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Ruthenium-NHC complex-catalyzed P(III)-directed C-H borylation of arylphosphines

Jompol Thongpaen,[a,b] Romane Manguin,[a,b] Tanakorn Kittikool,[a,d] Aurèle Camy,[a] Thierry Roisnel,[c] Vincent Dorcet,[c] Sirilata Yotphan,[d] Yves Canac,[a] Marc Mauduit,[b] and Olivier Baslé*[a]

(NHC)(arene)Ru(II) complexes with bidentate LX-type NHC-carboxylate ligands were efficiently synthesized and fully characterized including solid-state structures. The strong coordination of the NHC carboxylate ligand and the labile character of the arene ligand are highlighted. These unprecedented Ru(II) complexes demonstrated efficient catalytic activities in the selective P(III)-directed C-H borylation at *ortho* position of arylphosphines, representing the first report of the use of ruthenium-NHC based catalyst in C-H borylation.

Organoborons have been recognized as versatile intermediates in organic synthesis, material sciences and medicinal chemistry, and the direct transition metal-catalyzed C-H borylation has emerged as a straightforward strategy to access such platform molecules.[1] In this context, the control of the regioselectivity has remained challenging due to the ubiquity of C-H bonds.[2] To address this issue, the introduction of a directing group has been employed to bring the targeted C-H bond closed to transition metal center forming the kinetically favored five- or six-membered metallacycle.[3] Alternatively, regioselective borylation strategies involving hydrogen bonding,[4] Lewis acid-base interaction,[5] and electrostatic attraction[6] have also proved successful. Furthermore, phosphorous-containing molecules especially phosphines have played a critical role in innovative transition metal catalysis, and the direct C-H functionalization can offer a straightforward approach to extend the diversity of these compounds.[7] Nevertheless, and despite recent achievements in phosphine-directed C-H borylation,[8] the P(III)-directed C(sp^2)-H borylation at *ortho* position of arylphosphines ($ArPR_2$) has remained challenging due to their strong coordination and the formation of unfavored 4-membered metallacycle.[9] Of particular interest is the direct access to *o*-boronated phosphines that are an important class of ambiphilic compounds with unique features as ligands in coordination chemistry[10] or in metal-free catalysts.[11]

N-heterocyclic carbene (NHC) ligands have provided several advantages in homogeneous catalysis[12] including transition metal-catalyzed C-H bond functionalization.[13] Nevertheless, the use of NHC ligands in transition metal-catalyzed regioselective C-H borylation remains scarce.[14] On the other hand, while the use of ruthenium complexes has led in the past two decades to significant breakthroughs in C-H bond functionalization, much less interest has been given to the catalytic regioselective C-H borylation,[9b, 15] and the use of Ru-NHC based catalyst in C-H borylation has never been reported. Herein, we described the synthesis of new (NHC)(arene)Ru(II)-based complexes and their application as catalysts for the P(III)-directed *ortho* C-H borylation of arylphosphines (Figure 1).

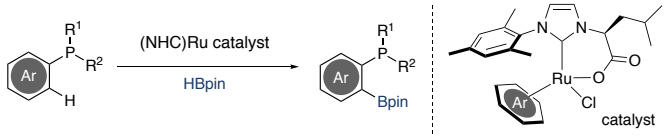


Figure 1. (NHC)(arene)Ru(II) complexes-catalyzed C-H borylation of arylphosphines.

