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FULL PAPER

Iridium complexes with a new type of *N*^*N*′-donor anionic ligand catalyze the *N*-benzylation of amines via borrowing hydrogen

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The development of efficient and eco-friendly methods for the synthesis of elaborate amines is highly desired as they are valuable chemicals. The catalytic alkylation of amines using alcohols as alkylating agents, through the so-called borrowing hydrogen process, satisfies several of the principles of green chemistry. In this paper, four neutral half-sandwich complexes of Ru(II), Rh(III), and Ir(III) have been synthesized and tested as catalysts in the *N*-benzylation of amines with benzyl alcohol. The new derivatives contain a *N*^*N*′ anionic ligand derived from 5-(pyridin-2-ylmethylene)hydantoin (Hpyhy) that has never been tested in metal complexes with catalytic applications. In particular, the Ir derivatives, [(Cp*)IrX(pyhy)] (X = Cl or H), exhibit high activity along with good selectivity in the process. Indeed, the scope of the optimized protocol has been proved in the benzylation of several primary and secondary amines. The selectivity towards monoalkylated or dialkylated amines has been tuned by adjusting the amine:alcohol ratio and the reaction time. Experimental results support a mechanism consisting of three consecutive steps, two of which are Ir catalyzed, and a favorable condensation step without the assistance of the catalyst. Moreover, an unproductive competitive pathway can operate when the reaction is performed in open-air vessels, due to the irreversible release of H_2. This route is hampered when the reaction is carried out in close vessels, likely because the release of H_2 is reversed through metal-based heterolytic cleavage. From our viewpoint, these results show the potential of the new catalysts in a very attractive and promising methodology for the synthesis of amines.

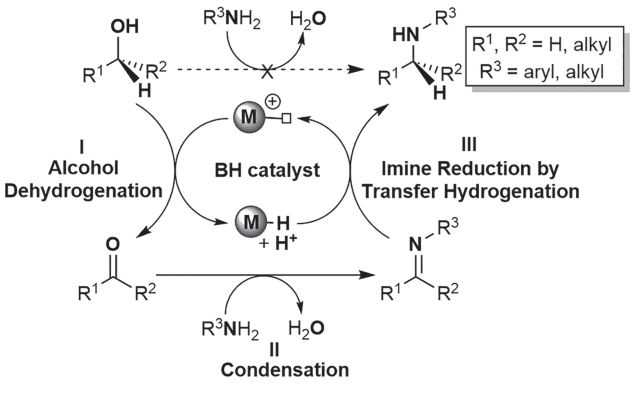
KEYWORDS
amines, benzylation, borrowing hydrogen, hydantoin, iridium, transfer hydrogenation

1 | INTRODUCTION

Amine groups are ubiquitous in natural products, pharmaceuticals, dyes, food additives, and other fine chemicals of commercial interest, so that the development of advantageous methods to produce more elaborate amines is of great interest.[1–3] Classical methods for the preparation of amines include the following: (a) reduction of nitro,[4–7] nitrile or amide groups[8]; (b) functionalization of alkenes or alkynes[9,10];

(c) alkylation of simple amines with alkyl halides[11,12]; and (d) reductive amination of carbonyl compounds.[13–15]

Alternatively, it is possible to obtain secondary or tertiary amines through alkylation of pre-existing primary or secondary amines, respectively, using alcohols as the alkylating agents. This methodology, called "borrowing hydrogen (BH)" or "hydrogen autotransfer,"[16] implies the use of less toxic and inexpensive starting materials and produces water as the only by-product.[17] These advantages have enormously boosted the interest of the scientific community in this process. BH is mediated usually by homogeneous catalysts, although heterogeneous systems have also been used,[6] and was first described by Grigg et al.,[18] Watanabe et al.,[19] and Murahashi et al.[20] in an independent way using [Ru], [Ir], or [Rh] complexes. This one-pot process occurs through three *in situ* consecutive reactions as shown in Scheme 1: Reaction I involves the dehydrogenation of the alcohol to give an aldehyde or ketone; Reaction II is the condensation between the primary or secondary amine and the aldehyde or ketone to give an imine or iminium ion; and Reaction III consists in the hydrogenation of the imine or iminium to give the secondary or tertiary amine.[17] Hence, the alcohol plays a dual role, as it acts as both the alkylating agent and the H_2 donor, which makes this BH chemical sequence a very efficient process in terms of atom economy. The condensation reaction is promoted by acidic species and except in a few cases does not involve the participation of the metallic catalyst.[21] Nevertheless, the BH methodology requires the participation of metal complexes able to promote processes I and III.[22,23] During the last years, several groups have contributed to the development of this strategy with metal complexes, mainly of Ir, including highly active



