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Rh^{III}-Catalyzed C–H Activation: A Versatile Route towards Various Polycyclic Pyridinium Salts

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Abstract: An efficient and convenient method for the synthesis of highly substituted polycyclic pyridinium salts from the reaction of various 2-aryl-pyridines and 2-aryl-sp^2-nitrogen-atom-containing heterocycles with alkynes through rhodium(III)-catalyzed C–H activation and annulation under an O_2 atmosphere is described. A possible mechanism that involves the chelation-assisted C–H activation of the 2-aryl-pyridine substrate, insertion of the alkyne, and reductive elimination is proposed. This mechanism was supported by the isolation of a five-membered rhodacycle (**I′**). In addition, kinetic isotope studies were performed to understand the intimate reaction mechanism.

Keywords: alkynes · C–H activation · fluorescence · pyridinium salts · rhodium

Introduction

Highly substituted pyridinium salts are important intermediates for the synthetic organic chemistry and are found in many naturally occurring compounds that exhibit a variety of biological activities.[1] Owing to their broad applications, several traditional and metal-mediated methods have been developed for the synthesis of pyridinium salts and related compounds.[2] In addition, the transition-metal-catalyzed syntheses of isoquinolines from *N-tert*-butyl *o*-halobenzaldimines,[3a–c] *N-tert*-butyl benzaldimines,[3d] aryl ketoximes,[3e–h] and alkynes have been reported. In these reactions, isoquinolinium salts were probably the intermediates. As part of our program concerning the synthesis and chemistry of isoquinolinium salts, we reported an efficient nickel-catalyzed synthesis of isoquinolinium salts from the reactions of 2-halobenzaldimines[4a,b] and *ortho*-iodoketimines with alkynes.[4c] In most of these reactions, a carbon–halogen moiety was used as the reactive species.

In recent years, Rh and Ru catalysts have stood out among the various transition-metal complexes for the functionalization of C–H bonds, owing to the high efficiency, selectivity, and functional-group tolerance of these catalysts.[5] Prompted by the various examples of C–H activation catalyzed by Rh and Ru complexes, we successfully demonstrated that isoquinolinium salts could also be synthesized through the rhodium- or ruthenium-catalyzed C–H activation of benzaldimines (or aryl aldehydes and amines) as the key step.[6] Earlier, Brennessel and Jones had shown that isoquinolinium salts were formed from the reactions of 2-phenylpyridine and benzo[*h*]quinoline with dimethyl acetylenedicarboxylate (DMAD), mediated by RhCp* complexes.[7] In 2011, Sanford and co-workers developed a Pd-catalyzed synthesis of cyclic pyridinium salts through the pyridine-directed olefination of the C(sp^3)–H bond and intramolecular Michael addition.[8] Our continued interest in transition-metal-catalyzed C–H activation[9] and the synthesis of N(sp^2)-containing salts[5,6] encouraged us to further explore the formation of polycyclic pyridinium salts by C–H activation. Herein, we report the synthesis of various polycyclic pyridinium salts by using substituted 2-phenylpyridine and N(sp^2)-containing substrates with alkynes in good-to-excellent yields under very mild reaction conditions. During the preparation of this manuscript, a report has appeared on the synthesis of similar compounds.[10] The reported reaction conditions required heating the reaction mixtures in MeOH at 120 °C for 22 h in the presence of O_2 and one equivalent of strong acid (HOTf) by using $[RhCp^*(H_2O)_3]^{2+}$ as a catalyst. In contrast, we carried out similar reactions in 1,2-dimethoxyethane (DME) at ambient temperature under 1 atmosphere of O_2 by using $[(RhCl_2Cp^*)_2]$ as the catalyst and $Cu(BF_4)_2$ as the co-catalyst and BF_4^- source. No acid was added during the reaction (see below for details). In addition, to understand the intimate mechanism of this rhodium-catalyzed reaction, we studied the kinetic isotope effects of the catalytic reaction to confirm that cleavage of the C–H bond was the product-determining step.

