ACS Catalysis

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Pyrene-Based Mono- and Di-N-Heterocyclic Carbene Ligand Complexes of Ruthenium for the Preparation of Mixed Arylated/Alkylated Arylpyridines

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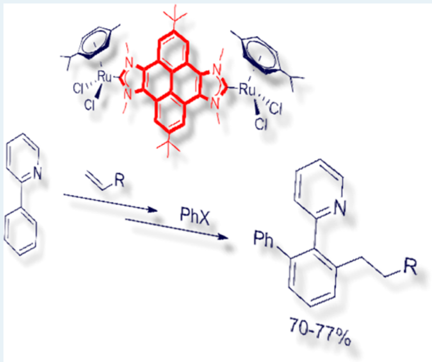
S *Supporting Information*

ABSTRACT: By using two pyrene-based mono- and di-N-heterocyclic carbene ligands, two ruthenium complexes (one monometallic and the other dimetallic) have been obtained and fully characterized. The molecular structure of the dimetallic complex has been determined by means of X-ray diffraction studies. The electrochemical studies reveal that the metal−metal communication in the dimetallic complex is weak. The catalytic activity of both complexes has been tested in the arylation of arylpyridines with aryl halides and in the hydroarylation of alkenes, where they showed similar activity. The sequential combination of these two catalytic processes (hydroarylation of alkenes followed by arylation of the resulting alkyl-substituted arylpyridine) allowed the preparation of mixed arylated/alkylated arylpyridines. In this tandem process, the dimetallic complex afforded activity higher than that of the monometallic complex. The activity was compared to that shown by the $[RuCl_2(p\text{-cymene})]_2$ complex. This reaction constitutes an efficient method for reaching unsymmetrically substituted arylpyridines.



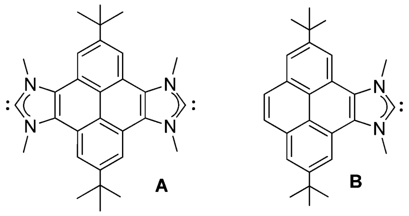
KEYWORDS: *ruthenium, N-heterocyclic carbene, Janus, tandem, arylation of arylpyridines, hydroarylation of alkenes*

■ INTRODUCTION

The replacement of salt-generating chemical synthesis with efficient catalyzed reactions that strive for atom economy is having a significant impact on the manufacturing of fine chemicals and pharmaceuticals. In this regard, the need for efficient synthetic procedures for sophisticated products may benefit from the use of tandem catalytic methods, which allow a sequence of reactions to be conducted in a single reaction vessel, without the need for purification of the reaction intermediates.[1] When considering the possibility of sequential combination of a series of catalytic reactions, it has to be taken into account that the catalyst has to be compatible with the reaction conditions needed for each catalytic process, and also with the generation of any residual materials in the preceding steps.[1a] This means that it is important to explore the compatibility of the individual catalytic reactions before they are combined in the full tandem process.