SCHEME 1 Sequence of reactions in the one-pot *N*-alkylation of amines with alcohols through borrowing hydrogen. The process indicated with the dotted arrow represent the global process, but the reaction takes place through three consecutive steps (I, II, and III) (The square in M^+-□ means a vacant coordination site)

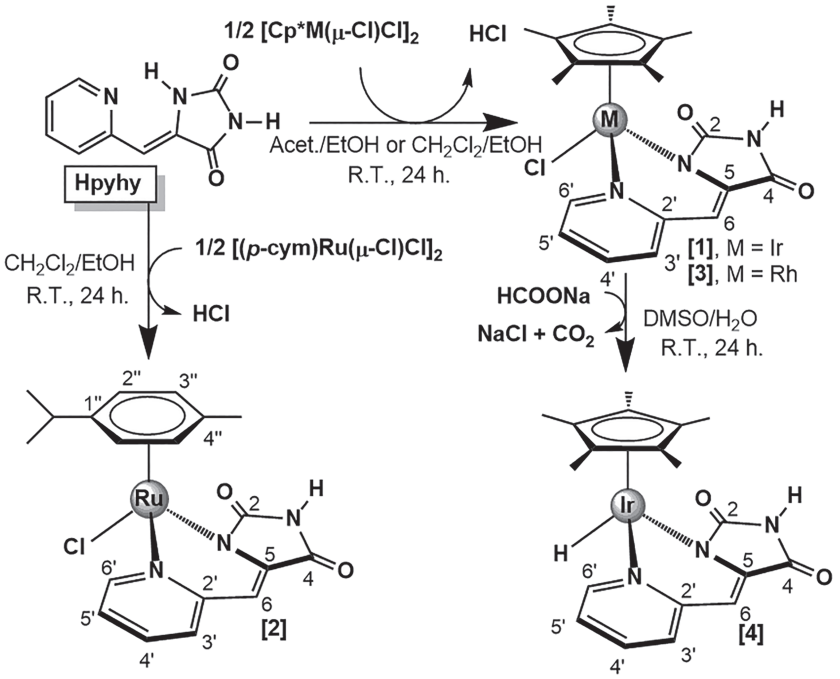
iridacyles,[13] Rh and Ru,[21,24–28] as well as other transition metals[29,30] and heterogeneous systems,[31–33] Catalysts active even in water and ionic liquids[34] or in solvent-free conditions[35] have been reported, but the majority of catalysts are used in organic solvent media. However, many of these processes suffer from incomplete amine conversion of the intermediate imine. As an alternative to the BH methodology, in recent years, TM-free *N*-alkylation reactions in basic media have been reported.[36] This procedure may work through an initial alcohol oxidation by air oxygen,[37,38] and it is autocatalyzed by the resulting carbonyl derivative (aldehyde or ketone). Other alternative is the previous addition of and aldehyde[39] or a ketone.[40] The transfer hydrogen step takes place by a Meerwein–Ponndorf–Verley process or by a hemiaminal intermediate.[41] Although this alternative method offers the advantage of not needing a metallic catalyst, suffers from drawbacks as long reaction times (e.g., 24 h), more exigent temperature conditions (130 °C to 180 °C) and relatively high loadings of base (20–40 mol%), whose nature and accompanying cation is critical in most of the reported examples.[39]

