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Heterobimetallic Iridium−Ruthenium Assemblies through an Ambidentate Triazole-Diylidene Ligand: Electrochemical Properties and Catalytic Behavior in a Cascade Reaction

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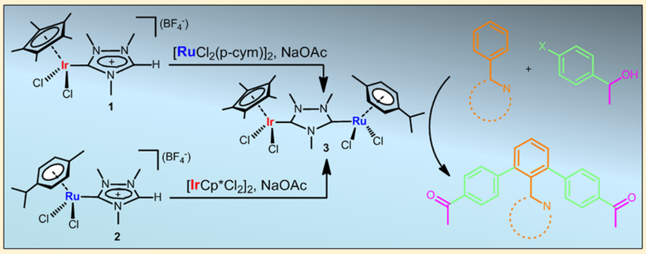
Ⓢ *Supporting Information*



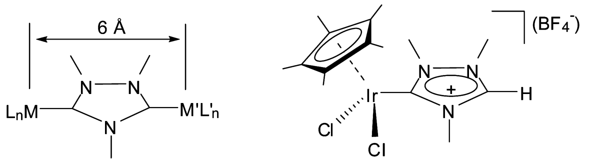
ABSTRACT: The preparation in high yield of a (*p*-cymene)-Ru^{II}(triazolium-ylidene) complex allows the synthesis of an heterobimetallic Ir^{III}−Ru^{II} complex with a triazole-diylidene bridge. The same complex can also be prepared by starting from the previously reported complex Cp*Ir^{III}(triazolium-ylidene). A full electrochemical study of the heterobimetallic complex has been performed, and the results have been compared with those for the related homobimetallic triazole-diylidene bridged complexes of ruthenium and iridium, where a weak metal−metal interaction (class II, according to the Robin and Day classification) has been detected. The Ir−Ru complex and some other related (*p*-cymene)Ru(NHC) complexes have been tested in a new tandem process, implying the chelation-assisted arylation of arylpyridines with 1-(4-halophenyl)ethanol. The arylation is accompanied by the transformation of the alcohol into a ketone, in the presence of acetone, through an Oppenauer oxidation process.

■ INTRODUCTION

Synthesis by means of catalytic processes is one of the most rapidly evolving research areas in chemistry. Natural catalysts are known to be far more efficient than those developed by chemists. While the mechanism of action of enzymes often benefits from the mutual cooperation provided by two or more metals, man-made catalysts rarely exploit this approach. In the past few years, many sophisticated metal-based multicatalyst systems have been reported and reviewed.[1−3] In most of the cases, the action of the one-pot cocatalyst refers to (i) two catalysts that carry out sequential organic transformations (each step carried out by one catalyst) or (ii) cooperative catalytic actions on substrates by suitable catalysts occurring in a substrate-selective manner, followed by the coupling of the resulting activated substrates.[2] In order to avoid the use of two different catalysts, the preparation of dinuclear complexes containing two metals in close proximity has become the subject of extensive investigations in order to design efficient bimetallic catalysts.[3] The bottleneck for such research is finding convenient synthetic routes to afford stable bimetallic structures, a goal that is far more complicated to achieve when heterobimetallic species are pursued.

The metal−metal separation in bimetallic catalysts plays a crucial role in the activity of the designed complexes. It has been proposed that the optimum separation of the two metals should be 3.5−6 Å, regardless of the existence of any direct interaction between the metal centers.[3] During the past few years we have reported an efficient method for the preparation of homo- and heterobimetallic complexes bound to a 1,2,4-triazolyl-3,5-diylidene (Scheme 1).[4−9] The preparation of such types of heterobimetallic complexes allowed us to study several catalyzed tandem reactions in which each of the metal fragments facilitates a mechanistically different cycle[6,7] and, more importantly, allowed us to find clear experimental evidence for catalytic cooperativity between the metals comprised in the bimetallic unit.[7,8] Due to the easy stepwise deprotonation of a dicationic 1,2,4-triazolium salt, we found a convenient method for the preparation of a monometallic complex containing a Cp*Ir fragment bound to a triazolium-ylidene, which still contains a C−H bond that can be used to generate a second carbene center (**1**; Scheme 1).[8] On the basis of this Cp*Ir(triazolium-ylidene), we obtained several heterometallic complexes in which the Cp*Ir fragment remained constant.[7−9] Until now, the preparation of monometallic complexes with the same triazolium-ylidene ligand but with metals other than iridium remained elusive.