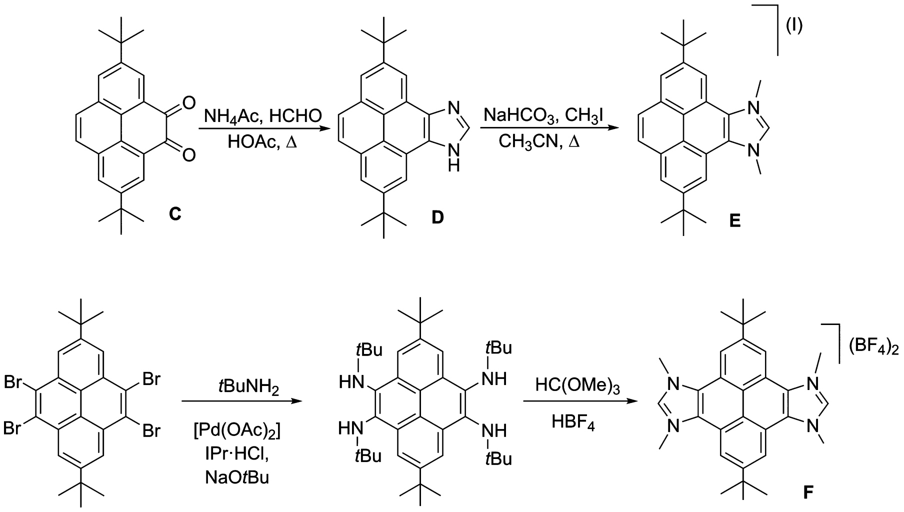
We have been recently interested in the preparation of heterometallic complexes for the design of sophisticated tandem processes.[2] Our idea was to combine two different metals linked to a single-frame ligand,[3] the idea being that each metal promotes a mechanistically independent catalytic cycle. We have also been interested in the preparation of improved catalysts based on N-heterocyclic carbene ligands (NHCs) decorated with rigid polyaromatic systems.[4] In our studies, we repeatedly observed that the use of polymetallic catalysts produces clear improvements in the catalytic efficiencies of the complexes compared to those provided by the monometallic analogue complexes, although we have tentatively attributed this improvement to the presence of the rigid polyaromatic ligand, rather than to the polymetallic nature of the catalyst. One of the rigid bis-NHC ligands that we recently described is a pyrene-based bis-NHC, which was coordinated to rhodium and iridium and displayed interesting photophysical properties as well as unusual geometrical features arising from the planar configuration of the ligand (**A**, Scheme 1).[5] On the basis of this ligand, and the related monometallic analogue (based on **B**), we now report the preparation of two complexes of ruthenium, and the exploration of their catalytic activity in a tandem process that combines the chelation-assisted arylation of arylpyridines and the subsequent hydroarylation of unactivated alkenes. We initially chose ruthenium for the coordination of these new

