ORGANOMETALLICS

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Dehydrative Coupling of Alcohols by Iridium(III) Complexes with N-Heterocyclic-Pyridine Chelating Ligands Decorated with Naphthalene-Diimide

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Cite This: *Organometallics* 2023, 42, 1487−1494 Read Online

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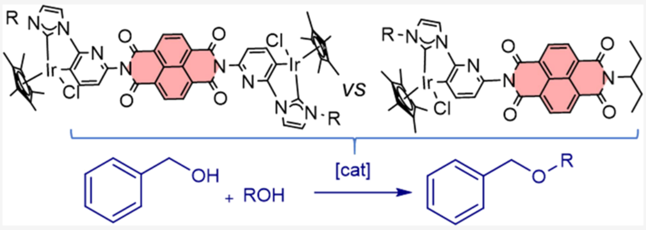
ABSTRACT: A series of dimetallic and monometallic Cp*Ir(III) complexes bearing naphthalene-diimide-decorated N-heterocyclic carbene/pyridine [NDI-(NHC-pyridine)] ligands were prepared and characterized. The complexes show a C,C-chelating coordination of the NHC-pyridine ligand, with the pyridine ring of the ligand bound to the metal via cyclometallation rather than by its nitrogen atom, although the coordination by the nitrogen atom could be achieved by subjecting one of the complexes to reaction with a strong acid. The spectroelectrochemical studies of the new compounds reveal that the complexes are able to undergo two successive reduction events, associated with the sequential reduction of the NDI moiety of the ligand. The new complexes were tested in the dehydrative etherification by cross-coupling of primary alcohols, where they showed good activity and selectivity toward the cross-coupled products. The mechanistic studies allowed us to propose a reaction mechanism which likely involves a redox-neutral acid-catalyzed pathway.



INTRODUCTION

N-Heterocyclic carbene ligands (NHCs) constitute one of the most widely used classes of ligands for the design of homogeneous catalysts.[1] Although myriads of NHCs have been described in the past, the development of new NHCs with exceptional donor or acceptor properties, and specific steric requirements, remains as one of the main focuses of current research interest. This continuous interest most often originates from the demand to adjust the steric and electronic properties of the metal complexes to face the activity and selectivity issues required in homogeneous catalysis. As an alternative to finding multiple ligands with different stereo-electronic properties, switchable ligands offer an atom-economical method for generating catalysts with tunable properties from a single precursor.[2] NHC ligands have been particularly rich in the design of switchable catalysts,[3] mostly because their preparation is often very straight forward and because they can be functionalized with essentially any imaginable functional group.

Naphthalene-diimides (NDIs) and perylene-diimides (PDIs) have attracted great attention due to their electron-deficient nature, rich photochemical and electrochemical properties, and easy functionalization.[4] Despite these advantageous properties, NDIs and PDIs have been scarcely used as tags appended to ligands for exploiting their photoelectrochemical properties in transition metal-based homogeneous catalysis. One of the earliest examples of the use of PDI chromophores in catalysis was reported in 2012,[5] when Wasielewski and co-workers described the ultrafast photo-driven intramolecular electron transfer from an iridium-based water-oxidation catalyst to a photooxidant PDI unit. In this case, the Ir(III) complex was appended to the PDI unit by the imide position—through which the PDI frontier orbitals have a nodal plane—but apparently, this did not hamper the effective PDI-Ir(III) charge transfer.

We recently became interested in the use of NDI and PDI functionalities for the preparation of NHC-based redox-switchable catalysts. The presence of the NDI or PDI moieties appended to the NHC ligands allowed toggling the properties of the metals between three electronic levels, and this was used for exploring the redox-switchable properties of the catalysts in the cycloisomerization of alkynoic acids,[6] the hydroamination of alkynes,[7] and the [3+2] cycloaddition of diphenylcyclopropenone and acetylenes.[8] In the incorporation of the NDI moieties into the NHC ligand, we used two strategies, which included the fusion of the NHC ligand at the core positions of the NDI moiety[6a,7,8] or the functionalization of the NDI at the imide positions.[6b] This last strategy is a simple and efficient one-step procedure, in which commercially available 1,4,5,8-naphthalenetetracarboxylic acid dianhydride (NDA) is condensed with a primary amine. By following this last strategy,

Received: March 3, 2023
Published: May 25, 2023

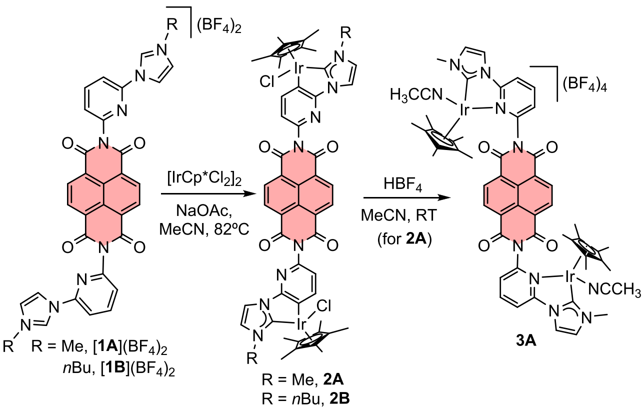
https://doi.org/10.1021/acs.organomet.3c00120

herein, we describe the preparation of two new NDI-functionalized NHC ligands for their coordination to iridium(III) and for studying their photoelectrochemical and catalytic properties. We thought that these two ligands could be especially relevant not only for exploring the redox-switchable properties of the catalysts which should be related to the presence of the NDI moiety but also because they offer a good opportunity for studying the differences associated with the presence of one or two metals on their catalytic outcomes. Thus, the present study describes the preparation and the study of the photoelectrochemical properties of two related monometallic and dimetallic Ir(III) complexes with a NDI-appended pyridine-NHC ligand. We also describe the catalytic properties of these complexes in the dehydrative cross-coupling of primary alcohols to form ethers.