Results and Discussion

The treatment of 2-phenylpyridine (**1a**) with diphenylacetylene (**2a**) in the presence of 1 mol% $[(RhCl_2Cp^*)_2]$ and Cu-

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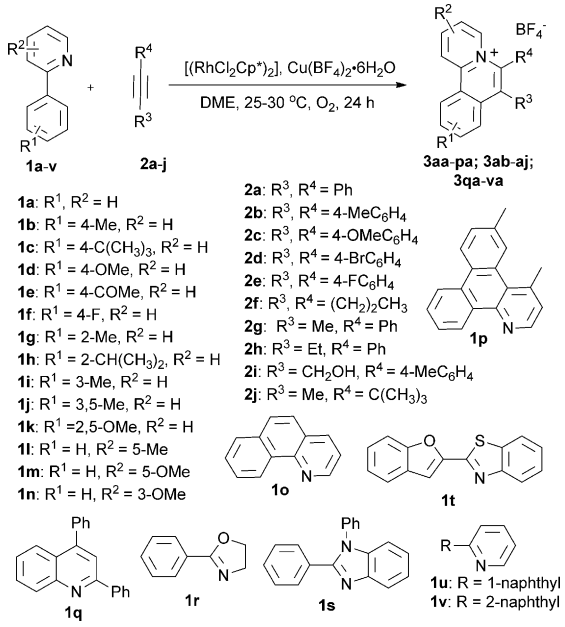
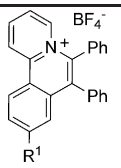
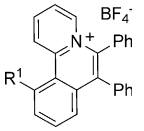
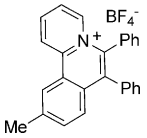
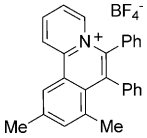
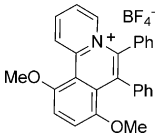
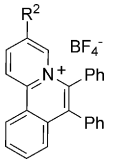
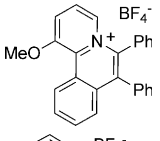
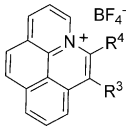
$(BF_4)_2{\cdot}6H_2O$ (0.5 equiv) in DME at room temperature under an O_2 atmosphere for 24 h gave pyrido[2,1-*a*]isoquinolin-5-ium salt **3aa** in 94% yield (Table 1, entry 1). The structure of compound **3aa**, which contained a pyridoisoquinolinium cation and a tetrafluoroborate anion, was confirmed by ^1H, ^{13}C, ^{19}F, and ^{11}B NMR spectroscopy and by mass spectrometry.

To evaluate the scope of this catalytic formation of pyridoisoquinolinium salts, we examined the reactions of several substituted 2-phenylpyridines (**1b**–**1n**) with diphenylacetylene (**2a**) under the same reaction conditions (Table 1). Thus, 4-methyl-, 4-*tert*-butyl-, 4-methoxy-, 4-acyl-, and 4-fluorophenylpyridines (**1b**–**1f**) effectively underwent C–H activation and annulation reactions with compound **2a**, thereby affording their corresponding pyridoisoquinolinium salts (**3ba**–**3fa**) in 97–88% yield (Table 1, entries 2–6). These results indicated that both electron-withdrawing and electron-donating arylpyridines worked well in the catalytic reaction. Similarly, the reactions of 2-(2-methylphenyl)pyridine (**1g**) and 2-(2-isopropylphenyl)pyridine (**1h**) with compound **2a** proceeded smoothly to give compounds **3ga** and **3ha** in 89 and 91% yield, respectively (Table 1, entries 7 and 8). In addition, 2-(3-methylphenyl)pyridine (**1i**) reacted nicely with compound **2a** to give compound **3ia** in 91% yield (Table 1, entry 9). In the reaction of 3-methylarylpyridine, there were two possible C–H activation sites, that is, at the C2 and C6 positions of compound **1i**, but the C–H activation only occurred at the C6 position, likely owing to the steric effect of the methyl group at the C3 position. In a similar manner, 2-(3,5-dimethylphenyl)pyridine (**1j**) and 2-(2,5-dimethoxyphenyl)pyridine (**1k**) gave pyridoisoquinolinium salts **3ja** and **3ka** in 88 and 91% yield, respectively (Table 1, entries 10 and 11). To evaluate the scope of the present catalytic reaction, we examined the reactions of substrates **1** that contained substituents on the pyridine ring (**1l**–**1n**) with compound **2a** under the standard reaction conditions. Thus, 5-methyl- (**1l**), 5-methoxy- (**1m**), and 3-methoxy-substituted pyridines (**1n**) effectively underwent C–H activation and annulation reactions with compound **2a**, thereby affording salt products **3la**, **3ma**, and **3na** in 90, 95, and 95% yield, respectively (Table 1, entries 12–14). Benzo[*h*]quinoline (**1o**) and 4,6-dimethyldibenzo[*f*,*h*]quinoline (**1p**) also reacted well with compounds **2c** and **2a** to give compounds **3oc** and **3pa** in 89 and 87% yield, respectively (Table 1, entries 15 and 16).