Scheme 1. NHC-Based Ligands Used in This Work

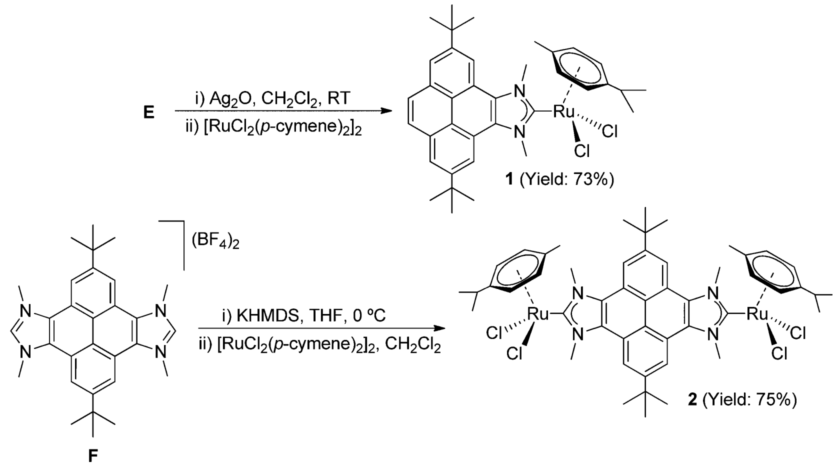


Received: May 29, 2014
Revised: July 14, 2014
Published: July 15, 2014

Scheme 2. Preparation of Mono- and Bis-azolium Salts E and F



Scheme 3. Preparation of Complexes 1 and 2



ligands, because ruthenium complexes have shown an extraordinary catalytic versatility in a wide set of non-metathetical reactions applied for the production of fine chemicals.[6] Specifically, ruthenium(II) complexes often combine a good stability with a high activity toward sp^2 C−H bond conversion, and the rapid development of this area has been achieved following the seminal works by Oi and Inoue,[7] as exemplified by the publication of a number of interesting review articles by Ackermann[6e,8] and Bruneau and Dixneuf.[9] This type of reaction has also allowed the design of interesting tandem processes, like those resulting from the combination of arylation and hydrosilylation, both facilitated by Ru(II) catalysts.[10] We also contributed to the field by describing the activities of a series of [RuCl$_2$(arene)(NHC)] complexes in the arylation and selective deuteration of a series of arylpyridines.[11] On the basis of these previous findings, and connecting with the recently described Ru(II)-catalyzed hydroarylations of unactivated alkenes described by Ackermann,[12] we decided to combine both processes for the preparation of arylpyridines with asymmetrically 2,2′-substituted phenyl rings. The reaction constitutes an interesting example of combination of two atom-economy reactions for the production of highly sophisticated products, by the sequential activation of two identical *ortho* C−H bonds of functional arenes. It has to be noted that this type of reaction has not yet been achieved, in spite of its potential to reach new mixed bifunctional polyaromatic molecules of interest for molecular materials and as polymer precursors.

■ RESULTS AND DISCUSSION

The pyrene imidazolium salt **E** was obtained starting from 2,7-di-*tert*-butylpyrene-4,5-dione, **C**, as shown in Scheme 2. The annulation of this diketone with ammonium acetate and formaldehyde in refluxing acetic acid afforded the related pyrene-imidazole, **D**, in almost quantitative yield (97%). **D** was dimethylated with MeI in refluxing acetonitrile in the presence of NaHCO$_3$, yielding the final pyrene-imidazolium, **E**, in 67% yield. Salt **E** was characterized by means of nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry, and elemental analysis. Bis-azolium salt **F** was prepared according to the method that we previously described (Scheme 2).[5]

Salt **E** and pyrene-bis-azolium salt **F** were used as NHC precursors for the synthesis of the related ruthenium complexes, as depicted in Scheme 3. The preparation of monometallic complex **1** was better achieved by trans-metallating the NHC ligand from the *in situ* prepared silver-NHC complex to [RuCl$_2$(*p*-cymene)]$_2$. Dimetallic complex **2** was obtained by deprotonation of bis-azolium salt **F** with potassium bis(trimethylsilyl)amide (KHMDS) and subsequent