■ RESULTS AND DISCUSSION

The NDI-connected bis(pyridine-imidazolylidene) di-iridium(III) complexes **2A** (R = Me) and **2B** (R = *n*Bu) were obtained following the method depicted in Scheme 1. The reaction of the NDI-connected bis(pyridine-imidazolium) salts [**1A**](BF_4)$_2$ (or [**1B**](BF_4)$_2$) with [IrCp*Cl_2]$_2$ in the presence of sodium acetate in refluxing acetonitrile afforded the formation of the dimetallic complexes **2A** and **2B** in 46 and 90% yield, respectively. Both **2A** and **2B** were characterized by means of NMR spectroscopy. The ^{1}H NMR spectra are consistent with the twofold symmetry of the complexes. For example, a single resonance is observed assigned to the four equivalent protons of the NDI core at 8.84 and 8.82 ppm for **2A** and **2B**, respectively, and the spectrum of **2A** shows a single resonance assigned to the protons of the *N*-methyl groups at 4.0 ppm. The aromatic region of the ^{1}H NMR spectra that show the resonances due to the protons at the pyridine and imidazolylidene rings is consistent with the cyclo-orthometallation of the pyridine ring, thus forming (C,C)- rather than (C,N)-chelating complexes. Such type of coordination is further confirmed by the corresponding ^{13}C NMR spectra, which show resonances at 164.4 and 161.5 ppm (for **2A**) and 163.2 and 160.7 ppm (for **2B**), which are attributed to the Ir−C$_{(carbene)}$ and Ir−C$_{(pyridine)}$ carbons, respectively. The Q-TOF mass spectra of the complexes displayed peaks at *m*/*z* values of 617.1508 and 1269.2744 for **2A** and 658.1958 and 1353.3688 for **2B**, which are assigned to [M−2Cl]$^{2+}$ and [M−Cl]$^+$, respectively.

Scheme 1. Synthesis of Complexes 2A, 2B, and 3A



All attempts to N-coordinate the NDI-bis(pyridine-imidazolium) salts [**1A**](BF_4)$_2$ (or [**1B**](BF_4)$_2$) were unsuccessful, most likely as a consequence of the steric hindrance imparted by the NDI moiety bound at C-6, next to the pyridyl group. Such type of cyclometallation of pyridine-imidazolylidene ligands in which N-coordination is entirely avoided due to the presence of bulky groups next to the pyridyl group has been observed previously.[9] In an attempt to protonate the uncoordinated nitrogen of the pyridyl groups of **2A**, we added tetrafluoroboric acid to an acetonitrile solution of the complex. After 12 h of reaction at room temperature, we obtained complex **3A**, which was characterized by ^{1}H NMR spectroscopy and mass spectrometry. Unfortunately, **3A** was obtained in a very low yield (<10%), thus preventing us from using it for manipulations beyond its full characterization.

Single crystals of **3A** suitable for X-ray diffraction studies were obtained from an acetonitrile solution of the complex. The molecular structure of **3A** (Figure 1) consists of two units of Ir(Cp*)(Pyr-NHC) [Pyr-NHC = pyridyl-2-(*N*-methyl-imidazolylidene] connected by a naphthalene-diimide (NDI) moiety. The structure shows important distortions due to the proximity of the NDI moiety to the methyl groups of the Cp* ligand. For example, the angle established between the NDI plane and the N(NDI)−C(pyr) bond is of 168.4°, which is thus significantly smaller than the expected 180° for an unhindered NDI-substituted molecule. The Ir−N bond distance measures 2.194(3) Å, which is thus longer than the related distance observed for other chelating pyr-NHC ligands bound to Cp*Ir(III).[10] The Ir−C$_{carbene}$ bond measures 2.027(4) Å. All other angles and distances are in the expected range.

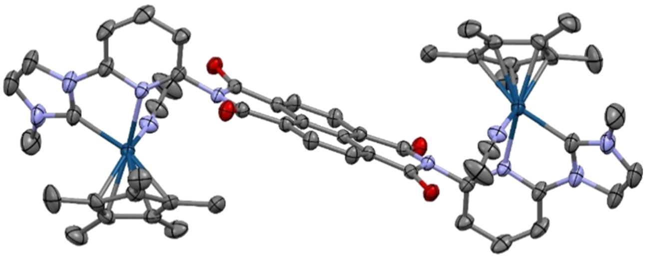


Figure 1. Molecular structure of complex **3A**. Hydrogen atoms, counter anions (BF_4), and solvent (CH_3CN) were omitted for clarity. Ellipsoids at 50% probability.

We carried out cyclic voltammetry studies on the bis-imidazolium salts [**1**](BF_4)$_2$ and the di-iridium(III) complexes **2**. The bisimidazolium salts [**1**](BF_4)$_2$ show two well-separated irreversible redox events associated with the sequential one-electron reduction of the NDI core (Figures S46−S49). The cyclic voltammograms of **2A** and **2B** (Figures S50−S53) show two reversible redox waves associated with the sequential reduction of the NDI core at −0.93 and −1.35 V for **2A** and −0.95 and −1.39 for **2B**. In addition, a quasi-reversible oxidation wave at 0.41 (**2A**) and 0.46 V (**2B**) associated with the one-electron oxidation of Ir(III) to Ir(IV) is also observed. This observation indicates that the iridium(IV) species obtained upon oxidation of **2A** or **2B** are relatively stable at room temperature but on a limited timescale. The electrochemical formation of stable Cp*Ir(IV) species is explained due to the presence of the strongly electron-donating NHC ligand and has been observed previously for other Cp*Ir(III) complexes bearing cyclometallated NHC-based ligands.[11]

https://doi.org/10.1021/acs.organomet.3c00120
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In order to obtain information about the stability of the species formed upon the reduction of the NDI moiety in complexes **2**, we performed UV−vis spectroelectrochemical (SEC) studies. The experiments were performed using an optically transparent thin-layer electrochemical (OTTLE) cell in CH_2Cl_2 by progressively applying more negative potentials, while UV−vis spectra were recorded using **2B** as the model compound. The resulting series of spectra (for **2B**) is shown in Figure 2. The UV−vis spectrum of **2B** shows one vibronically coupled band with its maximum peak at 379 nm. Upon applying a gradually increasing reduction potential, a featureless band centered at 478 nm associated with the one-electron reduced species $[\mathbf{2B}]^{-}$ appeared, with the concomitant disappearance of the band at 378 nm. The application of more negative potentials resulted in the disappearance of this band, with the concomitant appearance of a new vibronically coupled band centered at 422 nm related to the formation of $[\mathbf{2B}]^{2-}$. Once $[\mathbf{2B}]^{2-}$ was formed, the application of more positive potentials allowed recovering the starting neutral complex **2B**, thus confirming the reversibility of the two redox events.