Recently, we developed a multicomponent synthesis providing a direct access to a new class of unsymmetrical bidentate carboxylate NHC precursors.[16] These chelating ligands have notably shown advantages in stabilizing Cp*Rh(III)- and Rh(I)-based catalysts for C-H borylation under thermic and photocatalytic conditions, respectively.[14b, 14c] Therefore, we decided to evaluate this new family of chiral ligands in the synthesis of stable (arene)(NHC)Ru(II) complexes. To this end, a bidentate carboxylate NHC precursor **1** derived from L-leucine was readily converted to the corresponding silver complex, which was subsequently transmetallated using (arene)Ru(II)-dimers affording the desired (arene)(NHC)Ru(II) complexes **2a**-**2c** in excellent yield (Figure 2). First, complex **2a**, bearing *p*-cymene ligand, was obtained in 94% isolated yield as two air-stable inseparable diastereomers in the ratio of 1:1. The ^{13}C NMR analysis exhibits singlet peaks at 172.2 and 170.9 ppm, characteristic of carbenic carbon coordinating to Ru center.[17]

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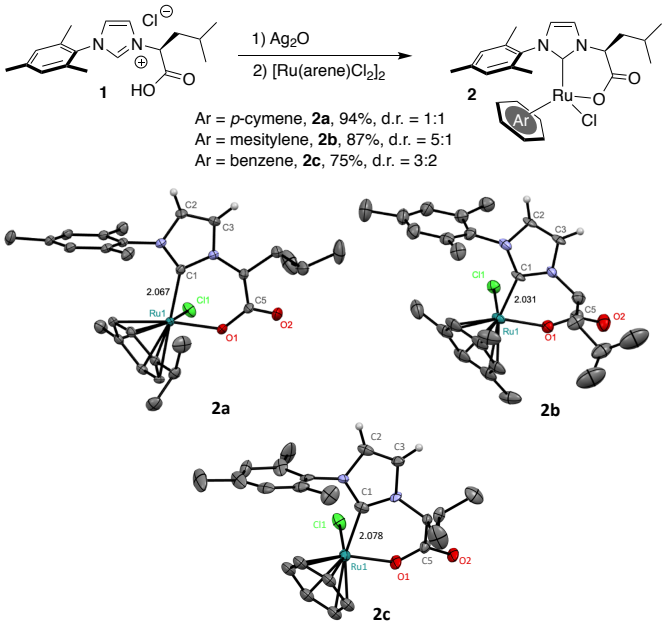


Figure 2. Synthesis of (arene)(NHC)ruthenium(II) complexes (top). X-ray crystal structure of **2a-c**.[18] Most hydrogen atoms are omitted for clarity. Both diastereomers co-crystallized and only $(S)_C(S)_{Ru}$ isomers are shown. *p*-cymene = 1-methyl-4-(propan-2-yl)benzene. Mesitylene = 1,3,5-trimethylbenzene.

Table 1. Selected bond lengths (Å) and angles (degree) for complexes **2a-c**. [18]

Bond length (Å)	$(S)_C(S)_{Ru}$-**2a**	$(S)_C(S)_{Ru}$-**2b**	$(S)_C(S)_{Ru}$-**2c**
Ru-C1	2.067(3)	2.030(6)	2.078(15)
Ru-$C_{arene(centroid)}$	1.699	1.702	1.678
Ru-Cl1	2.4241(9)	2.4083(17)	2.397(4)
Ru-O1	2.110(2)	2.077(5)	2.075(9)
O1-C5	1.279(4)	1.287(10)	1.280(17)
O2-C5	1.230(4)	1.231(9)	1.248(17)
C2-C3	1.339(5)	1.324(9)	1.32(2)
Angle (°)	$(S)_C(S)_{Ru}$-**2a**	$(S)_C(S)_{Ru}$-**2b**	$(S)_C(S)_{Ru}$-**2c**
Cl1-Ru-C1	89.37(9)	88.3(2)	83.5(4)
O1-Ru-C1	82.2(1)	85.2(3)	87.6(5)
O1-Ru-Cl1	92.43(7)	82.29(14)	81.8(3)