In addition to compound **2a**, other symmetrical alkynes (**2b**–**2f**) were also tested in the C–H activation and annulation reaction. Thus, methyl- (**2b**), methoxy- (**2c**), bromo- (**2d**), and fluoro-substituted

Table 1. Reactions of 2-phenylpyridines **1** with alkynes **2**.[a]



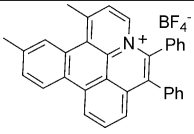
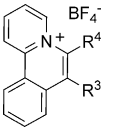
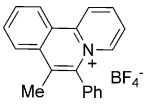
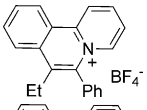
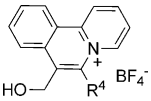
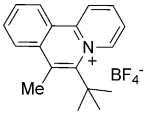
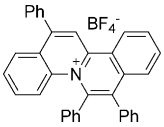
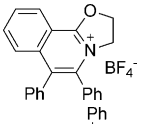
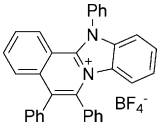
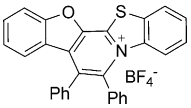
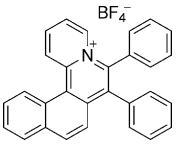
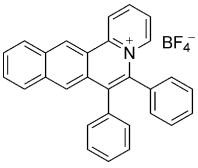
	1	2	Product 3	Yield [%][b]
1	**1a**	**2a**	 **3aa**: R^1 = H	94
2	**1b**	**2a**	**3ba**: R^1 = Me	91
3	**1c**	**2a**	**3ca**: R^1 = *t*Bu	89
4	**1d**	**2a**	**3da**: R^1 = OMe	97
5	**1e**	**2a**	**3ea**: R^1 = COMe	93
6	**1f**	**2a**	**3fa**: R^1 = F	88
7	**1g**	**2a**	 **3ga**: R^1 = Me	89[c]
8	**1h**	**2a**	**3ha**: R^1 = *i*Pr	91[d]
9	**1i**	**2a**	 **3ia**	91
10	**1j**	**2a**	 **3ja**	88[d]
11	**1k**	**2a**	 **3ka**	91[d]
12	**1l**	**2a**	 **3la**: R^1 = Me	90
13	**1m**	**2a**	**3ma**: R^1 = OMe	95
14	**1n**	**2a**	 **3na**	95[d]
15	**1o**	**2c**	 **3oc**: R^3, R^4 = 4-OMeC$_6$H$_4$	89

diphenylacetylenes (**2e**) underwent C–H activation and annulation with compound **1a** to afford the corresponding pyridoisoquinolinium salts (**3ab**–**3ae**) in good-to-excellent yields (Table 1, entries 17–20). Likewise, treatment of 4-octyne (**2f**) with compound **1a** provided the corresponding salt (**3af**) in 88% yield (Table 1, entry 21).