The catalytic *N*-alkylation of amines employing alcohols as alkylating reagents through BH exhibits several advantages compared with classical methods: (a) it generates water as the only by-product, with the consequent favorable contribution to the atom economy and eco-friendly principles; (b) avoids the use of often toxic alkyl halides as alkylating agents; (c) prevents the formation of overalkylation products when preparing secondary amines or in other words allows to control the degree of alkylation as a function of the reaction stoichiometry[17]; and (d) avoids the use of reductants compared with the reductive amination of carbonyl compounds.[13]

The ligands used in the metal complexes for BH processes are diverse although classical ligands such as phosphines are very common and half-sandwich complexes with Cp or arene ligands are also used frequently.[17] NHC ligands,[21,42] or diamido ligands,[43] such as those developed by Noyori and Ikariya, have been reported as well. The derivative 5-(pyridin-2-ylmethylene)hydantoin (Hpyhy) (see Scheme 2) has the appropriate conformation to form stable chelate complexes with transition metals, and, in fact, it has been used as proligand to synthesize nickel and copper complexes.[44,45] The ligand pyhy is a *N^N′* anionic ligand that could be considered reminiscent of the widely used Noyori–Ikariya ligands or even the *N^C* cyclometallating ligands.[13] However, metal derivatives with the ligand pyhy have never been explored in BH processes nor in other catalytic processes.

Thus, in this work, we have addressed the synthesis of four novel half-sandwich complexes of Ru(II), Rh(III), and Ir(III) with pyhy, including a hydrido derivative. We

SCHEME 2 Synthesis and structure of the Ir(III), Ru(II), and Rh (III) complexes bearing ligand pyhy$^-$



have demonstrated that some of the complexes are active in the catalytic *N*-benzylation of a variety of amines, and we have studied the influence of different factors on the efficiency and chemoselectivity of the process. A complete conversion of the starting amine is reported in many of the experiments, and optimization studies have allowed to get good to excellent chemoselectivity without the presence of the imine intermediate in the reaction products. Moreover, different NMR and catalytic experiments have shed light on the mechanism of this transformation.

2 | RESULTS AND DISCUSSION

2.1 | Synthesis and characterization of proligand and complexes

The proligand 5-(pyridin-2-ylmethylene)hydantoin (Hpyhy), formed from the heterocycles pyridine and hydantoin, was prepared as previously reported in the literature by reaction of pyridine-2-carbaldehyde and hydantoin.[46] The Rh(III) and Ir(III) neutral complexes of general formula [(Cp*)MCl(pyhy)] (M = Ir, **[1]**; M = Rh, **[3]**) were obtained by reacting the respective dimer $[(Cp^*)M(\mu\text{-}Cl)Cl]_2$ (M = Rh or Ir) with the proligand Hpyhy at room temperature in a mixture of acetone/ethanol or dichloromethane/ethanol (Scheme 2). The Ru(II) neutral *p*-cymene complex [(η^6-*p*-cym)RuCl(pyhy)], **[2]**, was prepared by reacting the dimer [(η^6-*p*-cym)Ru(μ-Cl)Cl]$_2$ with the same proligand Hpyhy at room temperature in a mixture of dichloromethane/ethanol (Scheme 2). The hydrido Ir(III) derivative [(Cp*)IrH(pyhy)] **[4]** was synthesized by reacting **[1]** with an excess of HCOONa in a mixture of DMSO:H_2O (1:5) at room temperature (Scheme 2).

The four derivatives are chiral (C_1 symmetry), and they were obtained as racemic mixtures of R and S enantiomers. The compounds were isolated in good yields as yellow (**[1]** and **[3]**) or red (**[2]** and **[4]**) solids and are air and moisture stable and soluble in common organic solvents such as DMSO, $CHCl_3$, and 2,2,2-trifluoroethanol (TFE).

The new complexes have been characterized by ^{1}H and $^{13}C\{^1H\}$ NMR. In addition, FT-IR, and FAB$^+$ MS spectra were also recorded, and elemental analysis was performed. The crystal structures of **[1]**, **[2]**, and the hydride derivative **[4]** were determined by single-crystal X-ray diffraction.