Scheme 1



We herein describe the preparation of a (*p*-cymene)Ru^{II} complex with a triazolium-ylidene ligand. This compound acts as an intermediate to the production of other Ru-containing

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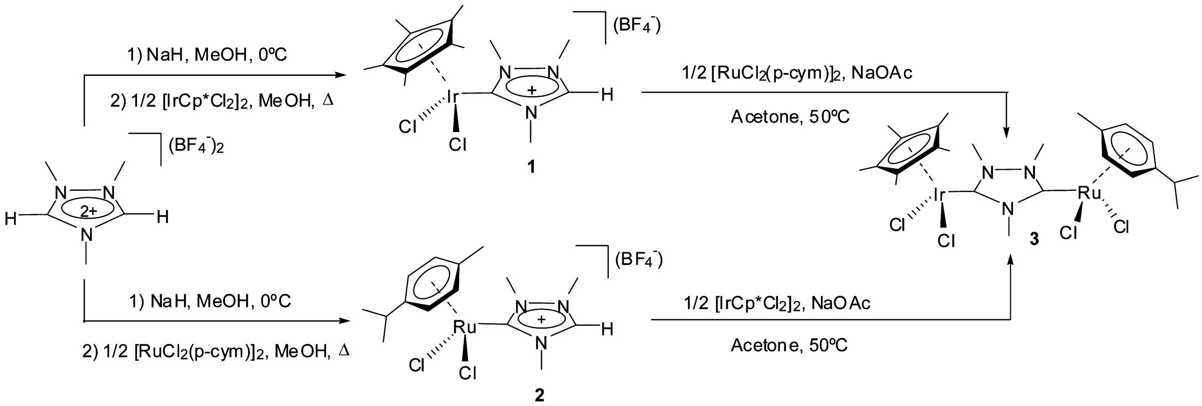
Scheme 2



heterobimetallic complexes. We have used this compound for the preparation of an heterometallic complex of Ru(II) and Ir(III). The final Ru−Ir complex can be obtained from two different routes, via the (*p*-cymene)Ru(triazolium-ylidene) or the Cp*Ir(triazolium-ylidene) intermediates. The new complexes obtained have been tested in a tandem process, implying the chelation-assisted arylation of arylpyridines with 1-(4-halophenyl)ethanol. The arylation is accompanied by the transformation of the alcohol into a ketone, in the presence of acetone, through an Oppenauer oxidation process.

RESULTS AND DISCUSSION

The reaction of 1,2,4-trimethyltriazolium tetrafluoroborate ($[ditzH_2](BF_4)_2$) in methanol at 0 °C in the presence of an equimolecular amount of NaH affords the methanolic adduct $[ditzH\text{-}MeOH](BF_4)$,[10] which can either be isolated or used in situ. The reaction of $[ditzH\text{-}MeOH](BF_4)$ with the corresponding amount of $[RuCl_2(p\text{-cymene})]_2$ in refluxing methanol affords the (*p*-cymene)Ru(triazolium-ylidene) complex **2** in high yield (80%). The reaction of **2** with $[IrCp^*Cl_2]_2$ in acetone at 50 °C in the presence of NaOAc affords the Ru(II)/Ir(III) complex **3** in 81% yield. Complex **3** can also be obtained by starting from the previously reported Cp*Ir(triazolium-ylidene) complex **1**,[8] by reaction with $[RuCl_2(p\text{-cymene})]_2$ in acetone at 50 °C in the presence of NaOAc, affording **3** in 70% yield. Scheme 2 summarizes the two possible routes to compound **3**.

Complexes **2** and **3** were characterized by NMR and mass spectroscopy. The ^1H NMR spectrum of **2** shows the characteristic signal for the acid NC*H*N proton at δ 9.54. The integration of this signal relative to the signals due to the three methyl groups (at δ 4.38, 4.21, and 4.17) indicates that only one of the two NC*H*N protons of the triazolium dicationic salt was lost upon coordination to the metal. The most relevant feature of the ^{13}C NMR spectrum is the signal due to the metalated $M-C_{carbene}$ carbon at 192.3 ppm.

The absence of any protic signal in the ^1H NMR spectrum of **3** indicates the deprotonation of both NC*H*N protons of the initial triazolium salt. The three distinct signals due to the methyl groups of the azole ring suggest the loss of the 2-fold symmetry of the ligand, upon coordination to the two different metal fragments. The ^{13}C NMR spectrum displays two representative signals due to the $Ru-C_{carbene}$ and $Ir-C_{carbene}$ signals at 186.4 and 168.1 ppm, respectively.

The molecular structure of **2** (Figure 1) was unambiguously determined by X-ray diffraction studies. The molecule can be regarded as a three-legged piano stool, with a *p*-cymene ligand, two chlorides, and a triazolium-ylidene completing the coordination sphere about the Ru(II) center. The cationic nature of the complex is confirmed by the presence of a BF_4^- counterion. The $Ru-C_{carbene}$ distance is 2.058(4) Å, in the same range as for other Ru complexes containing a bridging ditz ligand.[5]