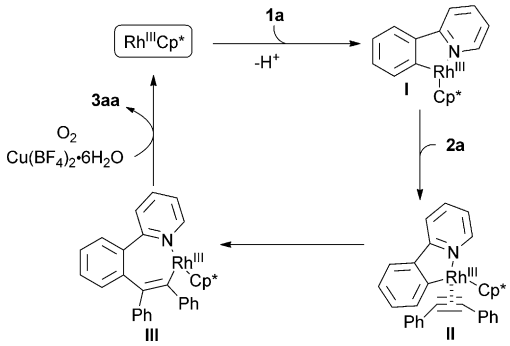
To understand the regioselectivity of this reaction, unsymmetrical alkynes **2g**–**2j** were also investigated. Thus, 1-phenyl-1-propyne (**2g**) and 1-phenyl-1-butyne (**2h**) reacted efficiently with compound **1a** to give two regioisomeric products in excellent yields with high regioselectivities (Table 1, entries 22 and 23). Similarly, two regioisomers were observed in the reaction of 3-(*p*-methylphenyl)propargyl alcohol (**2i**) with compound **1a**, thus forming regioisomeric products **3ai** and **3ai′** in 79% yield in a 95:5 ratio (Table 1, entry 24). The other internal alkyne that we tested in the reaction with compound **1a**, 4,4-dimethyl-2-pentyne (**2j**), afforded regioisomers **3aj** and **3aj′** in a 7:1 ratio in a combined 78% yield (Table 1, entry 25). The reaction of 2,4-diphenylquinoline (**1q**) with compound **2a** afforded pyridoisoquinolinium salt **3qa** in 93% yield. Similarly, 2-phenyl-4,5-dihydrooxazole (**1r**), 1,2-diphenyl-1*H*-benzo[*d*]imidazole (**1s**), and 2-(benzofuran-2-yl)benzo[*d*]thiazole (**1t**) reacted with compound **2a** at higher reaction temperatures to form their corresponding polycyclic pyridinium salts (**3ra–3ta**) in 84, 95, and 69% yield, respectively. The presence of five-membered heterocycles, including oxazoline, imidazole, and thiazole groups in these substrates (**1r**–**1t**) appeared to be the cause of the higher reaction temperatures. The presence of five-membered rings would require a higher activation energy in the reductive elimination step (Scheme 1) to give the final products, owing to the presence of angular strain. It is noteworthy that no such products (**3ra**–**3ta**) have been synthesized previously.[10] The reaction of 2-(naphthalen-1-yl)pyridine (**1u**) with compound **2a** provided compound **3ua** in excellent yield under similar reaction conditions (Table 1, entry 30). In a similar manner, 2-(naphthalen-2-yl)-pyridine (**1v**) also reacted with compound **2a** to form the corresponding pyridinium salt (**3va**) in 92% yield (Table 1, entry 31). There were two possible C–H activation sites in substrate **1v**, that is, at the C1 and C3 positions. However, the activation only occurred at the C3 position, owing to the steric effect of the fused aromatic ring.

On the basis of the known metal-catalyzed, directing-group-assisted C–H activation and annulation reactions,[5–11] a plausible mechanism for the rhodium-catalyzed annulation of 2-phenylpyridine (**1a**) with compound **2a** is proposed in Scheme 1. The first step likely involves the coordination of

Table 1. (Continued)

	1	2	Product 3	Yield [%][b]
16	**1p**	**2a**	 **3pa**	87
17		**2b**	 **3ab**: R^3, R^4 = 4-MeC_6H_4	85
18		**2c**	**3ac**: R^3, R^4 = 4-$OMeC_6H_4$	92
19	**1a**	**2d**	**3ad**: R^3, R^4 = 4-BrC_6H_4	91
20		**2e**	**3ae**: R^3, R^4 = 4-FC_6H_4	71
21		**2f**	**3af**: R^3, R^4 = $(CH_2)_2CH_3$	88
22	**1a**	**2g**	 **3ag**	90 (6:1)[e]
23	**1a**	**2h**	 **3ah**	89 (7:1)[e]
24	**1a**	**2i**	 **3ai**: R^4 = 4-MeC_6H_4	79 (95:5)[e]
25	**1a**	**2j**	 **3aj**	78 (7:1)[e]
26	**1q**	**2a**	 **3qa**	93[d]
27	**1r**	**2a**	 **3ra**	84[d,f]
28	**1s**	**2a**	 **3sa**	95[g]
29	**1t**	**2a**	 **3ta**	69[h,f]
30	**1u**	**2a**	 **3ua**	97[d]
31	**1v**	**2a**	 **3va**	92[d]

[a] All of the reactions were carried out by using 2-arylpyridine **1** (0.34 mmol), alkyne **2** (0.28 mmol), $[(RhCl_2Cp^*)_2]$ (1.0 mol%), and $Cu(BF_4)_2{\cdot}6H_2O$ (0.14 mmol) in DME (3 mL) at 25°C for 24 h under 1 atm O_2. [b] Yield of isolated product. [c] The reaction was carried out for 48 h. [d] The reaction was carried out at 60°C. [e] The ratio of the regioisomers was determined by ^{1}H NMR analysis and is given in parentheses; the major isomer is shown. [f] 10 mol% $AgBF_4$ was used. [g] The reaction was carried out in *t*AmylOH at 100°C. [h] The reaction was carried out with 2-ethoxyethanol at 120°C for 48 h.