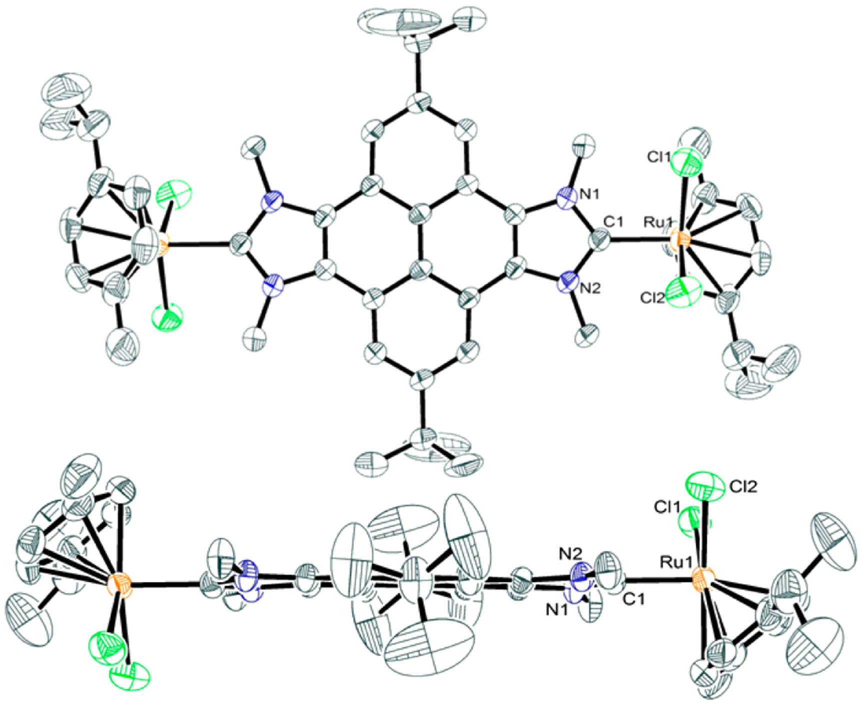


Figure 1. Two perspectives of the molecular structure of **2**. Hydrogen atoms and solvent (dichloroethane) have been omitted for the sake of clarity. Thermal ellipsoids are shown at the 50% level of probability. Selected bond distances (angstroms) and angles (degrees): Ru(1)−Cl(1), 2.4378(15); Ru(1)−Cl(2), 2.4231(17); Ru(1)−C(1), 2.097(5); Ru−(*p*-cymene)$_{\text{centroid}}$, 1.693(5); Cl(1)−Ru(1)−Cl(2), 84.65(6); C(1)−Ru(1)−Cl(1), 91.24(14); C(1)−Ru(1)−Cl(2), 88.14(15).

addition of $[\text{RuCl}_2(p\text{-cymene})]_2$. Both complexes were characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. The ^{1}H NMR spectrum of **1** confirms the 2-fold symmetry of the molecule caused by the presence of a mirror plane, as exemplified by the equivalency of the protons of the methyl groups of the *tert*-butyl substituents, and the three resonances assigned to the six protons of the pyrene. The ^{13}C NMR spectrum of **1** displays characteristic signals due to the carbene carbon at 184.2 ppm. The ^{1}H NMR spectrum of **2** is in agreement with the 2-fold symmetry of the complex, as illustrated by the presence of one single resonance due to the four protons of the pyrene. The ^{13}C NMR spectrum of **2** shows the signal due to the carbene carbons at 186.7 ppm.

The molecular structure of **2** could be determined by single-crystal X-ray diffraction studies. The molecule consists of a pyrene-bis-imidazolylidene bridging two ruthenium centers, which complete their coordination sphere with a *p*-cymene and two chloride ligands. The relative configuration of the ligands about the ruthenium atoms is *anti*, based on the orientation of the *p*-cymene ligands, therefore affording pseudo-C_{2h} symmetry. The bridging ligand is planar, as can be confirmed by the side-on perspective of the molecule given in Figure 1. The Ru−C$_{\text{carbene}}$ distance is 2.097 Å, and the through-space distance between the metals is 13.39 Å, very similar to the M−M distance provided by the same ligand in our previously reported complexes of rhodium and iridium.[5]

Cyclic voltammetry (CV) studies were conducted to determine whether there is any significant metal−metal electronic communication across the pyrene-di-imidazolylidene ligand in dimetallic complex **2**. The complex displays a single quasi-reversible one-electron oxidation wave centered at an $E_{1/2}$ of 1.336 V. Complex **1** displays two oxidation waves corresponding to the oxidation of the ruthenium center ($E_{1/2}$ = 1.271 V) and to the oxidation of the pyrene fragment ($E_{1/2}$ = 1.462 V),[13] with the first being quasi-reversible and the second irreversible (see the Supporting Information for details). The differencial pulse voltammetry (DPV) analysis of both complexes allowed us to observe that the metal-centered wave for dimetallic complex **2** is slightly broader than the related wave displayed by monometallic complex **1**. Taking the DPV signal of **1** as a reference, we found the deconvolution of the DPV curve for **2** shows two bands separated by 40 mV (Figure 2). This separation indicates an essentially decoupled

