
2	**3a**	K_2CO_3	toluene	80	8
3	**3a**	NaO^{t}Bu	toluene	80	12
4	**3a**	NaO^{i}Pr	toluene	80	61
5	**3a**	NaOMe	toluene	80	71
6	**3a**	NaOMe	THF	80	34
7	**3a**	NaOMe	*n*-octane	80	9
8	**3a**	**NaOMe**	**benzene**	**80**	**86**
9	**3a**	NaOMe	benzene	70	43
10	**3a**	NaOMe	benzene	r.t.	n.r.
11[c]	**3a**	NaOMe	benzene	80	20
12	**3b**	NaOMe	benzene	80	80
13	**3c**	NaOMe	benzene	80	54
14	[Rh][e]	NaOMe	benzene	80	25
15	[Rh][e]/IMes	NaOMe	benzene	80	29
16	**3a**	-	benzene	80	n.r.
17	-	NaOMe	benzene	80	n.r.

[a] Reaction conditions: 2-phenylpyridine (0.2 mmol), B_2pin_2 (0.4 mmol), Catalyst (0.01 mmol of Rh), base (0.02 mmol), solvent (2 mL), 16 hrs, under Ar. [b] NMR yield using 1,3,5-trimethylbenzene as an internal standard. [c] HBpin was used instead of B_2pin_2. [e] [Rh] = $[Cp^*RhCl_2]_2$. n.r. = no reaction, r.t. = room temperature.

To test the viability of this method, we first turned our attention to other 2-arylpyridine based-substrates (Table 2). The yield of the *ortho*-borylated product **5** was determined by ^{1}H NMR spectroscopy and subsequent quantitative oxidation with Oxone® allowed efficient isolation of the corresponding hydroxylated product **6**.[2b] Under the optimized reaction conditions with catalyst **3a**, substrates bearing an ether electron-donating (**4b** and **4c**) and an ester electron-withdrawing *para*-substituents (**4d** and **4e**) behave comparably to the parent substrate **4a**. A slight decrease of reactivity was observed with **4e** bearing a trifluoromethane group in the *para* position. On the other hand, while electronic effects may be neglected, the reaction was sensitive to the steric environment at the aryl ring.[2,7] In fact, the borylation process was considerably affected by a methyl substituent in the *ortho* or *meta* position and thus affording the products **5g** and **5h** with low 10 and 25% yield, respectively. Moreover, the borylation of (2-naphthylene-1-yl)pyridine **4i** did not take place. 2-phenylpyridine having a methyl (**4j**), trifluoromethyl (**4k**) or phenyl substituent (**4l**) on the pyridyl group were also tolerated. The isoquinoline-based substrates were effective in *ortho* borylation,[16] affording the functionalized products (**6m**-**6p**) in good yields. A decrease of activity was observed

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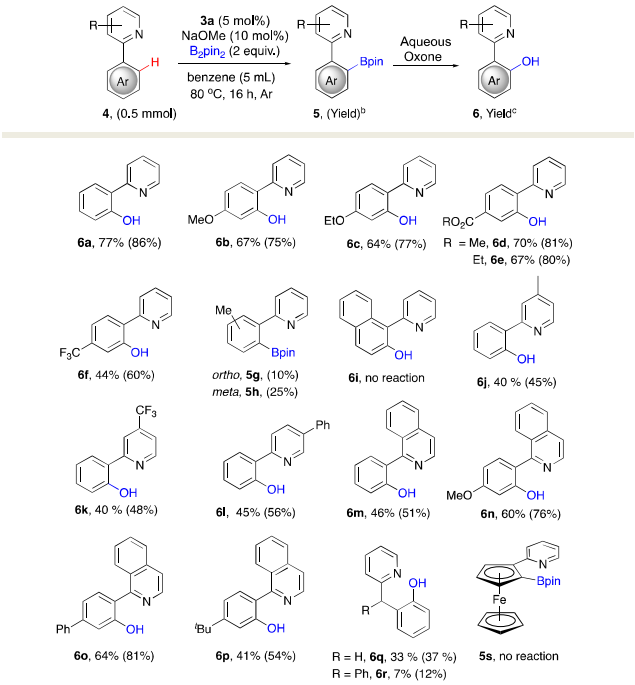
with 2-benzylpyridine-based substrates that allowed poor conversion with the prochiral bulkier substrate **4r** affording the racemic product **6r** in low yield.[4i] Finally, the ferrocenyl group was ineffective in C-H borylation and did not allow the synthesis of the planar chiral borylated product **5s**.