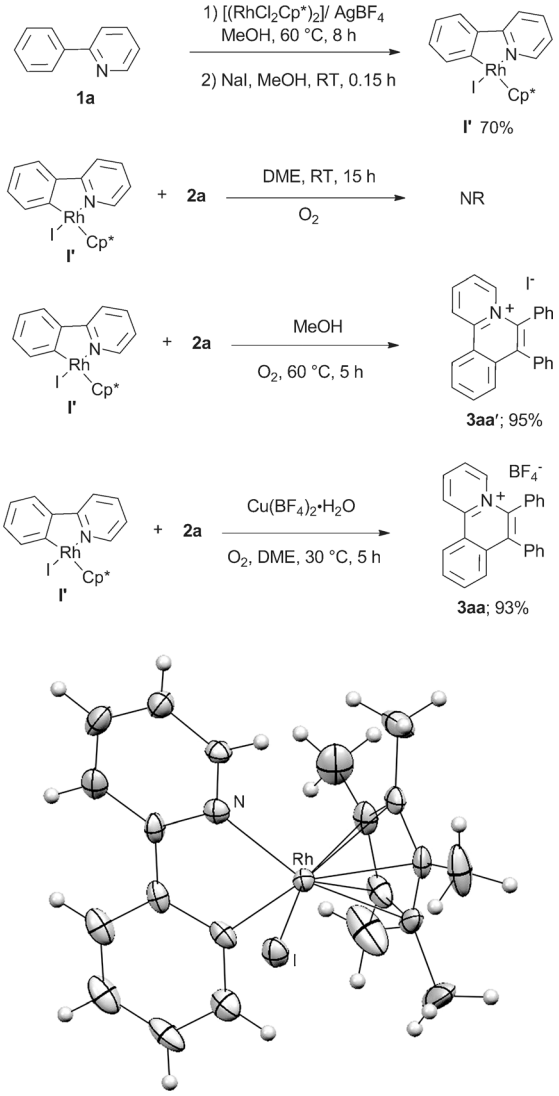


Scheme 1. Proposed mechanism for the formation of pyridoisoquinolinium salt **3aa**.

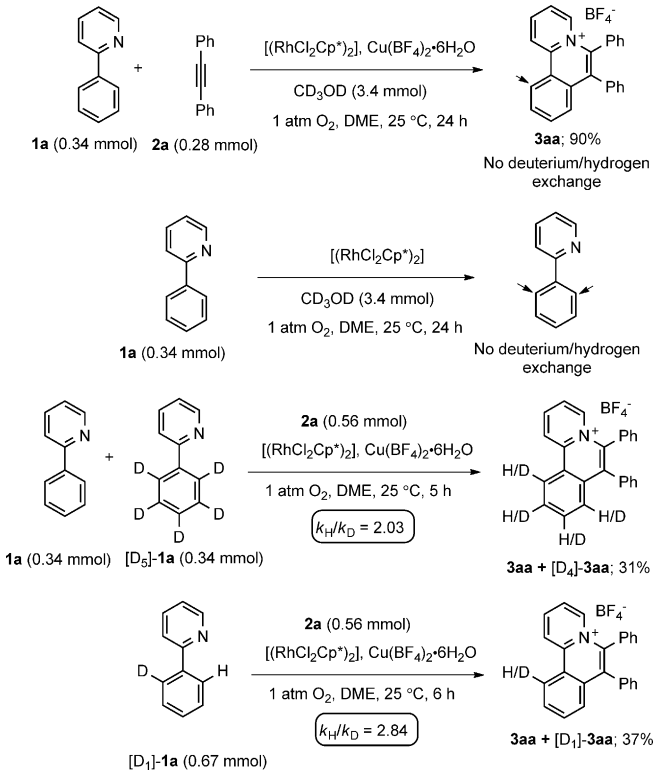
the pyridine group of compound **1a** to the rhodium metal center, followed by cyclometalation of an *ortho*-phenyl C–H bond to the rhodium(III) center to form five-membered rhodacycle **I**. The coordination of alkyne **2a** to complex **I** gives intermediate **II** and subsequent insertion of the coordinated alkyne to the Rh–C bond affords seven-membered rhodacycle **III**. Finally, reductive elimination from structure **III** gives the pyridoisoquinolinium salt product (**3aa**) and a rhodium(I) species. Oxidation of the latter species regenerates the active rhodium(III) catalyst.