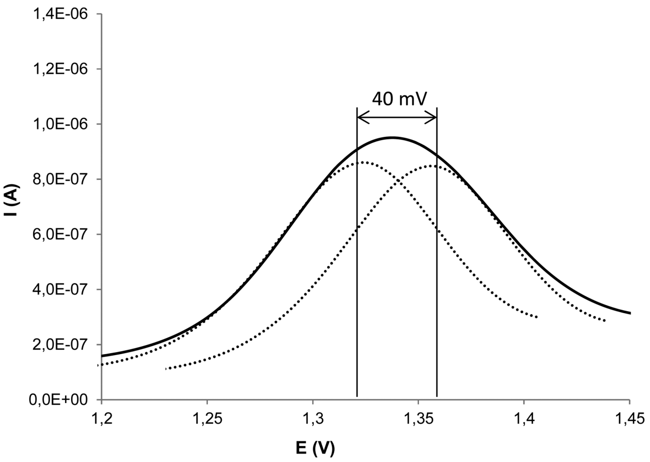
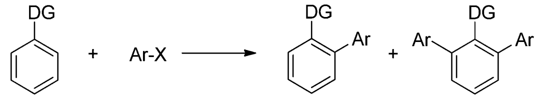
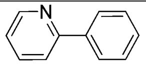
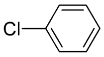
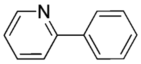
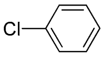
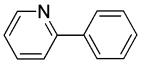
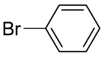
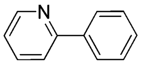
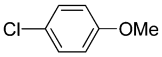
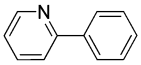
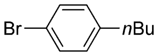
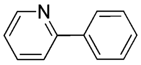
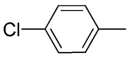
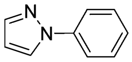
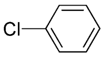
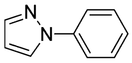
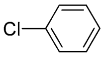
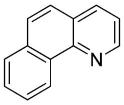
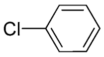


Figure 2. Relevant DPV section of complex **2** (1 mM in dry CH_2Cl_2 with 0.1 mM $[\text{NBu}_4][\text{PF}_6]$ as the supporting electrolyte, scan rate of 50 mV s^{-1}, Fc$^+$/Fc used as an internal standard with $E_{1/2}$ (Fc/Fc$^+$) = 0.44 V vs the saturated calomel electrode). The convoluted curves (gray dotted lines) were obtained from adding two potential-shifted and weighted signals of monometallic complex **1**.

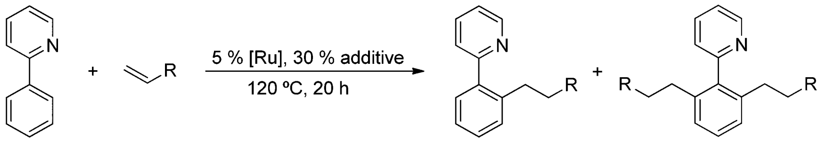
Table 1. Arylation of Arylpyridines Using Catalysts **1** and **2**[a]



Entry	Pyridine	Ar-X	Cat	t (h)	Monoarylated (%)[b]	Bisarylated (%)[b]
1			**2**	3	1	98 (85)
2			**1**	3	-	98
3			**2**	2	-	98
4			**2**	5	-	99
5			**2**	2	-	99
6			**2**	4	-	99
7			**2**	1	-	99 (82)
8			**1**	1	-	99
9			**2**	2	-	95

[a]Reaction conditions: KOAc (0.05 mmol), 5% catalyst loading (based on metal), 2 mL of NMP, room temperature for 1 h, then substrate (0.5 mmol), Ar-X (1.25 mmol), K_2CO_3 (1.25 mmol), 120 °C. [b]Yields determined by gas chromatography using anisole (0.5 mmol) as an internal standard. Isolated yields in parentheses.

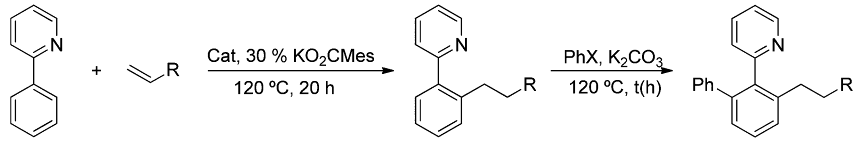
Table 2. Hydroarylation of Terminal Alkenes with 2-Phenylpyridine, Using Catalysts **1** and **2**[a]



entry	R	catalyst	additive	solvent	monoalkylated (%)[b]	bisalkylated (%)[b]
1	*n*-octyl	**2**	KOAc	NMP	6	–
2	*n*-octyl	**2**	KO_2CMes	NMP	14	–
3	*n*-octyl	**2**	KOAc	toluene	72	–
4	*n*-octyl	**2**	KO_2CMes	toluene	93 (81)	–
5	*n*-octyl	**1**	KO_2CMes	toluene	95	–
6[c]	*n*-octyl	**2**	KO_2CMes	toluene	93	–
7	*n*-hexyl	**2**	KO_2CMes	toluene	94 (79)	–
8	*n*-hexyl	**1**	KO_2CMes	toluene	96	–
9	*n*-butyl	**2**	KO_2CMes	toluene	94 (80)	–
10	*n*-butyl	**1**	KO_2CMes	toluene	97	–
11	trimethylsilyl	**2**	KO_2CMes	toluene	90 (80)	9 (7)