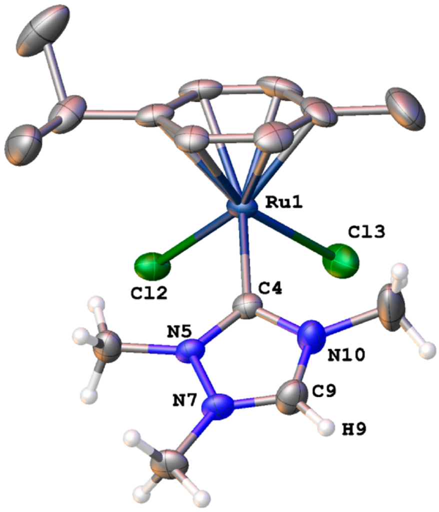


Figure 1. Molecular diagram of complex **2**. Ellipsoids are shown at the 50% probability level. Hydrogen atoms of the *p*-cymene ligand and the counteranion (BF_4^-) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−Cl(2) = 2.4045(11), Ru(1)−Cl(3) = 2.4172(10), Ru(1)−C(4) = 2.058(4), $Ru(1)-C_{centroid}$ = 1.699; C(4)−Ru(1)−Cl(2) = 90.95(11), C(4)−Ru(1)−Cl(3) = 88.37(10), Cl(2)−Ru(1)−Cl(3) = 84.91(4), N(5)−C(4)−N(10) = 102.8(3).

Cyclic voltammetric (CV) studies have recently been proposed as a valuable means to study the electronic properties of NHC ligands in rhodium and iridium complexes.[11] The same technique has also been used to ascertain whether there is any metal−metal electronic communication across ditopic bis(NHCs).[12,13] It has been claimed that the potential M═C π-bonding may stimulate electronic communication between remote metal centers connected by π-delocalized connecting ligands.[13] We have carried out CV measurements of complex **3** and for comparative purposes also on complexes **4**−**7** depicted in Scheme 3. In order to obtain more accurate data about the peak separation in the dimetallic complexes, we also performed differential pulse voltammetry (DPV) experiments (Table 1).

Scheme 3

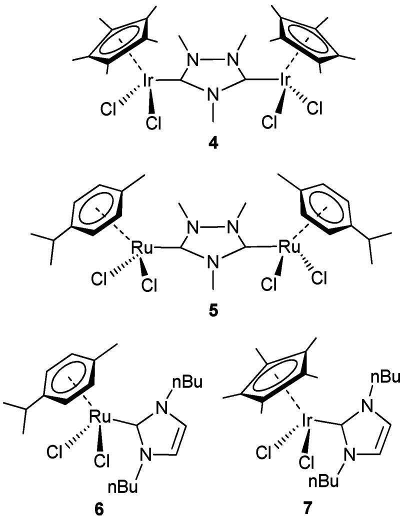


Table 1. Electrochemical Data from Cyclic Voltammetry (CV) and Difference Pulse Voltammetry (DPV)[a]

entry	complex	$E_{1/2}$ (V) (ΔE (mV))		$\Delta E_{1/2}$ (mV)
1	3	1.29 (80)	1.35 (110)	120
2	4	1.15[b]		
3	5	1.34 (−)	1.46(60)	120
4	6	1.13 (109)		
5	7	1.17 (112)		

[a] Measured in CH_2Cl_2, 0.1 M $TBAPF_6$ electrolyte, calibrated to Fc^+/Fc ($E_{1/2}$ = 0.46 V vs SCE). [b] Irreversible peak measured at 100 mV s^{-1}.

The redox potential of the monometallic Ru compound **6** is 1.13 V, attributed to the $E(Ru^{II}/Ru^{III})$ process. For the Ir complex **7**, the redox potential is 1.17 V and is attributed to an $E(Ir^{III}/Ir^{IV})$ process. These values can be compared to those shown by the dimetallic complexes **3**−**5**. The heterobimetallic complex **3** displays two independent redox processes attributed to the Ru and Ir centers, at 1.29 and 1.41 V, respectively. These values confirm that the triazolyl-diylidene ligand in **3** has a lower electron-donating character than the monocarbenes in **6** and **7**. Also, we have to take into account that the redox values shown for complexes **6** and **7** are very similar (ΔE = 40 mV); therefore, the fact that we observed the two peaks separated by 120 mV in **3** may be due to the influence of the oxidation of the Ru center over the oxidation of the Ir center, suggesting that the two centers are (weakly) electronically coupled.

Both the CV and DPV experiments on complex **5** reveal that two oxidation bands are present, separated by 120 mV (Figure 2). This separation corresponds to a class II system according to the Robin and Day classification.[14] Although this interaction can be classified as weak, it has to be taken into account that it is the highest electronic coupling measured among all other Janus-type bis-NHC related ligands reported to date, which have shown weaker couplings, ranging from 60 to 80 mV.[12,13] The first oxidation peak in **5** appears at 1.34 V, at a value slightly higher than the same process attributed to the Ru center in **3** (1.29 V), indicating that the presence of the Ru(*p*-cymene)Cl_2 fragment in **5** instead of $IrCp^*Cl_2$ reduces the electron-donating character of the part of the ligand bound to Ru(*p*-cymene)Cl_2, although this effect is small. Unfortunately, the bis-iridium complex **4** gave an irreversible CV wave; thus, we could not obtain suitable data for analysis.