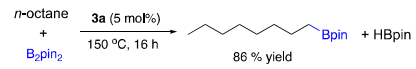
Table 2 Scope of substrates[a]



[a] Reaction conditions: **4** (0.5 mmol), B_2pin_2 (1.0 mmol), **3a** (5 mol%), NaOMe (10 mol%), benzene (5 mL), 16 h, under Ar; then Oxone (1.0 mmol). [b] NMR yield of the borylated product **5**. [c] Isolated yield of the hydroxylated product **6**.

To gain some mechanistic insight into the present reaction, the following experiments were conducted. First, the kinetic study of the reaction performed in C_6D_6, revealed a relatively long induction period (45-60 min under the optimized conditions), followed by a striking color change from dark red to dark green that is concomitant with the initiation of the catalytic C-H borylation process (Scheme S1, ESI†). Interestingly, the intermediacy of a metal-hydride was probe by NMR experiments. The reaction of a stoichiometric amount of complex **3a**, NaOMe and Bpin-Bpin at 80 °C in C_6D_6 led after 45 min to a dark green solution that allowed the observation of a Rh-H resonance by ^{1}H NMR at δ –10.90 (d, J_{RhH} = 24 Hz, Fig. S3, ESI†).[18] Moreover, mass and ^{1}H NMR spectroscopy analyses of the crude reaction also allowed the detection of Cp*H. Reductive elimination of Cp* with hydride ligands has been previously observed from Cp*Rh^{III} hydride complexes,[19] with possible dissociation of the free Cp*H diene.[20] Based on the above results, we surmise that the Rh-H intermediate originated from complex **3a** could undergo Cp* ligand dissociation allowing liberation of coordination sites to accommodate arylpyridine substrates for *ortho* C-H borylation.[20] However, no cyclometalated intermediate could be isolated or clearly identified from stoichiometric reaction in the presence of substrate **4a**.[22] Several other mechanisms can be envisioned, such as dissociation of the NHC-carboxylate ligand to generate high oxidation state Cp*Rh^V boryl complexes that are established catalysts in C-H borylation.[9] Nevertheless, neither the [Cp*Rh(H)$_2$(Bpin)$_2$] nor the [Cp*Rh(H)(Bpin)$_3$] with characteristic signals in ^{1}H and ^{11}B NMR could be detected from the crude of stoichiometric reactions. Furthermore, while rhodium(V) boryl complex were recently established as efficient catalysts in C-F bond borylation,[23] our catalytic system appeared totally inefficient in the *ortho* borylation of 2-(perfluorophenyl)pyridine (Scheme S2, ESI†). In addition, the deuterium kinetic isotope effect value of 1.3 determined in the cross-experiment using **4a** and its pentadeuterated analogue d_5-**4a** indicated that the *ortho* C-H bond cleavage was not the rate-limiting step (Fig. S4, ESI†). Finally, additional experiments in the presence of butylated hydroxytoluene (BHT) and mercury metal suggested that catalytic processes involving radicals or heterogeneous metal are unlikely to be operative. Despite these observations, the exact mechanism through which complexes **3** catalyze the pyridine-directed regioselective *ortho*-C-H borylation of arenes remains uncertain.

Finally, we decided to evaluate the potential of complex **3a** to catalyze alkane functionalization.[9] While no reaction was observed under the standard conditions at 80 °C, the desired regiospecific borylation of *n*-octane proved effective at 150 °C, affording 1-octylBpin in high 86 % isolated yield. Analysis of the isolated borane product by gas chromatography-mass spectroscopy confirmed the high selectivity for terminal C-H bond functionalization with 1-octylBpin being the only isomer detected.



Scheme 2. Complex **3a** catalyzed terminal borylation of n-octane

In conclusion, an efficient strategy for the synthesis of Cp*Rh(III)-based complexes bearing bulky chiral bidentate NHC-carboxylate ligands was developed. The newly synthesized Cp*Rh(NHC) complexes demonstrated catalytic activities in the pyridine-directed regioselective *ortho*-C-H borylation of arenes. The selective catalytic process was found to be applicable to a broad range of pyridine based substrates under mild reaction conditions. Further investigations on the application of the chiral-NHC/Rh system to asymmetric C-H activation reactions and to elucidate the reaction mechanism are currently underway in our laboratory.

We are grateful to the CNRS, the Ecole Nationale Supérieure de Chimie de Rennes. This work was supported by the Agence Nationale de la Recherche (ANR-15-CE07-0012-01 "CHADOC" grant to OB and JT), the region Bretagne (SAD n° 8734 grant to MM and TS).

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DOI: 10.1039/C8CC03144D

Conflicts of interest

The authors declare no conflict of interest

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