The main features in the ^{1}H NMR spectra of these derivatives are (i) a broad singlet at 7.4–7.5 ppm for **[1]** and **[4]** and at 8.17 ppm for **[2]** in $CDCl_3$ attributed to the N—H group of the hydantoin moiety. (ii) Singularly, **[4]** exhibits a singlet at −9.5 ppm ($CDCl_3$) for the hydride group. (iii) In the case of **[2]**, the C_1 symmetry is reflected in the existence of four resonances for the aromatic *p*-cymene protons and two doublets for the isopropylic methyl groups.

The IR spectra, apart from the two different bands for the vibrations of the two C═O groups,[46] exhibit the expected band for the stretching vibration of the NH group. The position of this band is sensitive to the

formation of hydrogen bonds, and indeed, it appears at different positions depending on the complex (3159 cm^{-1} for **[1]**, 3366 cm^{-1} for **[2]**, 3149 cm^{-1} for **[3]**, and 3318 cm^{-1} for **[4]**).

From FAB^+ spectrometry, it has been found that the base peak corresponds to fragments of the type $[M - Cl]^+$ for all the complexes with the exception of the hydrido derivative **[4]** where the pseudo-molecular cation, $[M]^+$, is detected. Complementary NMR techniques and elemental analysis are also in agreement with the expected structures for these complexes.

The crystal structures of **[1]·$CHCl_3$**, **[2]·$(CH_3CH_2OH)_{0.5}$**, and **[4]** were determined by X-ray diffraction. Single crystals of **[2]·$(CH_3CH_2OH)_{0.5}$** were obtained from a saturated chloroform solution of **[2]**. Surprisingly, single crystals of **[1]·$CHCl_3$** were formed in a saturated chloroform solution of **[4]**. In the case of **[4]**, the single crystals were obtained by slow diffusion of a dimethylformamide solution of **[1]** in an aqueous solution of HCOONa. The ORTEP diagrams are shown in Figures 1–3, whereas selected bond lengths and angles with estimated standard deviations are gathered in Table 1, and relevant crystallographic parameters are given in Table S1. A full list of bond lengths (Å) and angles (°) for these structures is compiled in Tables S5–S7. In the case of **[2]·$(CH_3CH_2OH)_{0.5}$**, two independent molecules (Molecules 1 and 2 with Ru(1) and Ru(2), respectively) are present in the unit cell. The molecular structures of the three derivatives exhibit the expected three-legged piano-stool design, with a π-bonded ligand (Cp* or *p*-cymene), plus the pyhy *N*^*N*′-donor ligand forming a six-membered metallacycle and a monodentate

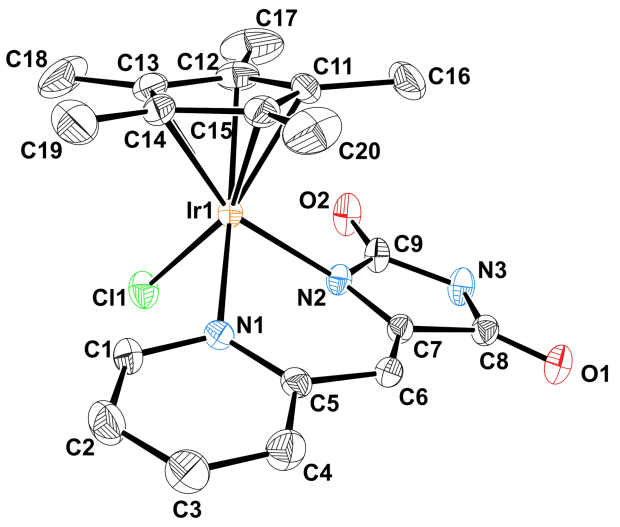


FIGURE 1 ORTEP diagram for the molecular structure of **[1]**. Thermal ellipsoids are shown at the 30% probability. Only the R enantiomer is shown. Hydrogen atoms have been omitted for clarity. Solvent molecules have been omited as well