In order to study the catalytic activity of the dimetallic complexes **3** and **5**, we decided to test them in a combination of two reactions: the chelation-assisted arylation of arylpyridines with aryl halides (a reaction which is typically catalyzed by Ru(II) complexes)[15] and the Oppenauer oxidation of alcohols. We wanted to explore the effect of the two metal centers in the dimetallic complexes on the final outcome of this tandem reaction. Although this tandem reaction presumably can be catalyzed by one only metal (Ru), there are no examples of such tandem reaction reported in the literature; thus, we believed that the study of this reaction might provide some interesting results. We first studied one individual step of the reaction consisting of the arylation of 2-phenylpyridine with chlorobenzene. For comparative purposes, we also tested the activity of the monometallic Ru complex **6**, a very effective catalyst for the arylation and also the deuteration of a wide set of substantially different pyridines.[16]

As can be seen from the results shown in Table 2, for the reactions carried out with 5 mol % catalyst loading (entries 1−3), the diruthenium complex **5** proved to be the most active catalyst, in terms of both conversion and selectivity toward the bis-arylated product. Interestingly, **5** provides a better catalytic outcome than the Ir−Ru complex **3**, a fact that may seem rather logical if we take into account that **5** contains two ruthenium centers while **3** contains only one. This result indicates not only that the iridium fragment is formally inactive in this reaction but also that the two metals in **5** behave as active catalytic centers, meaning that we can discard a situation in which one ruthenium is acting as a spectator center while the other is catalyzing the process. For the reaction carried out with **3**, the reduction of the catalyst loading to 2.5 mol % (entry 4, 5 mol % based on metal), results in a decrease of conversion and a loss of selectivity, and the overall catalytic outcome is very similar to that provided by the monometallic catalyst **6**. Also, under these reaction conditions, catalyst **5** is far more effective than the Ir−Ru catalyst **3**, despite the fact that the reaction was carried out with the same concentration of Ru.

Table 3 shows the most representative results from a comparative study of the catalytic behavior of complexes **3**−**6** in the Oppenauer oxidation of 1-phenylethanol in acetone. For this reaction, the best catalyst was the monometallic ruthenium complex **6** (Table 3, entry 1). All the rest of the catalysts showed less catalytic activity, in terms of both the conversions achieved and reaction times. The bis-iridium catalyst **4** was the best catalyst among all the bimetallic complexes tested (entry 4).

Once we proved the activity of our complexes in both the arylation of arylpyridines and the oxidation of alcohols with acetone, we decided to combine both processes into a one-pot tandem reaction; thus, we used catalysts **3**−**6** in the arylation of arylpyridines with 1-(4-chlorophenyl)ethanol (or 1-(4-bromophenyl)ethanol) in a mixture of *N*-methylpyrrolidine and acetone, aiming to obtain the arylated pyridines with carbonyl functionalities. The monitoring of this reaction allowed us to observe that only the starting substrates and the final product are detected along all the reaction time course, indicating that once the oxidation of the alcohol had taken place, the arylation step is fast. On the other hand, in a parallel experiment, we decided to perform the reaction in the absence of acetone; therefore, we avoided the oxidation of the alcohol. Under these reaction conditions, the arylation of 1-(4-