[a]Reaction conditions: 0.5 mmol of 2-phenylpyridine, 1.5 mmol of alkene, 0.15 mmol of additive, 5% catalyst loading (based on metal), 2 mL of solvent, 120 °C, 20 h. Mes = 2,4,6-trimethylphenyl. [b]Yields determined by gas chromatography using anisol (0.5 mmol) as an internal standard. Isolated yields in parentheses. [c]Reaction conducted in the presence of a drop of mercury.

Table 3. Sequential Hydroarylation of Alkenes and Arylation of Arylpyridines Catalyzed by **1**, **2**, and $[\mathrm{RuCl_2}(p\text{-cymene})]_2$[a]



entry	R	catalyst	PhX	t (h)	yield (%)[b]
1	*n*-octyl	**1**	PhBr	24	38
2	*n*-octyl	**1**	PhBr	72	51
3	*n*-octyl	**2**	PhCl	24	48
4	*n*-octyl	**2**	PhBr	24	52
5[c]	*n*-octyl	**2**	PhBr	24	3
6[d]	*n*-octyl	**2**	PhBr	24	15
7	*n*-octyl	**2**	PhBr	72	61
8	*n*-octyl	**2**	PhBr	90	71 (64)
9[e]	*n*-octyl	**2**	PhBr	24	50
10	*n*-octyl	$[\mathrm{RuCl_2}(p\text{-cymene})]_2$	PhBr	24	52
11	*n*-hexyl	**1**	PhBr	24	32
12	*n*-hexyl	**1**	PhBr	48	42
13	*n*-hexyl	**2**	PhBr	24	44
14	*n*-hexyl	**2**	PhBr	72	73 (62)
15	*n*-hexyl	$[\mathrm{RuCl_2}(p\text{-cymene})]_2$	PhBr	24	51
16	*n*-butyl	**1**	PhBr	24	37
17	*n*-butyl	**1**	PhBr	48	49
18	*n*-butyl	**2**	PhBr	24	45
19	*n*-butyl	**2**	PhBr	72	70
20	*n*-butyl	**2**	PhBr	90	77 (65)
21	*n*-butyl	$[\mathrm{RuCl_2}(p\text{-cymene})]_2$	PhBr	24	45
22	*n*-butyl	$[\mathrm{RuCl_2}(p\text{-cymene})]_2$	PhBr	48	60

[a] Reaction conditions: 0.5 mmol of 2-phenylpyridine, 1.5 mmol of alkene, 0.15 mmol of $\mathrm{KO_2CMes}$, 5% catalyst loading (based on metal), 2 mL of toluene, 120 °C, 20 h. Then 1 mmol of PhX and 1 mmol of $\mathrm{K_2CO_3}$, 120 °C for the appropriate time. [b] Yields determined by GC using anisol (0.5 mmol) as an internal standard. Isolated yields in parentheses. [c] Two milliliters of H_2O was added in the second step of the reaction. [d] Two milliliters of NMP was added in the second step of the reaction. [e] The reaction was conducted in the presence of a drop of mercury.

system, as the ones that we found for our previously dimetallic complexes of iridium(I), based on the same ligand (the coupling was 30 mV).[5] This weak coupling compares well to those of other π-linked di-NHCs[14] and is in agreement with our previous suggestion that the electronic communication across polyaromatic-linked di-NHCs is mostly due to a σ-interaction,[15] unless a proper orientation of the carbene and metal orbitals is achieved by the use of the appropriate chelating ligands.[16]