Similarly, complexes **2b** and **2c**, respectively bearing mesitylene and benzene ligands, were obtained in 87% and 75% isolated yield. According to ^{1}H NMR analysis, both complexes were obtained as a mixture of two diastereomers with the ratio of 5:1 for **2b** and 3:2 for **2c**. These novel Ru(NHC) complexes were crystallized and their structures could be confirmed by X-ray diffractometry analyses (Figure 2). The selected geometrical parameters of $(S)_C(S)_{Ru}$ isomer for each complex are shown in Table 1. All complexes featuring a six-membered metallacycle exhibited a three-legged piano-stool-typed geometry, which is commonly observed in half-sandwich complex. The distance of Ru1-C1 which refers to the Ru-$C_{carbenic}$ bond in each complex was found to be 2.067(3), 2.030(6) and 2.078(15) Å for **2a**, **2b** and **2c**, respectively. The measured distance between ruthenium atom and the centroid of arene ligands was found to be approximately 1.70 Å which is similar for all complexes. The same trend was observed in the case of Ru1-Cl1 and Ru1-O1 with a slight decrease of the bond length from **2a** to **2c**. Importantly, the distance between the oxygen atom (O1) that binds to the ruthenium atom and carbonyl carbon atom (C5) is longer than the bond length of O2-C5 in every case; confirming that the carboxylate arm of the NHC ligands serves as an X-typed ligand in these NHC-ruthenium(II) complexes.[14]

In analogy with recent mechanistic studies that evidenced the implication of arene-ligand-free active ruthenium catalysts in C-H bond functionalization processes,[19] we surmised that these new (arene)(NHC)Ru(II) complexes could liberate the arene ligands to accommodate the substrates and subsequently undergo C-H bond functionalization. Therefore, to evaluate the potential of these coordination-saturated complexes to catalyzed C-H bond functionalization reactions, experiments were conducted to demonstrate the labile character of the arene ligands (Figure 3). To this end, the model complex **2a** bearing *p*-cymene was treated with 3 equivalents of KPF_6 in acetonitrile at 100 °C for 4 days leading to the total consumption of starting complex and affording the tetra(acetonitrile)NHC-ruthenium analogue **3a** in 80 % isolated yield (Figure 3). The signal at 174.6 ppm in ^{13}C NMR analysis which belong to the Ru-$C_{carbenic}$ resonance could unambiguously confirm the presence of NHC-carboxylate ligand binding to the ruthenium center. This result proved both the labile character of the *p*-cymene ligand and the strong coordination of the bidentate NHC ligand to the ruthenium center, even under relatively harsh conditions. Furthermore, the facile exchange of one acetonitrile co-ligand by triphenylphosphine afforded complex **3b** in excellent yield.[20]

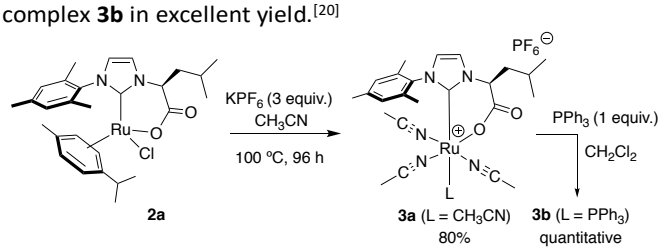
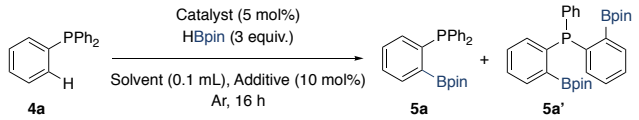


Figure 3. Synthesis of cationic arene-free Ru complexes **3a** and **3b**.