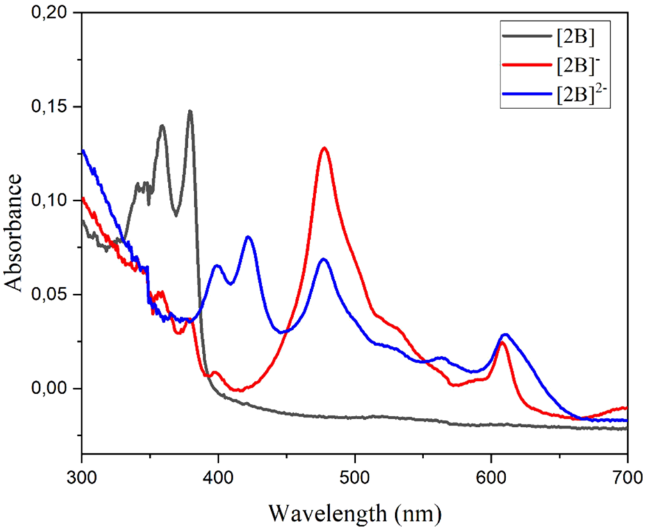
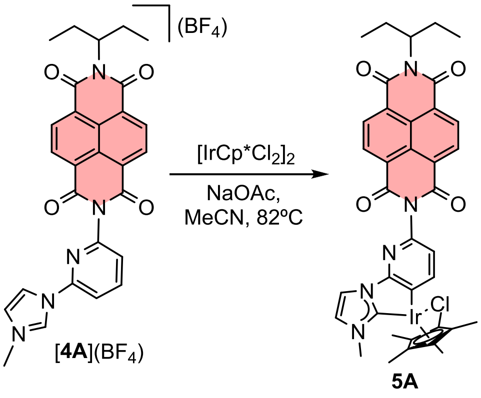


Figure 2. UV−vis SEC monitoring of the reduction of **2B** in CH_2Cl_2. Lines represent the spectra of the starting neutral (black), singly reduced (red), and doubly reduced (blue) species.

We thought that exploring the catalytic properties of complexes **2A** and **2B** could be interesting for several reasons. First, the presence of the redox-active NDI moiety would allow us to study if the complexes showed redox-switchable catalytic properties, as we showed above that the reduction of the NDI unit is governed by reversible processes. In addition, given the tendency of NDI-based complexes to form $\pi-\pi$-stacking aggregates, we were also interested in studying about the possibility that self-aggregation of the catalysts could have any influence on their catalytic outcome, or even if the addition of external π-stacking additives, such as polycyclic aromatic hydrocarbons (PAHs), would affect the activity of the catalysts.[12] Finally, due to the dimetallic nature of the complexes, we thought that it would also be interesting to explore the possibility that the two metals could show any kind of cooperativity in their catalytic performances. In order to address this last point, we decided to obtain the related monometallic NDI-(pyr-NHC) complex **5A**, which was obtained in 85% yield from the NDI-functionalized pyridine-imidazolium salt $[\mathbf{4A}](BF_4)$, according to the procedure depicted in Scheme 2. The ^{1}H NMR spectrum of **5A** is consistent with the asymmetric substitution of the NDI moiety, as evidenced by the appearance of an AB system centered at 8.77 ppm assigned to two pairs of unequivalent protons of the naphthalene core of the NDI unit. As for complexes **2A** and **2B**, in **5A**, the ligand is coordinated to the Ir(III) center via a (C_{NHC},C_{pyr})-chelating form, as evidenced by the two doublets observed at 8.25 and 6.95 ppm assigned to the protons of the pyridine ring, and to the resonances at 164.6 and 163.8 ppm that appear on the ^{13}C NMR spectrum, assigned to the Ir−$C_{carbene}$[13] and Ir−$C_{(pyridine)}$ carbons, respectively.

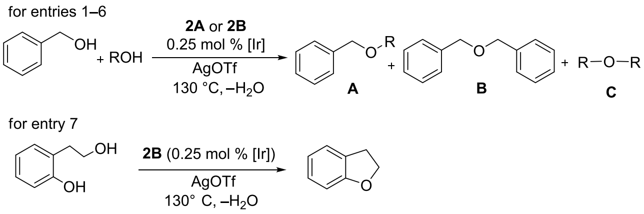
Scheme 2. Synthesis of Complex 5A



We decided to test the catalytic activity of complexes **2A**, **2B**, and **5A** in the dehydrative cross-etherification by cross-coupling of primary alcohols. Ethers are an important class of compounds widely used in a variety of applications, including their use as solvents, pharmaceuticals, agricultural products, and perfumes.[14] The direct coupling of alcohols to ethers is an atom-economical and environmental benign process, as it produces water as the only byproduct, thus avoiding the generation of copious amounts of salt byproducts resulting from the use of inorganic bases and organic halides and alkoxides, which are generated by the currently used industrial scale methods.[15] Several authors,[10d,10,13,16] including us,[17] have used Ir(III) complexes as catalysts for the etherification by cross-coupling of primary alcohols. Two different redox neutral reaction mechanisms have been proposed for the Ir(III) etherification of alcohols. The first mechanism involves a borrowing-hydrogen pathway, in which the dehydrogenation of one of the alcohols (normally the aromatic one) generates an aldehyde, which reacts with the second primary alcohol to form the final ether product, via the formation of a hemiacetal intermediate, which dehydrates and hydrogenates by the iridium catalyst to form the final ether product.[16a] An alternative pathway is an acid-catalyzed process involving a nucleophilic substitution.[10d,16a]