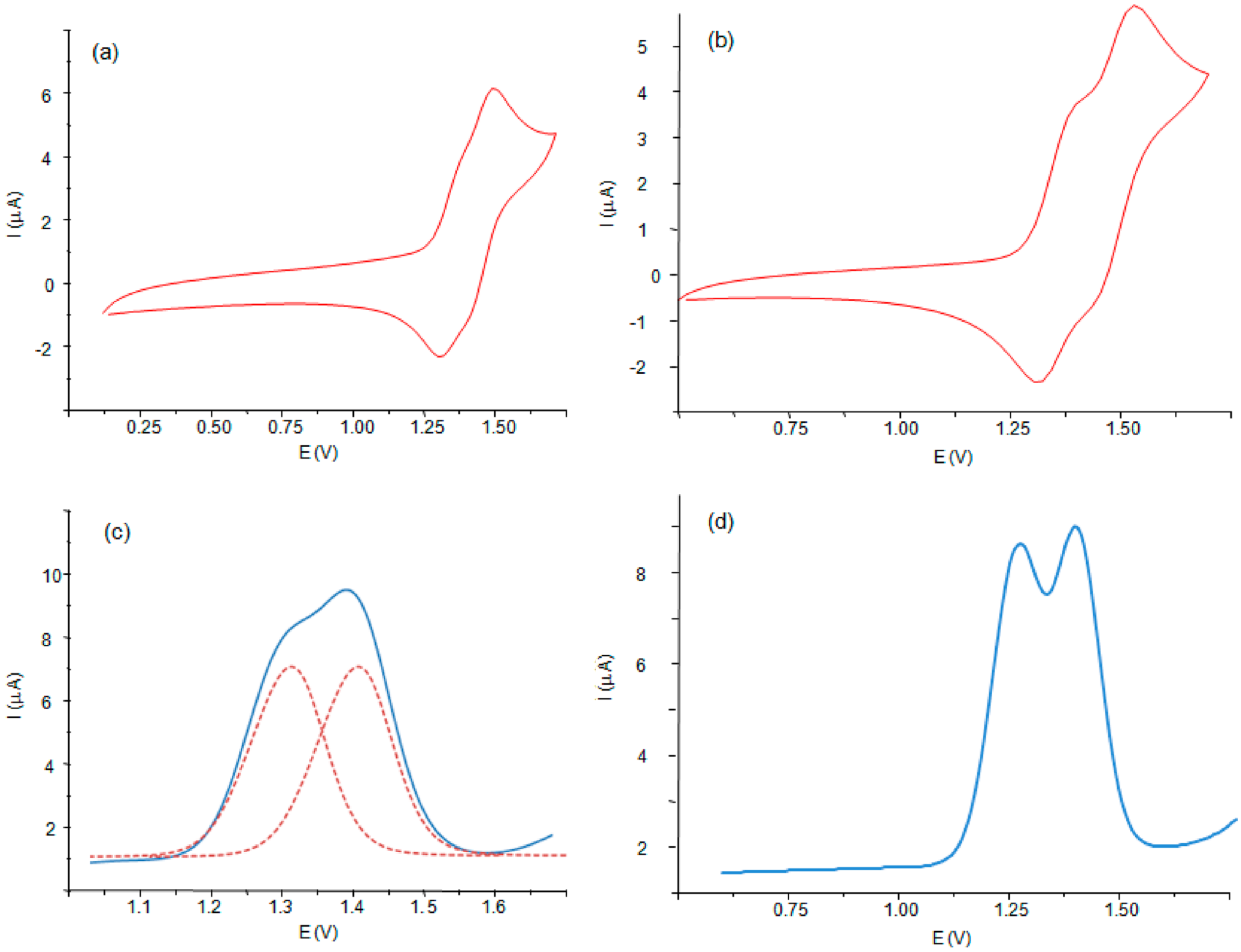
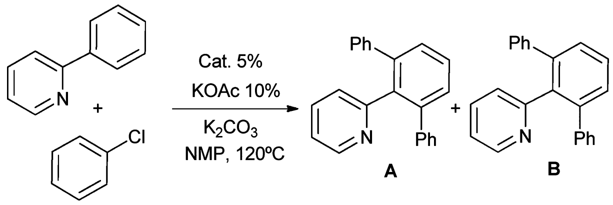


Figure 2. Cyclic voltammetry (top) and differential pulse voltammetry (bottom) of complexes **3** (b, d) and **5** (a, c). Deconvolution was performed by superimposition of multiple DPV signals of **6**.

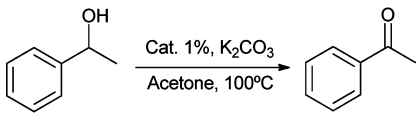
Table 2. Chelation-Assisted Arylation of 2-Phenylpyridine with Chlorobenzene[a]



entry	cat.	*t* (h)	**A** (%)[b]	**B** (%)[b]
1	**6**	12	25	74
2	**5**	5		99
3	**3**	12	56	18
4	**5**[c]	12	25	74

[a] Reaction conditions: KOAc (10 mol %), catalyst (5 mol %), 2 mL of NMP as solvent, room temperature for 1 h, then 2-phenylpyridine (0.5 mmol), chlorobenzene (1.25 mmol), K_2CO_3 (1.5 mmol), 120 °C. [b] Yields and ratios determined by GC (internal standard anisole) and by ^1H NMR. [c] 5 mol % of metal.

Table 3. Oppenauer Oxidation of 1-Phenylethanol[a]



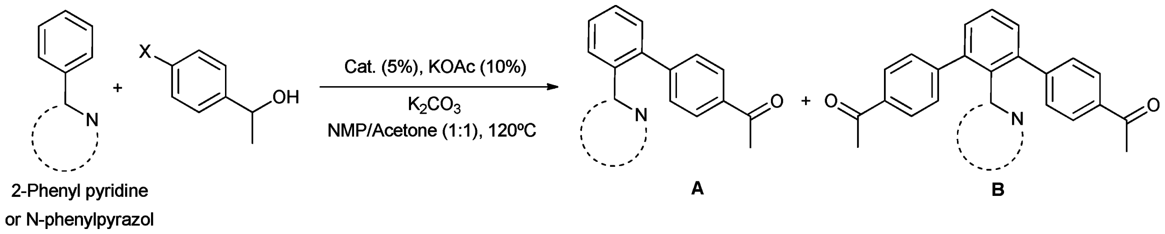
entry	cat.	*t* (h)	yield (%)[b]
1	**6**	1	99
2	**5**	9	76
3	**3**	9	88
4	**4**[c]	9	94
5	**5**[c]	9	37