With these preliminary results in hand, we decided to evaluate our novel complexes in the P(III)-directed C-H borylation of triphenylphosphine (**4a**) using pinacolborane (HBpin) as a borylating agent (Table 2 & Table S1). First, at 110 °C under neat condition, the use of 5 mol% of the arene-free complexes **3a** or **3b** as catalyst afforded the desired *ortho* borylated product **5a** with 65% and 72% yield, respectively (entries 1 & 2). Under the same conditions, the complex **2a**, bearing *p*-cymene ligand, furnished 76% of product **5a** together with 16% of the diborylated product **5a'** (entry 3).[9a] The introduction of KPF_6 as cationizing agent to facilitate the release of the arene ligand could improve both activity and selectivity to deliver the desired product in 87% yield with lower 7% of diborylated by-product (entry 4).[19a] On the other hand, the variation of catalysts employing mesitylene (**2b**) or benzene (**2c**) analogues provided lower reactivity and selectivity affording respectively the desired products with 55% and 66% yield (entries 5-6). Aiming

to further improve the catalytic efficiency, the P(III)-directed C-H borylation was performed at 100 °C under neat condition (entry 7). However, the reaction proceeded with lower conversion, and the desired product was obtained with 73% yield. To our delights, the introduction of solvent could improve the reactivity and selectivity at this temperature (entries 8-10). First, employing toluene as solvent, the reaction proceeded with high conversion affording 84% of the desired product with low 3% of diborylated by-product (entry 8). While the use of 1,4-dioxane could produce similar results (entry 9), the optimal conditions were found using benzene as a solvent at 100 °C in the presence of **2a** as catalyst, affording 90% yield of the desired product **5a** with low 3% of **5a'** (entry 10). The decrease of the reaction temperature to 90 and 80 °C lowered the reactivity even though the formation of diborylated products was prevented (entries 11-12). Finally, a modest but significant catalytic activity was observed upon UV-light irradiation (λ_{max} = 365 nm) at room temperature affording 30 % of the desired borylated product **5a** after 3 days (entry 13).[14c]

Table 2. Optimization studies.[a]

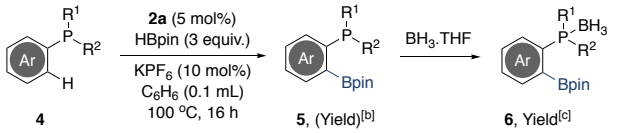


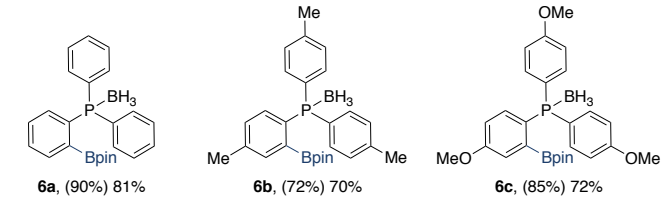
Entry	Catalyst	Solvent	Additive	Temp. (°C)	Conv.[b]	Yield (%)[c]	
						5a	**5a'**
1	**3a**	neat	-	110	87	65	8
2	**3b**	neat	-	110	90	72	12
3	**2a**	neat	-	110	92	76	16
4	**2a**	neat	KPF_6	110	94	87	7
5	**2b**	neat	KPF_6	110	81	55	26
6	**2c**	neat	KPF_6	110	76	66	10
7	**2a**	neat	KPF_6	100	86	73	9
8	**2a**	toluene	KPF_6	100	96	84	4
9	**2a**	1,4-dioxane	KPF_6	100	97	88	3
10	**2a**	C_6H_6	KPF_6	100	98	90	3
11	**2a**	C_6H_6	KPF_6	90	80	78	-[d]
12	**2a**	C_6H_6	KPF_6	80	16	14	-[d]
13[e]	**2a**	C_6D_6	KPF_6	rt[f]	64	30	-[d]

[a] Reaction conditions: PPh_3 (**4a**, 0.2 mmol), Catalyst (**2**, 0.01 mmol), KPF_6 (0.02 mmol), HBpin (0.6 mmol), Solvent (0.1 mL) in preheated oil bath at stated temperature for 16 hours under Ar. [b] Determined by ^{31}P NMR. [c] %Yield was determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard. [d] Not detected. [e] Irradiated at 365 nm for 72h. [f] Room temperature (25-30°C).