We first screened the activity of the catalysts in the cross-coupling of benzyl alcohol with a variety of aliphatic alcohols. The reactions were performed at 130 °C using benzyl alcohol and the corresponding alkylating alcohol in a 1:5 molar ratio using a 0.25 mol % loading of the catalyst (based on the amount of metal) and silver triflate as the halide scavenger. As can be observed form the results shown in Table 1, **2A** and **2B** are very effective catalysts in the coupling of benzyl alcohol

Table 1. Etherification of Primary Alcohols Using 2A and 2B as Catalysts[a]



entry	alcohol	cat.	*t* (h)	conv. (%)	A (%)[d]	B (%)[d]	C (%)[d]
1	*n*-butanol	2B	7	98	97	0	12
2[b]	*n*-butanol	2B	24	1	1	0	0
3	*n*-butanol	2A	7	98	98	0	11
4	*n*-hexanol	2B	12	98	90	7.5	10
5	*n*-dodecanol	2B	12	94	87	7.5	15
6	cyclohexanol	2B	15	86	56	29	20
7[c]	2-hydroxyphenethyl alcohol	2B	12	>99			

[a] All reactions were performed by mixing benzyl alcohol (1.6 mmol), alkylating alcohol (8.0 mmol), catalyst (0.25 mol % based on iridium), and silver triflate (0.3 mol % based on metal) at 130 °C in a thick-walled glass tube fitted with a Teflon cap. Conversions and yields were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as the integration standard. [b] 0.5 mol % of cobaltocene was added to the reaction mixture. [c] A mixture of 2-hydroxyphenethyl alcohol (1.6 mmol), catalyst (0.25 mol % based on metal), and silver triflate (0.3 mol % based on metal) in toluene-d_6 (800 μL) was heated at 130 °C in a thick-walled glass tube fitted with a Teflon cap. [d] Yield based on the amount of benzyl alcohol. [e] Yield based on the amount of alkylating alcohol.

with *n*-butanol, affording quasi-quantitative conversion of the product with excellent selectivity toward the cross-coupling product (A) in just 7 h of reaction (entries 1 and 3). The substrate scope was performed using **2B** as the model catalyst. The coupling of benzyl alcohol with three other aliphatic alcohols required longer times (12−15 h) for achieving quantitative conversions and, while a good selectivity was maintained toward the cross-coupling product, small amounts of dibenzyl-ether (B) were observed as a consequence of the homocoupling of benzyl alcohol (entries 4−6). In the case of the coupling of cyclohexanol, the production of B was particularly relevant (entry 6), most likely because the higher hindrance exerted by this cyclic alcohol lowered the kinetics in the production of the cross-coupling product A. Catalyst **2B** was also found to be very effective in the cycloetherification of 2-hydroxyphenethyl alcohol to form 2,3-dihydrobenzofuran as it afforded quantitative yields of the desired product without the detection of any other reaction byproducts (entry 7). To put these results in context, our results compare well with those found by us in a previous study using a series of [IrCp*Cl$_2$(NHC)] complexes under the same reaction conditions, although then we used a significantly higher catalyst loading (1 mol %).[17] Albrecht and co-workers observed the homocoupling etherification of benzyl alcohol using a Ir(*III*)Cp* complex with a chelating pyridine-NHC ligand, but the reaction was not selective (benzaldehyde was also produced), and the reaction conditions used were harsher than those used by us (150 °C, catalyst loading 2 mol %).[10d] In a more recently published work, Fujita and co-workers described the homocoupling of a series of primary alcohols at a lower temperature (120 °C) using a series of Cp*Ir(III) complexes, but the reaction required a hydrogen atmosphere and a catalyst loading of 1 mol %,[13] and the product yields were slightly below 90%. As for the activity of [IrCp*Cl$_2$]$_2$, in our previous studies, we showed that it was able to produce the cross-coupling etherification of benzyl alcohol and *n*-butanol under the exact same reaction depicted in Table 1, affording 90% of the cross-coupling product, although a 2 mol % of catalyst loading (based on the amount of metal) was required.[17] It is also important to mention that in none of the above-mentioned works, studies on the mechanism of the process were performed.

We were interested in studying if the presence of the NDI moiety in the catalyst could be used as a redox-active tag and hence if it could be used for modifying the catalytic properties of the catalyst upon application of a redox stimulus. As can be seen from the results shown in Table 1 (entry 2), the addition of an equivalent of cobaltocene (with respect to the catalyst) to the reaction mixture completely inhibited the activity of the catalyst, which was only able to produce 1% of the cross-coupling product generated from the reaction of benzyl alcohol and *n*-butanol after 24 h of reaction. With this result in hand, we decided to explore whether we could toggle between the active and inactive forms of the catalyst by subsequently adding a reducing (cobaltocene) and an oxidizing (acetylferrocenium tetrafluoroborate) agent along the reaction course (Figure 3). First, we allowed the reaction to evolve for 2 h, and we

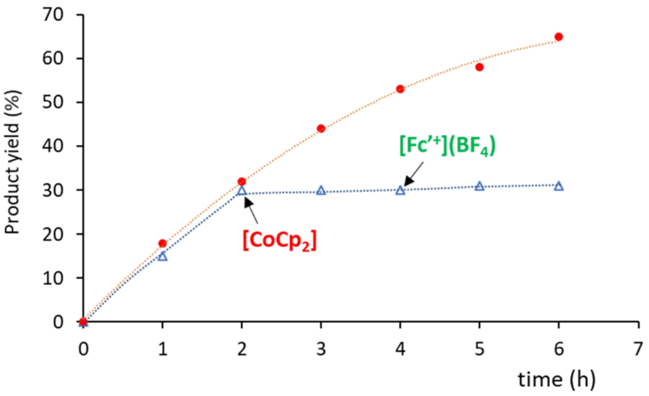


Figure 3. Plots showing the cross-coupling of benzyl alcohol and *n*-butanol using 0.25 mol % of **2B** (red solid circles) and with sequential additions of cobaltocene and $[\mathrm{Fe}(\eta^5\text{-}C_5H_4COCH_3)\mathrm{Cp}](\mathrm{BF}_4)$ ($[\mathrm{Fc'^+}](\mathrm{BF}_4)$) (blue triangles). The reactions were performed at 130 °C using benzyl alcohol (1.6 mmol), *n*-butanol (8.0 mmol), and silver triflate (0.3 mol % based on metal).