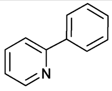
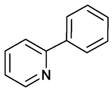
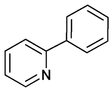
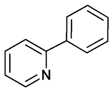
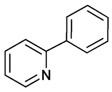
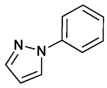
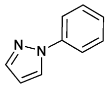
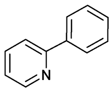
[a] Reaction conditions: catalyst (0.01 mmol), 1 mmol of phenylethanol, 1.5 mmol of K_2CO_3, 2 mL of acetone as solvent, 100 °C. [b] Yields and ratios determined by GC (internal standard anisole). [c] 1 mol % of metal.

chlorophenyl)ethanol did not occur, therefore indicating that the aryl chloride is activated by the oxidation of the alcohol functionality to the ketone.

As can be seen from the data shown in Table 4, the best catalyst from all those that we used was compound **6**, when a catalyst loading of 5 mol % (based on metal) was used. The homobimetallic complex **5** was also an excellent catalyst and performed better than the Ir−Ru heterobimetallic complex **3** under the same reaction conditions (compare entries 1 and 2). The best outcome shown by catalyst **6** may be understood if we take into account that the oxidation of the alcohol is the rate-determining step of the process, a step in which **6** is more active, as seen from the results shown in Table 3. Catalyst **6** was also active in the bis-arylation of *N*-phenylpyrazole, when both 1-(4-chlorophenyl)ethanol and 1-(4-bromophenyl)ethanol were used as arylating agents (Table 4 entries 4−7). The bis

Table 4. Tandem Oxidation of 1-(4-Halophenyl)ethanols and Arylation of Arylpyridines[b]



Entry	Catalyst	Arylpyridine	X	T(h)	A(%)[a]	B(%)[a]
1	**3**		Br	9	--	76
2	**5**		Br	9	--	98
3	**5**[c]		Br	9	--	72
4	**6**		Br	9	--	90
5	**6**		Cl	9	10	75
6	**6**		Br	9	--	95
7	**6**		Cl	9	7	80
8	**4**		Cl	9	0	0

[a]Yields and ratios determined by GC (internal standard anisole) and by ^{1}H NMR. [b]Reaction conditions: KOAc (10 mol %), catalyst (5 mol %), 2 mL of NMP/acetone (1/1) as solvent, room temperature for 1 h, then arylpyridine (0.5 mmol), Ar−X (1.25 mmol), K_2CO_3 (2.5 mmol), 120 °C. [c]5 mol% of metal.

iridium catalyst **4** was inactive in the overall process, because it could not facilitate the second step of the reaction (arylation of the pyridine).

CONCLUSIONS

A new triazolium-ylidene complex of ruthenium (**2**) has been prepared. This complex is a useful intermediate in the formation of ruthenium-containing heterobimetallic complexes bridged by the triazole-diylidene (ditz) ligand. In this present work we have prepared a heterobimetallic Ir−Ru complex (**3**), which can also be obtained by starting from our previously reported iridium triazolium-ylidene complex **1**.[8]

Electrochemical studies of complexes **3**−**5** reveal that there is an electronic interaction between the two metals bound by the triazole-diylidene ligand. Although this interaction can be considered as weak (class II according to the Robin and Day classification[14]), it is remarkably stronger than the communication shown for other related NHC-based Janus type ligands.[12,13]

Complex **3** and some other related (*p*-cymene)Ru(NHC) complexes have been tested in a new tandem process, implying the chelation-assisted arylation of arylpyridines with 1-(4-halophenyl)ethanol, where the monometallic (*p*-cymene)Ru(NHC) complex **6** has shown the best activities. In this catalytic process the arylation is accompanied by the transformation of the alcohol into a ketone, in the presence of acetone, through an Oppenauer oxidation process. This tandem process is unprecedented in the literature.

EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out under nitrogen using standard Schlenk techniques and high vacuum, unless otherwise stated. Compound **1** was prepared according to the literature procedure.[8] Anhydrous solvents were dried using a solvent purification system (SPS, MBraun) or purchased from Aldrich and degassed prior to use by purging with dry nitrogen and kept over molecular sieves. All other reagents were used as received from commercial suppliers. NMR spectra were recorded on Varian Innova spectrometers operating at 300 or 500 MHz (^{1}H NMR) and 75 or 125 MHz (^{13}C NMR), respectively, using $CDCl_3$ as solvent at room temperature unless otherwise stated. Elemental analyses were carried out in an Carlo Erba EA 1108 CHNS-O analyzer. Electrospray mass spectra (ESI-MS) were recorded on a MicromassQuatro LC instrument, and nitrogen was employed as the drying and nebulizing gas.