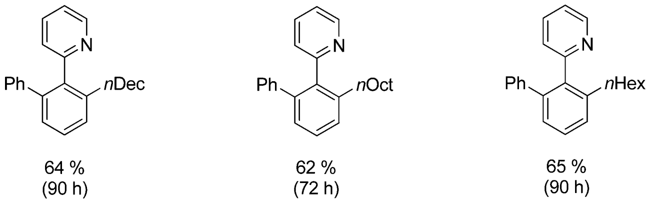
Complexes **1** and **2** were tested in the arylation of arylpyridines with a series of arylhalides. The results are listed in Table 1. For the study of this reaction, we used previously described reaction conditions (120 °C in NMP)[7b,17] and a catalyst loading of 5 mol %, based on the amount of metal. As shown in the results listed in the table, both complexes afforded almost quantitative yields to the bisarylated arylpyridines, in relatively short reaction times (1−5 h). These results clearly improve the activity shown by other related $[\mathrm{RuCl_2}(p\text{-cymene})(\mathrm{NHC})]$ complexes in the same reaction, for which longer reaction times were needed and poorer selectivities were achieved.[11] The comparison of the activities afforded by monometallic catalyst **1** and dimetallic complex **2** reveals that there are not any significant differences in the activities afforded by these two complexes.

Encouraged by these results, we then decided to test both catalysts in the hydroarylation of unactivated alkenes. This carboxylate-assisted reaction, recently developed by Ackerman and co-workers,[12] constitutes a convenient atom-economical addition of sp^2 C−H bonds to unactivated alkenes and has the potential to provide access to a wide variety of alkyl-substituted bicyclic compounds, which are important motifs in medicinal chemistry.[18] The reactions were conducted using 2-phenylpyridine and a terminal alkene, in the presence of a carboxylate at 120 °C, and using a 5 mol % of catalyst loading (based on the amount of metal). We were interested in determining whether the reaction could be efficient using NMP as a solvent, to explore the compatibility of this reaction with the arylation of arylpyridines (reactions shown in Table 1), but the process was completely inefficient. As shown by the results listed in Table 2, the optimal reaction conditions were obtained when $\mathrm{KO_2CMes}$ and toluene were used, and the activities of the two catalysts compare well with the previously reported results.[12] As observed before, we did not find any significant differences in the catalytic activities provided by monometallic and dimetallic catalysts **1** and **2**, respectively. Interestingly, although the reactions were very selective in the formation of the monoalkylated phenylpyridines, for the reaction with trimethylvinylsilane a small amount of the bisalkylated compound was observed. Because the reaction is conducted at a high temperature and needs a long time to reach completion, we considered it convenient to perform a mercury drop experiment to discard the possibility that the reaction could be heterogeneously catalyzed.[19] As shown by the comparison of the results listed in the table (compare entries 4 and 6), the yields obtained do not dependently vary upon addition of the drop of mercury, and therefore, we believe that the heterogeneity of the process may be ruled out.