observed the formation of 30% of reaction product. Then, 1 equiv of [$CoCp_2$] was added to the reaction mixture, thus transforming the catalyst into its reduced form [**2B**$^-$], which showed null activity during the following 2 h of reaction. After this time, acetylferrocenium tetrafluoroborate ([$Fe(\eta^5$-$C_5H_4COCH_3)Cp](BF_4)$) was added in order to oxidize the catalyst back to its active form, **2B**, and we let the reaction to evolve for two more hours, after which we observed that no further product was formed. Although, as we mentioned above, we found that the reduced form of the catalyst [**2B**$^-$] was stable at room temperature and that it could be reversibly converted into **2B**, we think that most likely [**2B**$^-$] could not stand the harsh reaction conditions used for this catalytic reaction, and therefore, it could not be reoxidized to its active form.

In order to get further insight into mechanistic aspects of the catalytic performance of **2B**, we decided to perform some kinetic studies. We first aimed to determine the reaction rate order with respect to the substrates. The reaction order in benzyl alcohol was determined by measuring the initial rates of the reaction by changing the concentration of this substrate while maintaining a constant concentration of *n*-butanol. By doing this, we obtained a first-order dependence on the concentration of benzyl alcohol (see ESI file for details), thus indicating that the attack of this substrate is involved in the rate-determining step (RDS) of the process. Next, we performed kinetic studies in order to determine the reaction rate order with respect to the catalyst. For this purpose, we used the variable time normalization analysis, consisting of the visual comparison of the variably normalized concentration profiles.[18] The reactions were monitored using four different concentrations of **2B** (1, 0.5, 0.25, and 0.125 mol %). As can be seen from the graphics shown in Figure 4, the normalized profiles match with a half-order order in **2B**, thus strongly suggesting that the reaction mechanism involves the formation of inactive off-cycle species resulting from the dimerization of the catalyst.[19]

We wondered whether this half-order reaction rate with respect to the catalyst could be due to the formation of a self-aggregated dimer formed by π–π-stacking association by the naphthalene-diimide moiety. We previously observed that self-aggregation due to π-stacking may have dramatic effects on the reaction order with respect to the catalyst, when catalysts decorated with moieties that are amenable to π-stacking are used.[20] In order to address this point, we carried out a series of ^{1}H NMR spectra of **2B** in CD_3OH at different concentrations of the complex, ranging from 0.02 to 2 mM, but we did not observe any shifting of the signals due to the protons of the NDI moiety, so the self-association of the complex was discarded.

We were also interested in determining if the dimetallic nature of the catalyst may have an influence on the catalytic performance of the catalyst, in terms of cooperativity between the two metals, or even if this could be related to the fractional reaction order in **2B** that we observed. In order to address this point, we studied the reaction profiles of the reaction between benzyl alcohol and *n*-butanol using catalysts **2A**, **2B**, and **5A** at a catalyst loading of 0.25 mol %. The resulting reaction profiles of these catalysts are quasi-superimposable, indicating that all three catalysts display quasi-identical activity (Figure 5). This observation indicates that the two metals in **2A** and **2B** behave as independent catalytic active sites, rather than showing any kind of catalytic cooperativity. It is also important to mention that the fact that **2A** and **2B** show identical activity indicates that the presence of the *N*-methyl or *N*-*n*But wingtips in the catalysts has negligible effect in their activity. By monitoring the catalytic reactions using four different concentrations of **5A**, in a similar manner to the studies that we described above for **2B**, we determined that the reaction order with respect to **5A** is 0.5, thus indicating that, for this monometallic catalyst, the mechanism also involves non-active off-cycle dimeric species.

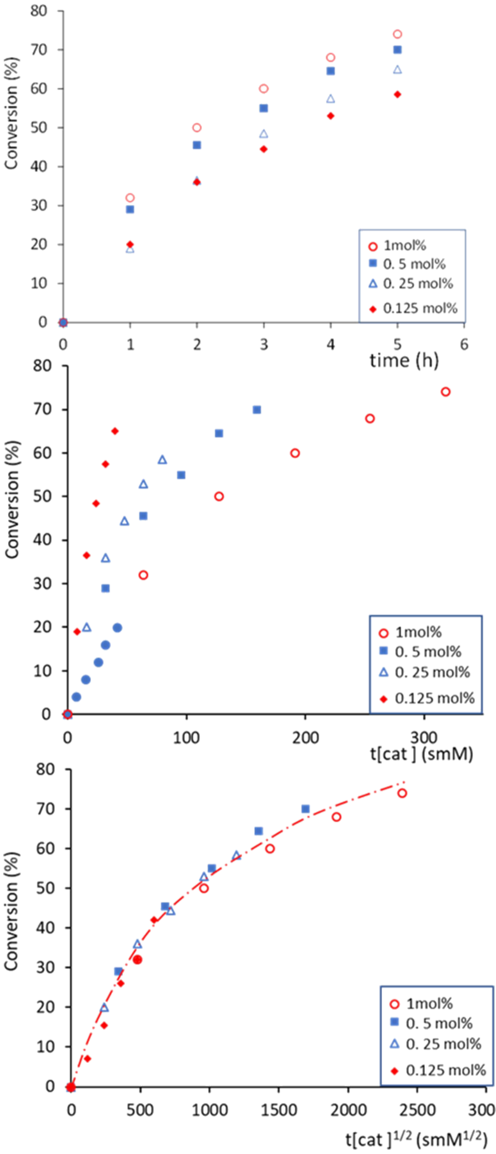


Figure 4. Determination of the reaction order with respect to catalyst **2B** using the variable time normalization analysis.[18b] The reactions were performed at 130 °C using benzyl alcohol (1.6 mmol) and *n*-butanol (8.0 mmol).