To test the viability of this method, several commercially available arylphosphines were engaged in P(III)-directed C-H borylation under the optimal thermic conditions (Table 3). The yield of *ortho*-borylated product **5** was determined by ^1H NMR analysis, and subsequent quantitative treatment with BH_3.THF could facilitate the isolation and purification of the phosphine-borane adducts **6**. First, the model substrate triphenylphosphine (**4a**) could afford 81% isolated yield of the desired borylated product **6a**. Then, the electronic effect of the aryl groups was studied employing substrates **4b**-**4e**. First, C-H borylation of triarylphosphines bearing an electron-donating group at *para*-position including a methyl- (**4b**) or a methoxy- (**4c**) group provided the corresponding products **6b** and **6c** in 70% and 72% isolated yield, respectively. On the other hand, the borylation of electron-deficient triarylphosphines bearing fluoro- (**4d**) or trifluoromethyl- (**4e**) substituents at the *para*-position could lead to the corresponding borylated products **5d** and **5e** with 60% and 76% yield under modified conditions employing only one equivalence of HBpin. In fact, electron-deficient triarylphosphines seems to display higher reactivity in the borylation process,[9b] resulting in a loss of selectivity and rendering purification slightly more challenging with detrimental impact on isolated yields. When one aryl ring of the model substrate was replaced by an alkyl group such as for cyclohexyldiphenylphosphine (**4f**), the yield of the desired borylated product was halved under the standard conditions. However, the reactivity was improved when the reaction was conducted under neat condition at 110 °C for 48 hours and the desired product **6f** was isolated with good 77% yield. The borylation of smaller size cone angle phosphines with stronger binding to ruthenium was adversely affected.[21] In fact, ethyldiphenylphosphine (**4g**) could provide the desired products with only 12% yield while no reactivity was observed

Table 3. Scope of the reaction.[a]





[a] Reaction conditions: **4** (0.2 mmol), **2a** (0.01 mmol), KPF_6 (0.02 mmol), HBpin (0.6 mmol), C_6H_6 (0.1 mL) in preheated oil bath at 100 °C for 16 hours under Ar then BH_3.THF for 2h under Ar. [b] %Yield was determined by ^1H NMR using 1,3,5-trimethylbenzene as an internal standard. [c] Isolated yield over 2 steps. [d] HBpin (0.2 mmol). [e] isolated yield of **5**. [f] 48h. [g] Neat at 110 °C.

when methyldiphenylphosphine (**4h**) was used as substrate. Noteworthy, borylation of dicyclohexylphenylphosphine **4i** could proceed quite satisfactorily with 54% yield to furnish 32% of the corresponding isolated product **6i**. Finally, additional experiments in the presence of butylated hydroxytoluene and Hg metal suggested that catalytic processes involving radicals or heterogeneous metal are unlikely to be operative (see SI).[22]

In conclusion, the bidentate LX-type NHC-carboxylate ligand was successfully engaged in the synthesis of half-sandwiched ruthenium arene complexes. The nature of the arene ligand noticeably affected the catalytic activities of the corresponding complexes. Thanks to the labile character of arene ligand and a strong coordination of NHC-carboxylate ligand, the newly developed complexes demonstrated efficient catalytic activities in the challenging P(III)-directed C-H borylation of arylphosphines under thermal conditions, representing the first report of the use of ruthenium-NHC based catalyst in C-H borylation. Further investigations on the application of these ruthenium-NHC complexes as chiral (photo)catalysts for C-H borylation reactions are currently underway in our laboratory.

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Conflicts of interest

There are no conflicts to declare

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20 Attempts to exchange the *p*-cymene ligand by PPh_3 afforded complex crude mixtures with complex **3b** as main product.

21 L. Luo and S. P. Nolan, *Organometallics*, 1994, **13**, 4781-4786.

22 For kinetic isotope effect with $P(C_6D_5)_3$, see figure S4.