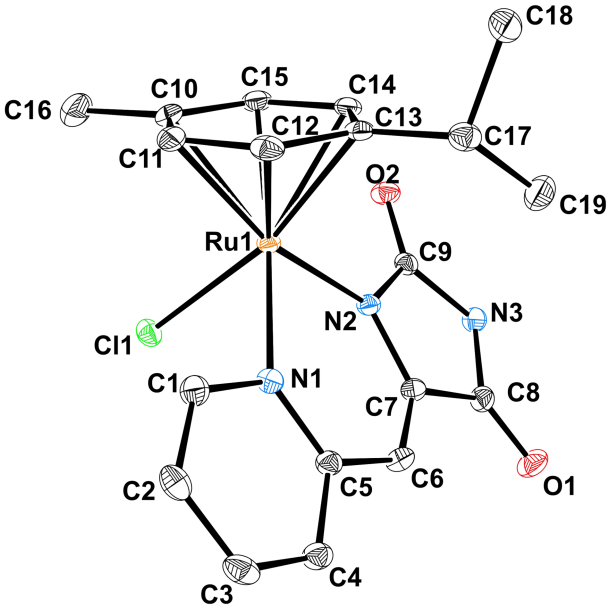


FIGURE 2 ORTEP diagram for the molecular structure of **[2]** (Molecule 1). Thermal ellipsoids are shown at the 30% probability. Only the R enantiomer is shown. Hydrogen atoms have been omited for clarity. Solvent molecules have been omited as well

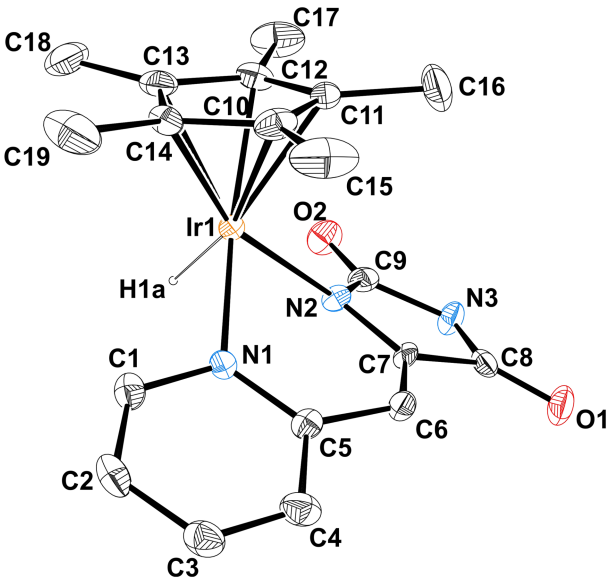


FIGURE 3 ORTEP diagram for the molecular structure of **[4]**. Thermal ellipsoids are shown at the 30% probability. Only the R enantiomer is shown. Hydrogen atoms, except the hydride have been omited for clarity

group (chloride or hydride). The M—N(1) (pyridine) bonding distances are longer than the respective M—N (2) (hydantoin) distances in all the cases, likely as a consequence of the strong σ-donor character of the anionic N of hydantoin. The M—Cl bond distances for **[1]** and **[2]** and the metal-centroid lengths for the three derivatives are conventional when compared with those reported for

TABLE 1 Selected bond lengths (Å) and angles (°) for compounds **[1]·$CHCl_3$**, **[2]·$(CH_3CH_2OH)_{0.5}$**, and **[4]**.