On the basis of our results, we propose a working mechanistic hypothesis for the formation of unsymmetrical ethers (Scheme 3). The reaction follows a redox-neutral acid-catalyzed mechanistic pathway. The first step of the process is the removal of the chloride ligand by silver triflate forming the cationic species **I**, which is followed by the coordination of benzyl alcohol forming intermediate **II**. Then, the nucleophilic substitution with the second alcohol (nucleophilic attack of the oxygen of the second alcohol at the carbon atom of the

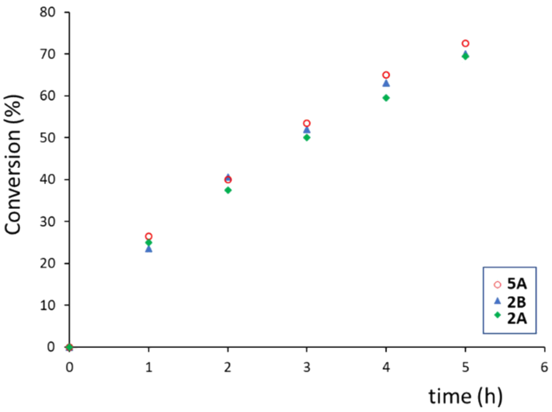
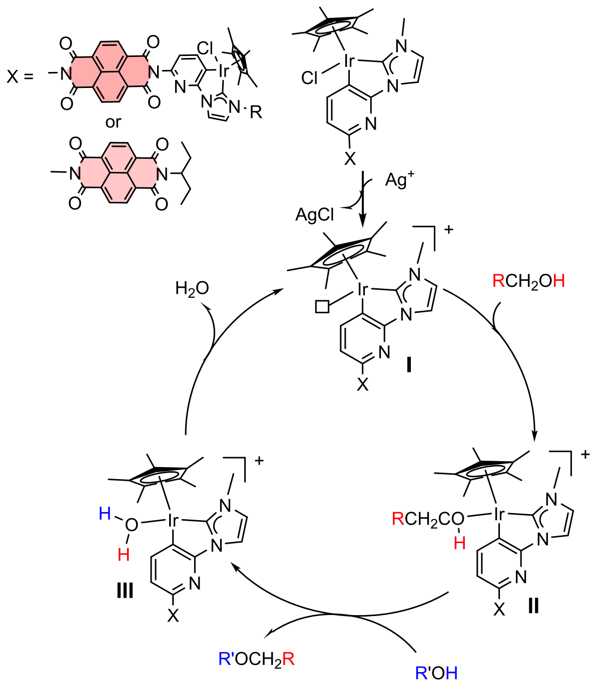


Figure 5. Comparative time-dependent reaction profiles of the cross-coupling etherification of benzyl-alcohol and *n*-butanol using catalysts **2A**, **2B**, and **5A**. The reactions were carried out using a catalyst loading of 0.25 mol % (based on the amount of Ir) at 130 °C using benzyl alcohol (1.6 mmol) and *n*-butanol (8.0 mmol).

Scheme 3. Proposed Mechanism for the Etherification of Alcohols



coordinated one, forming the new C−O bond) would generate the ether product, together with the iridium intermediate **III**, which has a H_2O ligand arising from the −OH group of the first alcohol and the proton of the second one. The fact that the reaction is first order in benzyl alcohol is in accordance with this nucleophilic attack (step **II**−**III**) being the RDS of the cycle. This conclusion is also supported by the fact that the reduction of the catalyst with cobaltocene quenches the activity of the catalyst since the formation of a neutral form of the Ir(III) complex would make the nucleophilic attack less likely. The mechanism is in agreement with previous studies by Martin-Matute and co-workers, who proposed the acid-catalyzed cyclodehydration of electron-rich diols by a Cp*Ir(III) complex bearing a NHC-based bifunctional ligand.[16a] The mechanism is also in agreement with previous studies by Albrecht and co-workers[10d] describing how the etherification of benzyl alcohol by Cp*Ir(III)(NHC) complexes is dictated by a dehydration mechanism which is independent from the dehydrogenation of alcohols, therefore indicating that the etherification does not involve a hydrogen-borrowing mechanism. Our proposed mechanism is also supported by the fact that we did not observe the formation of benzaldehyde along the course of the reaction. The high selectivity in the formation of the ethers may also be due to the fact that our catalysts only have one coordination vacant site (two would be needed for the hydrogen-borrowing process) as a consequence of the formation of the strong C−Ir bond derived from the cyclometalation of the pyridine ring. A N-coordination of the pyridine ring would very likely generate a hemilabile ligand, which would open the possibility that the catalyst could operate via a borrowing-hydrogen mechanism, as has been observed previously for related Ir(III) complexes bearing chelating (C,N)-NHC-pyridine ligands.[10d]

CONCLUSIONS

In summary, we prepared a series of NDI-functionalized NHC-pyridine ligands that were coordinated to iridium(III) affording a series of NDI-di(NHC-pyridine)-based dimetallic complexes of Ir(III) and one monometallic Ir(III) complex with a NDI-(NHC-pyridine) ligand. In all cases, the NHC-pyridine ligand is coordinated to the metal in a chelating form but, due to the steric hindrance exerted by the NDI moiety connected by the carbon adjacent to the nitrogen atom of the pyridine, the chelating coordination of the ligand was produced via the cyclo-orthometalation of the pyridine ring, rather than from the coordination of the pyridine by its nitrogen atom. Only when one of the dimetallic complexes was subjected to a reaction with a strong acid, the formation of a new complex with a (C,N) (NHC-pyridine)-chelating coordination of the ligand could be observed.

The presence of the NDI moiety on the dimetallic complexes allowed us to perform SEC studies of the complexes. The reduction of the NDI fragment allowed the spectroscopic detection of the mono- and doubly reduced species, which could be reoxidized back to the original neutral complexes, therefore showing the reversibility of the process and, consequently, the relative high stability of the species in all three electronic states.