Given the activity of **1** and **2** in the arylation of arylpyridines and in the hydroarylation of alkenes, we decided to combine these two reactions in a tandem process to afford unsymmetrically substituted phenylpyridines. Because of the deactivation of the hydroarylation in NMP, which is the optimal solvent for the arylation of arylpyridines, we decided to conducted the sequence of reactions in toluene, a solvent that has already proven to be adequate for this process.[20] Considering that the hydroarylation of alkenes selectively yields the monoalkylated products, leaving an unfunctionalized C−H bond at position 2′ of the phenylpyridine, we designed the sequence by first proceeding with the hydroarylation to form the monoalkylated phenylpyridine and then adding the arylhalide to arylate the remaining C−H bond and afford the final alkyl,aryl-substituted phenylpyridine. The inversion of the sequence would facilitate the formation of the bisarylated phenylpyridine, because arylation is favored over hydroarylation. The reactions were conducted by reacting 2-phenylpyridine with the terminal alkene in toluene at 120 °C for 20 h, in the presence of KO_2CMes and 5 mol % of catalyst (based on metal), and then adding the arylhalide and K_2CO_3. The results for the overall process are listed in Table 3, where *t* (time) refers to the time for the second step of the reaction (arylation). As shown by the data listed in the table, the catalysts afford moderate yields to the final unsymmetrically substuted phenylpyridines after 24 h [gas chromatography (GC) yields 38−52%], but longer reaction times (90 h) allow the achievement of the final products in higher yields (GC, 71−77%; isolated, 62−65%), which in fact indicates that the catalyst remains active for the very long reaction process. Some previous works have suggested that the arylation of arylpyridines may be favored in the presence of water,[21] and this is why we also performed a reaction in which water was added to the second step of the process. As shown in Table 3, the addition of water clearly reduces the efficiency of the process, compared to that of the reaction in which toluene is used (compare entries 4 and 5). Interestingly, although dimetallic complex **2** showed activities similar to that shown by monometallic complex **1** in the individual steps of the reactions (Tables 1 and 2), now dimetallic complex **2** shows an activity higher than that of **1**, as shown by the higher product yields provided by the dimetallic complex. For comparative purposes, we also conducted the reactions using $[RuCl_2(p\text{-cymene})]_2$ as a catalyst, and we observed that the activity of this complex is very similar to that afforded by dimetallic complex **2**. Because the overall process requires a very long reaction time at a very high temperature, we also considered it important to discard the possibility that the process may be heterogeneously catalyzed, and therefore, we performed the mercury drop test. As shown by the results listed in the table (compare entries 4 and 9), when the reaction was conducted in the presence of a drop of mercury, the final yields were quasi-identical to the results obtained in the absence of mercury. This result suggests that the process is homogeneously catalyzed.

Scheme 4 shows the maximal yields obtained and the reaction conditions used in the preparation of each unsymmetrically substituted phenylpyridine using catalyst **2**. Given the complexity of the process, we consider these yields to be remarkable.

Scheme 4. Maximal Isolated Yields Obtained in the Production of Unsymmetrically Substituted Arylpyridines Using Catalyst 2



■ CONCLUSIONS

In summary, we have obtained a new diruthenium complex based on a pyrene-bis-NHC Janus-type ligand and a related monometallic complex of ruthenium with a pyrene-based-NHC ligand. The catalytic activity of both complexes has been tested in the arylation of arylpyridines with aryl halides and in the hydroarylation of alkenes, where they showed very similar catalytic activities. The sequential combination of these two catalytic processes (hydroarylation of alkenes followed by arylation of the resulting alkyl-substututed arylpyridine) allowed the preparation of mixed arylated/alkylated arylpyridines, by the successive C−H bond activation of two identical C−H bonds. In this tandem process, dimetallic complex **2** afforded an activity higher than that of related monometallic complex **1**. The $[RuCl_2(p\text{-cymene})]_2$ complex provided a catalytic activity similar to that of **2**. This reaction constitutes an efficient method for reaching unsymmetrically substituted arylpyridines and widens the accessibility to a wide range of new materials that may have important applications in materials chemistry and pharmaceuticals. To the best of our knowledge, only one recent example describing the sequential chelating-assisted monoarylation with two different arylhalides to reach unsymmetrical *ortho* diarylated arenes has been reported, which also included an interesting example of mixed *ortho*-arylated and alkenylated arenes,[21] but our work constitutes the first example describing the access to mixed *ortho*-substituted alkyl/aryl-phenylpyridines.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and characterization data of all new complexes and crystallographic details of complex **2** in the form of a cif file. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge financial support from Ministerio de Economia y Competitividad of Spain (CTQ2011-24055/BQU). S.G. thanks the Ministerio de Ciencia e Innovación for a fellowship. We are grateful to the Serveis Centrals d’Instrumentació Científica (SCIC) of the Universitat Jaume I for providing us with all characterization techniques. We thank Dr. Macarena Poyatos for conducting the cyclic voltammetric studies and for revising the writing of the manuscript.

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