X-ray Studies. Diffraction data were collected on a Agilent SuperNova diffractometer equipped with an Atlas CCD detector using Mo Kα radiation (λ = 0.710 73 Å). Single crystals were mounted on a MicroMount polymer tip (MiteGen) in a random orientation. Absorption corrections based on the multiscan method were applied.[17]

The structures were solved by direct methods in SHELXS-97 and refined by the full-matrix method based on F^2 with the program SHELXL-97 using the OLEX software package.[18]

Synthesis of Compound 2. A suspension of sodium hydride (60% in mineral oil, 15.7 mg, 0.39 mmol) in dry methanol was stirred at 0 °C under a nitrogen atmosphere until a clear solution of sodium methoxide was formed. 1,2,4-Trimethyltriazolium tetrafluoroborate (93.6 mg, 0.32 mmol) was added, and the mixture was stirred at room temperature for 1 h. After addition of $[\mathrm{RuCl_2}(p\text{-cymene})]_2$ (100 mg, 0.16 mmol), the mixture was refluxed for 2 h. The suspension was filtered, and the solution was concentrated under reduced pressure. Compound **2** was obtained as an orange solid after crystallization from acetonitrile/methanol. Yield: 129 mg (80%).

^{1}H NMR (300 MHz, $\mathrm{CD_3CN}$): δ 9.54 (s, 1H, NC*H*N), 5.66 (d, $^3J_{\mathrm{H,H}}$ = 6 Hz, 1H, C$H_{p\text{-cym}}$), 5.43 (d, $^3J_{\mathrm{H,H}}$ = 6 Hz, 1H, C$H_{p\text{-cym}}$), 4.38 (s, 3H, NCH_3), 4.21 (s, 3H, NCH_3), 4.17 (s, 3H, NCH_3), 2.94 (sept, $^3J_{\mathrm{H,H}}$ = 7.5 Hz, 1H, C$H_{\mathrm{isop}\ p\text{-cym}}$), 2.10 (s, 3H, C$H_{3\ p\text{-cym}}$), 1.33 (d, $^3J_{\mathrm{H,H}}$ = 6 Hz, 6H, C$H_{3\ \mathrm{isop}\ p\text{-cym}}$). ^{13}C{^{1}H} NMR (75 MHz, $\mathrm{CD_3CN}$): δ 192.3 (C_{carbene}−Ru), 145.7 (NCHN), 112.6, 99.8 ($C_{\mathrm{q}\ p\text{-cym}}$), 88.2, 85.3 ($\mathrm{CH}_{p\text{-cym}}$), 40.1, 39.6, 38.1 ($\mathrm{NCH_3}$), 31.6 ($\mathrm{CH}_{\mathrm{isop}\ p\text{-cym}}$), 22.4 ($\mathrm{CH}_{3\ \mathrm{isop}\ p\text{-cym}}$), 18.7 ($\mathrm{CH}_{3\ p\text{-cym}}$). Anal. Calcd for $\mathrm{C_{15}H_{24}N_3BCl_2F_4Ru}$ (505.15): C, 35.66; H, 4.79; N, 8.32. Found: C, 35.50; H, 5.05; N, 7.99. Electrospray MS (cone 15 V; *m/z*, fragment): 418.2 $[\mathrm{M}]^+$. HRMS ESI-TOF-MS (positive mode): $[\mathrm{M}-\mathrm{Cl}]^+$ monoisotopic peak 418.0385, calcd 418.0389, ε_{r} = 0.9 ppm.

Synthesis of Compound 3. *Method A.* Compound **2** (100 mg, 0.198 mmol), NaOAc (17 mg, 0.207 mmol), and $[\mathrm{IrCp^*Cl_2}]_2$ (79 mg, 0.099 mmol) were stirred under nitrogen in deoxygenated acetone (10 mL) at 50 °C for 16 h. The final suspension was filtered, giving an orange solid, which was extracted with dichloromethane (3 × 10 mL). Crystallization from dichloromethane/diethyl ether gave compound **3** as an orange crystalline solid. Yield: 130 mg (81%).

Method B. Compound **1** (150 mg, 0.247 mmol), NaOAc (20.6 mg, 0.247 mmol), and $[\mathrm{RuCl_2}(p\text{-cymene})]_2$ (75.3 mg, 0.123 mmol) were stirred under nitrogen in deoxygenated acetone (10 mL) at 50 °C for 16 h. The final suspension was filtered, giving an orange solid, which was extracted with dichloromethane (3 × 10 mL). Crystallization from dichloromethane/diethyl ether gave compound **3** as an orange crystalline solid. Yield: 141 mg (70%).