One of the dimetallic complexes was tested in the cross-coupling etherification of alcohols, where it showed excellent activity and selectivity toward the resulting ethers. The comparison of the activity of the dimetallic complex with a related monometallic one indicated that the two metals in the dimetallic unit act independently, without showing any indication of catalytic cooperativity. The presence of the NDI moiety in the complexes allowed us to observe that the activity of the catalyst could be suppressed by adding a reducing agent to the reaction mixture. This observation, together with our kinetic studies, allowed us to conclude that the reaction follows a redox-neutral acid-catalyzed mechanistic pathway, in which the nucleophilic substitution is the RDS.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.3c00120.

Experimental details about the synthesis, characterization, and catalytic experiments and electrochemical and SEC studies (PDF)

Accession Codes

CCDC 2245772 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge financial support from the Ministerio de Ciencia y Universidades (PID2021-127862NB-I00 and the Universitat Jaume I (UJI-B2020-01 and UJI-B2021-39). We are grateful to the Serveis Centrals d'Instrumentació Científica (SCIC-UJI) for providing spectroscopic facilities.

■ REFERENCES

(1) (a) Peris, E. Smart N-heterocyclic carbene ligands in catalysis. *Chem. Rev.* **2018**, *118*, 9988−10031. (b) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. An overview of N-heterocyclic carbenes. *Nature* **2014**, *510*, 485−496. (c) Herrmann, W. A. N-heterocyclic carbenes: A new concept in organometallic catalysis. *Angew. Chem., Int. Ed.* **2002**, *41*, 1291−1309. (d) Gaillard, S.; Cazin, C. S. J.; Nolan, S. P. N-Heterocyclic Carbene Gold(I) and Copper(I) Complexes in C-H Bond Activation. *Acc. Chem. Res.* **2012**, *45*, 778−787.

(2) (a) Crabtree, R. H. Multifunctional ligands in transition metal catalysis. *New J. Chem.* **2011**, *35*, 18−23. (b) Berben, L. A.; de Bruin, B.; Heyduk, A. F. Non-innocent ligands. *Chem. Commun.* **2015**, *51*, 1553−1554. (c) Lyaskovskyy, V.; de Bruin, B. Redox Non-Innocent Ligands: Versatile New Tools to Control Catalytic Reactions. *ACS Catal.* **2012**, *2*, 270−279. (d) de Bruin, B. Special Issue: Cooperative & Redox Non-Innocent Ligands in Directing Organometallic Reactivity (Cluster Issue). *Eur. J. Inorg. Chem.* **2012**, 340−342. (e) Luning, U. Switchable Catalysis. *Angew. Chem., Int. Ed.* **2012**, *51*, 8163−8165. (f) Blanco, V.; Leigh, D. A.; Marcos, V. Artificial switchable catalysts. *Chem. Soc. Rev.* **2015**, *44*, 5341−5370. (g) Choudhury, J. Recent developments on artificial switchable catalysis. *Tetrahedron Lett.* **2018**, *59*, 487−495.

(3) (a) Ryu, Y.; Ahumada, G.; Bielawski, C. W. Redox- and light-switchable N-heterocyclic carbenes: a ″soup-to-nuts″ course on contemporary structure-activity relationships. *Chem. Commun.* **2019**, *55*, 4451−4466. (b) Rosen, E. L.; Varnado, C. D.; Tennyson, A. G.; Khramov, D. M.; Kamplain, J. W.; Sung, D. H.; Cresswell, P. T.; Lynch, V. M.; Bielawski, C. W. Redox-Active N-Heterocyclic Carbenes: Design, Synthesis, and Evaluation of Their Electronic Properties. *Organometallics* **2009**, *28*, 6695−6706.

(4) (a) Al Kobaisi, M.; Bhosale, S. V.; Latham, K.; Raynor, A. M.; Bhosale, S. V. Functional Naphthalene Diimides: Synthesis, Properties, and Applications. *Chem. Rev.* **2016**, *116*, 11685−11796. (b) Bhosale, S. V.; Jani, C. H.; Langford, S. J. Chemistry of naphthalene diimides. *Chem. Soc. Rev.* **2008**, *37*, 331−342. (c) Maniam, S.; Higginbotham, H. F.; Bell, T. D. M.; Langford, S. J. Harnessing Brightness in Naphthalene Diimides. *Chem. − Eur. J.* **2019**, *25*, 7044−7057. (d) Kumar, S.; Shukla, J.; Kumar, Y.; Mukhopadhyay, P. Electron-poor arylenediimides. *Org. Chem. Front.* **2018**, *5*, 2254−2276. (e) Pan, M.; Lin, X. M.; Li, G. B.; Su, C. Y. Progress in the study of metal-organic materials applying naphthalene diimide (NDI) ligands. *Coord. Chem. Rev.* **2011**, *255*, 1921−1936. (f) Zhan, X. W.; Facchetti, A.; Barlow, S.; Marks, T. J.; Ratner, M. A.; Wasielewski, M. R.; Marder, S. R. Rylene and Related Diimides for Organic Electronics. *Adv. Mater.* **2011**, *23*, 268−284.

(5) Vagnini, M. T.; Smeigh, A. L.; Blakemore, J. D.; Eaton, S. W.; Schley, N. D.; D'Souza, F.; Crabtree, R. H.; Brudvig, G. W.; Co, D. T.; Wasielewski, M. R. Ultrafast photodriven intramolecular electron transfer from an iridium-based water-oxidation catalyst to perylene diimide derivatives. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 15651−15656.

(6) (a) Ruiz-Zambrana, C.; Gutierrez-Blanco, A.; Gonell, S.; Poyatos, M.; Peris, E. Redox-Switchable Cycloisomerization of Alkynoic Acids with Napthalenediimide-Derived N-Heterocyclic Carbene Complexes. *Angew. Chem., Int. Ed.* **2021**, *60*, 20003−20011. (b) Gutierrez-Pena, C. L.; Poyatos, M.; Peris, E. A redox-switchable catalyst with an 'unplugged' redox tag. *Chem. Commun.* **2022**, *58*, 10564−10567.

(7) Ruiz-Zambrana, C.; Poyatos, M.; Peris, E. A redox-switchable gold(I) complex for the hydroamination of acetylenes: a convenient way for studying ligand-derived electronic effects. *ACS Catal.* **2022**, *12*, 4465−4472.