To support this proposed mechanism, we tried to isolate key intermediate **I** (Scheme 1). Thus, 2-phenylpyridine (0.40 mmol) was heated in the presence of $[(RhCl_2Cp^*)_2]$ (0.16 mmol) and $AgBF_4$ (0.80 mmol) in MeOH at 60 °C for 8 h, which led to the isolation of five-membered rhodacycle **I** in 75 % yield. However, attempts to crystalize intermediate **I** by using various solvents under different conditions failed. Based on our previous experiments,[6] intermediate **I** was treated with NaI in MeOH at room temperature for 0.15 h to afford rhodium intermediate **I′**, which was isolated in 70 % yield (Scheme 2). Single crystals of complex **I′** were readily obtained from its solution in MeOH and its structure was determined by X-ray diffraction. As shown in Scheme 2, the rhodium complex is an 18-electron system that contains a cyclometalated 2-phenylpyridine moiety and a pentamethylcyclopentadienyl ligand, in addition to a directly coordinated iodide ligand. The reaction of complex **I′** with compound **2a** in DME did not afford any pyridoisoquinolinium product (**3**) at room temperature; the starting materials were recovered in almost-quantitative yield after 15 h at room temperature.[7,12a] However, complex **I′** reacted with compound **2a** in MeOH at 60 °C to afford compound **3aa′** in 95 % yield with an I^- counteranion; the structure was confirmed by ^1H and ^{13}C spectroscopy, HRMS, and X-ray diffraction. On the other hand, the addition of 0.5 equivalents of $Cu(BF_4)_2{\cdot}6H_2O$ to the reaction of complex **I′** with compound **2a** in DME led to the corresponding pyridoisoquinolinium salt (**3aa**) in 93 % yield at room temperature.

To gain more-detailed information on the mechanism of this catalytic reaction, we carried out the reaction between compounds **1a** and **2a** under standard conditions with the addition of 10 equivalents of CD_3OD. The reaction produced compound **3aa** in 90 % yield, but with no incorporation of deuterium into the product, thus indicating that no deuterium/hydrogen exchange had occurred during the catalytic reaction (Scheme 3). To validate this result, we treated compound **1a** under our standard reaction conditions for 24 h and compound **1a** was recovered in quantitative yield, with no deuterium/hydrogen exchange observed. These experiments indicated that the cyclometalation of Rh^{III} with substrate **1a** was irreversible. To further understand the inherent nature of the mechanism of this catalytic reaction, we determined the inter- and intramolecular kinetic isotopic effects (KIEs) in the catalytic reaction of compound **1a** with compound **2a**. An intermolecular KIE (k_H/k_D) of 2.03 was observed for the competition reaction between compound **1a** and deuterium-labeled compound $[D_5]$-**1a** with compound **2a** (Scheme 3). In addition, an intramolecular competition experiment between compounds $[D_1]$-**1a** and **2a** showed a k_H/k_D of 2.84. The difference between the intermolecular and intramolecular KIE values indicated that the



Scheme 2. Structure and reactivity of intermediate **I′**.