^{1}H NMR (300 MHz, $\mathrm{CD_3Cl}$): δ 5.53 (d, $^3J_{\mathrm{H,H}}$ = 6 Hz, 1H, C$H_{p\text{-cym}}$), 5.49 (d, $^3J_{\mathrm{H,H}}$ = 6 Hz, 1H, C$H_{p\text{-cym}}$), 5.42 (d, $^3J_{\mathrm{H,H}}$ = 6 Hz, 1H, C$H_{p\text{-cym}}$), 5.25 (d, $^3J_{\mathrm{H,H}}$ = 6 Hz, 1H, C$H_{p\text{-cym}}$), 4.37 (s, 3H, NCH_3), 4.32 (s, 3H, NCH_3), 4.27 (s, 3H, NCH_3), 2.93 (m, 1H, C$H_{\mathrm{isop}\ p\text{-cym}}$), 2.18 (s, 3H, C$H_{3\ p\text{-cym}}$), 1.63 (s, 15H, $\mathrm{C_5}(CH_3)_5$), 1.32 (d, $^3J_{\mathrm{H,H}}$ = 6 Hz, 6H, C$H_{3\ \mathrm{isop}\ p\text{-cym}}$). ^{13}C{^{1}H} NMR (75 MHz, $\mathrm{CD_2Cl_2}$): δ 186.4 (C_{carbene}−Ru), 168.1 (C_{carbene}−Ir), 109.6, 98.5 ($C_{\mathrm{q}\ p\text{-cym}}$), 90.2 ($C_5(\mathrm{CH_3})_5$), 86.6, 85.4, 84.9, 83.9 ($\mathrm{CH}_{p\text{-cym}}$), 42.1, 39.2, 38.1 ($\mathrm{NCH_3}$), 30.8 ($\mathrm{CH}_{\mathrm{isop}\ p\text{-cym}}$), 22.3, 21.9 ($\mathrm{CH}_{3\mathrm{isop}\ p\text{-cym}}$), 18.6 ($\mathrm{CH}_{3\ p\text{-cym}}$), 8.8 ($\mathrm{C_5(CH_3)_5}$). Anal. Calcd for $\mathrm{C_{25}H_{38}N_3Cl_4RuIr}$ (815.69): C, 36.81; H, 4.69; N, 5.15. Found: C, 36.76; H, 4.73; N, 4.75. Electrospray MS (cone 15 V; *m/z*, fragment): 780.3 $[\mathrm{M}-\mathrm{Cl}]^+$, 372.5 $[\mathrm{M}-2\mathrm{Cl}]^{2+}$. HRMS ESI-TOF-MS (positive mode): $[\mathrm{M}-\mathrm{Cl}]^+$ monoisotopic peak 780.0796, calcd 780.0789, ε_{r} = 0.9 ppm.

Catalytic Studies. *Arylation of Arylpyridines.* The ruthenium complex (5 mol %) and KOAc (10 mol %) were placed together in a thick-walled Schlenk tube with a Teflon cap. The tube was then evacuated and filled with nitrogen three times. NMP (1 mL) and acetone (1 mL) were added, and the mixture was stirred at room temperature for 1 h. Then arylpyridine (0.5 mmol), Ar−X (1.25 mmol), and $\mathrm{K_2CO_3}$ (2.5 mmol) were added. The resulting mixture was stirred at 120 °C for the desired time. $\mathrm{H_2O}$ and EtOAc were added to the cold reaction mixture. The organic phase was dried with $\mathrm{Na_2SO_4}$ and concentrated under vacuum. The remaining residue was purified by column chromatography on silica gel (hexanes/$\mathrm{Et_2O}$ mixture) to yield the corresponding ortho-arylated products. Yields and ratios were determined by ^{1}H NMR spectroscopy and by GC analyses using anisole (0.5 mmol) as internal standard. Products were identified according to previously reported spectroscopic data.[19]

Transfer Hydrogenation. The catalyst (1 mol %), 1-phenylethanol (1 mmol), $\mathrm{K_2CO_3}$ (1 mmol), and deoxygenated acetone (2 mL) were placed together in a thick-walled glass tube. The mixture was stirred at 100 °C for the desired time. Yields were determined by GC chromatography using anisole (1 mmol) as internal standard. Products were identified according to the spectroscopic data of the commercially available compounds.

Electrochemical Measurements. The measurements were carried out using a GPES equipped PGSTAT-30 potentiostat from Autolab at room temperature. A three-electrode configuration was used, where two Pt microelectrodes were connected to the working electrode and counter electrode and a Ag wire was used as the pseudo reference electrode. The redox potential of ferrocene was used to calibrate the potential scale. Dichloromethane was used as the solvent for all experiments. $[\mathrm{NBu_4}]\mathrm{PF_6}$ was used as the supporting electrolyte.

■ ASSOCIATED CONTENT

Supporting Information

Text, tables, figures, and a CIF files giving details of the catalytic experiments, high-resolution mass spectra (HR/MS) of compounds **2** and **3**, electrochemical data including CV and DPV, ^{1}H and ^{13}C NMR of new complexes, and X-ray diffraction data for complex **3**. 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.

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