(8) Ruiz-Zambrana, C.; Dubey, R. K.; Poyatos, M.; Mateo-Alonso, A.; Peris, E. Redox-Switchable Complexes Based on Nanographene-NHCs. *Chem. − Eur. J.* **2022**, *28*, No. e202201384.

(9) Specht, Z. G.; Grotjahn, D. B.; Moore, C. E.; Rheingold, A. L. Effects of Hindrance in N-Pyridyl Imidazolylidenes Coordinated to Iridium on Structure and Catalysis. *Organometallics* **2013**, *32*, 6400−6409.

(10) (a) Xiao, X. Q.; Jin, G. X. Functionalized N-heterocyclic carbene iridium complexes: Synthesis, structure and addition polymerization of norbornene. *J. Organomet. Chem.* **2008**, *693*, 3363−3368. (b) Huang, M.; Li, Y. W.; Liu, J. H.; Lan, X. B.; Liu, Y.; Zhao, C. Y.; Ke, Z. F. A bifunctional strategy for N-heterocyclic carbene-stabilized iridium complex-catalyzed N-alkylation of amines with alcohols in aqueous media. *Green Chem.* **2019**, *21*, 219−224. (c) Kaur, M.; Reshi, N. U. D.; Patra, K.; Bhattacherya, A.; Kunnikuruvan, S.; Bera, J. K. A Proton-Responsive Pyridyl-(benzamide)-Functionalized NHC Ligand on Ir Complex for Alkylation of Ketones and Secondary Alcohols. *Chem. − Eur. J.* **2021**, *27*, 10737−10748. (d) Vivancos, A.; Petronilho, A.; Cardoso, J.; Muller-Bunz, H.; Albrecht, M. Unveiling the role of ancillary ligands in acceptorless benzyl alcohol dehydrogenation and etherification mediated by mesoionic carbene iridium complexes. *Dalton Trans.* **2018**, *47*, 74−82. (e) Valencia, M.; Muller-Bunz, H.; Gossage, R. A.; Albrecht, M. Enhanced product selectivity promoted by remote metal coordination in acceptor-free alcohol dehydrogenation catalysis. *Chem. Commun.* **2016**, *52*, 3344−3347.

(11) Brewster, T. P.; Blakemore, J. D.; Schley, N. D.; Incarvito, C. D.; Hazari, N.; Brudvig, G. W.; Crabtree, R. H. An Iridium(IV)

Species, Cp*Ir(NHC)Cl(+), Related to a Water-Oxidation Catalyst. *Organometallics* **2011**, *30*, 965−973.

(12) Peris, E. Polyaromatic N-heterocyclic carbene ligands and pi-stacking. Catalytic consequences. *Chem. Commun.* **2016**, *52*, 5777−5787.

(13) Onoda, M.; Fujita, K. Dehydrogenative Esterification and Dehydrative Etherification by Coupling of Primary Alcohols Based on Catalytic Function Switching of an Iridium Complex. *ChemistrySelect* **2022**, *7*, No. e202201135.

(14) (a) Arca, H. C.; Mosquera-Giraldo, L. I.; Bi, V.; Xu, D. Q.; Taylor, L. S.; Edgar, K. J. Pharmaceutical Applications of Cellulose Ethers and Cellulose Ether Esters. *Biomacromolecules* **2018**, *19*, 2351−2376. (b) Hu, F.; Song, T. Application of functionalized ether in lithium ion batteries. *RSC Adv.* **2017**, *7*, 54203−54212. (c) Zheng, B.; Wang, F.; Dong, S. Y.; Huang, F. H. Supramolecular polymers constructed by crown ether-based molecular recognition. *Chem. Soc. Rev.* **2012**, *41*, 1621−1636. (d) Pitsinos, E. N.; Vidali, V. P.; Couladouros, E. A. Diaryl Ether Formation in the Synthesis of Natural Products. *Eur. J. Org. Chem.* **2011**, *2011*, 1207−1222.

(15) Larock, R. C. *Comprehensive Organic Transformations*, 2nd edition; Wiley-VCH: New York, 1999.

(16) (a) Miera, G. G.; Lopez, A. B.; Martinez-Castro, E.; Norrby, P. O.; Martin-Matute, B. Nonclassical Mechanism in the Cyclodehydration of Diols Catalyzed by a Bifunctional Iridium Complex. *Chem. − Eur. J.* **2019**, *25*, 2631−2636. (b) Petronilho, A.; Vivancos, A.; Albrecht, M. Ether formation through reductive coupling of ketones or aldehydes catalyzed by a mesoionic carbene iridium complex. *Catal. Sci. Technol.* **2017**, *7*, 5766−5774.

(17) Prades, A.; Corberan, R.; Poyatos, M.; Peris, E. [IrCl2Cp*-(NHC)] Complexes as Highly Versatile Efficient Catalysts for the Cross-Coupling of Alcohols and Amines. *Chem. − Eur. J.* **2008**, *14*, 11474−11479.

(18) (a) Bures, J. A Simple Graphical Method to Determine the Order in Catalyst. *Angew. Chem., Int. Ed.* **2016**, *55*, 2028−2031. (b) Bures, J. Variable Time Normalization Analysis: General Graphical Elucidation of Reaction Orders from Concentration Profiles. *Angew. Chem., Int. Ed.* **2016**, *55*, 16084−16087.

(19) Blackmond, D. G. Kinetic Profiling of Catalytic Organic Reactions as a Mechanistic Tool. *J. Am. Chem. Soc.* **2015**, *137*, 10852−10866.

(20) (a) Ibáñez, S.; Poyatos, M.; Peris, E. Gold Catalysts with Polyaromatic-NHC ligands. Enhancement of Activity by Addition of Pyrene. *Organometallics* **2017**, *36*, 1447−1451. (b) Ruiz-Botella, S.; Peris, E. Unveiling the Importance of -Stacking in Borrowing-Hydrogen Processes Catalysed by Iridium Complexes with Pyrene Tags. *Chem. − Eur. J.* **2015**, *21*, 15263−15271.