Scheme 3. Kinetic isotope study of the Rh^{III}-catalyzed formation of the pyridoisoquinolinium salts.

pre-binding of substrate **1a** (likely through the pyridine-nitrogen atom) to the Rh^{III} center took place prior to an irreversible cleavage of the C–H bond to form intermediate **I**. The observed primary KIE of 2.84 suggests that direct C–H bond cleavage is involved in the cyclometalation step and is the product-determining step.[13]

As shown in Figure 1, the synthesized polycyclic pyridinium salts showed deep-blue-to-green fluorescence emission, depending on the structures of the salts. These salts appear to be a new class of fluorescent materials that contain a pyridinium functional group. We have been interested in the search for highly efficient materials for application in organic light-emitting diodes (OLEDs).[14] It is known that improved OLED device performance has been achieved by using ionic materials as the dopants.[15] Moreover, pyridinium salts are also found to be potential candidates for use in the electron-injection layer in organic light-emitting diodes, owing to their relatively low HOMO and LUMO levels.[16] The ionic character of these materials also make them excellent candidates as OLED materials for solution processing. Investigations in this direction are underway.

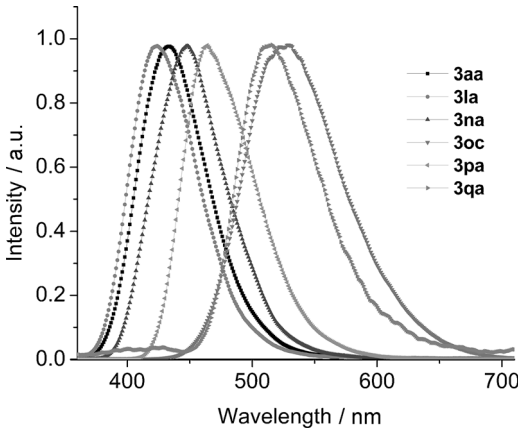


Figure 1. Fluorescence spectra of selected pyridinium salts at a concentration of 1×10^{-5} M in CH_2Cl_2.

Conclusion

We have successfully developed a convenient method for the synthesis of highly substituted isoquinolinium salts through a rhodium-catalyzed C–H activation/cyclization sequence in one pot under very mild reaction conditions. Our proposed mechanism was strongly supported by the isolation of a five-membered rhodacycle intermediate. Kinetic isotope labeling studies implied that the C–H activation step followed the irreversible cyclometalation step and that the initial C–H activation may be the rate-limiting step. Primary photophysical studies were also performed on the new pyridinium salt compounds. Further studies towards intramolecular C–H activation and the application of these compounds in OLED materials are underway in our laboratory.

Experimental Section

General procedure for the synthesis of pyridinium salts: A sealed tube that contained [(RhCl$_2$Cp*)$_2$] (1.0 mol%) and Cu(BF$_4$)$_2$•6H$_2$O (0.14 mmol) was evacuated and purged with oxygen gas three times. Then, a solution of 2-arylpyridine **1** (0.34 mmol) and alkyne **2** (0.28 mmol) in 1,2-dimethoxyethane (3.0 mL) was added to the system by syringe under an oxygen atmosphere and the reaction was stirred at 25 °C for 24 h under an O_2 atmosphere. At the end of the reaction, the mixture was diluted with CH_2Cl_2 (10 mL) and filtered through a pad of celite, which was washed several times with CH_2Cl_2 (50 mL). The combined filtrate was concentrated in vacuo and the mixture was purified by column chromatography on silica gel (CH_2Cl_2/MeOH, 95:5) to afford the desired pure product (**3**).

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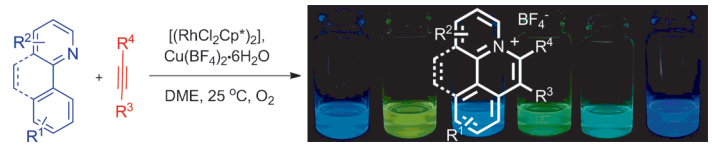

Rh^{III} and easy: A convenient synthesis of polycyclic pyridinium salts in excellent yields through Rh^{III}-catalyzed C–H activation under an O_2/Cu^{II} atmosphere at ambient temperature is described (see scheme). These salts showed strong fluorescence in CH_2Cl_2. DME = 1,2-dimethoxyethane.

C–H Activation

*C.-Z. Luo, P. Gandeepan, J. Jayakumar, K. Parthasarathy, Y.-W. Chang, C.-H. Cheng** ▮▮▮▮–▮▮▮▮

Rh^{III}-Catalyzed C–H Activation: A Versatile Route towards Various Polycyclic Pyridinium Salts