Distances/angles	[1]·$CHCl_3$	Distances/angles	[2]·$(CH_3CH_2OH)_{0.5}$ (Molecule 1/Molecule 2)	Distances/angles	[4]
Ir(1)—N(1)	2.116 (4)	Ru(1)—N(1)/Ru(2)—(4)	2.159 (2)/2.136 (2)	Ir(1)—N(1)	2.107 (9)
Ir(1)—N(2)	2.072 (3)	Ru(1)—N(2)/Ru(2)—N(5)	2.085 (2)/2.079 (2)	Ir(1)—N(2)	2.082 (9)
Ir(1)—Cl(1)	2.387 (1)	Ru(1)—Cl(1)/Ru(2)—Cl(2)	2.4315 (5)/2.4194 (6)	Ir(1)—H(1a)	1.6 (1)
Ir(1)—C(11)	2.140 (5)	Ru(1)—C(10)/Ru(2)—C(30)	2.226 (2)/2.223 (2)	Ir(1)—C(10)	2.23 (1)
Ir(1)—C(12)	2.149 (5)	Ru(1)—C(11)/Ru(2)—C(31)	2.217 (2)/2.192 (2)	Ir(1)—C(11)	2.235 (9)
Ir(1)—C(13)	2.182 (5)	Ru(1)—C(12)/Ru(2)—C(32)	2.175 (2)/2.158 (2)	Ir(1)—C(12)	2.16 (1)
Ir(1)—C(14)	2.186 (5)	Ru(1)—C(13)/Ru(2)—C(33)	2.207 (2)/2.183 (2)	Ir(1)—C(13)	2.18 (1)
Ir(1)—C(15)	2.146 (5)	Ru(1)—C(14)/Ru(2)—C(34)	2.174 (2)/2.156 (2)	Ir(1)—C(14)	2.13 (1)
		Ru(1)—C(15)/Ru(2)—C(35)	2.176 (2)/2.211 (2)		
Ir-Ct (Cp*)	1.79	Ru-Ct (*p*-cym)	1.68/1.67	Ir-Ct (Cp*)	1.82
C(5)—C(6) (F)	1.450 (7)	C(5)—C(6)/C(25)—C(26)	1.436 (3)/1.443 (3)	C(5)—C(6) (F)	1.459 (16)
N(2)—Ir(1)—N(1)	83.75 (14)	N(2)—Ru(1)/N(1)/N(4)—Ru(2)—N(5)	88.00 (7)/87.20 (7)	N(2)—Ir(1)—N(1)	84.4 (4)
N(2)—Ir(1)—Cl(1)	87.58 (11)	N(2)—Ru(1)—Cl(1)/N(4)—Ru(2)—Cl(2)	87.60 (5)/84.02 (5)		
N(1)—Ir(1)—Cl(1)	87.21 (10)	N(1)—Ru(1)—Cl(1)/N(5)—Ru(2)—Cl(2)	80.42 (5)/86.25 (5)		
α	14.8	α	6.3/11.6	α	27.7
β	33.8	β	4.5/16.9	β	35.1

Note: Ct = centroid. α is the angle between the planes of the pyridine and hydantoin rings. β is the dihedral angle formed by the N(2)—M—N(1) and N(1)C(5)N(2)C(7) planes (see Chart 1).

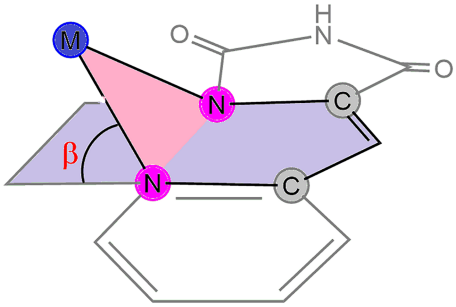


CHART 1 β angle

similar complexes.[47–52] It is noteworthy that the hydride atom has been located in the Fourier difference map and refined freely.

The hydantoin part of the ligand is essentially planar, reflecting an electron delocalization around this ring. The same situation has been found in the Ni and Cu complexes previously described.[44,45] The respective distance ranges determined for this ring are reflected in Figure S1a where it is observed that distances B and D are the longest. In accordance with the electron delocalization, there is no pyramidalization on the NH group (sum of the angles around the N atom = 358.5° to 360°). The dihedral angle (α) between the two rings of the pyhy ligand in general is low (14.8° for **[1]** and 6.3° and 11.6° for Molecules 1 and 2 of **[2]**), but it is higher for the hydrido complex **[4]** (27.7°). This fact could reflect different degrees of delocalization in the metallacycle. Interestingly, there is a clear correlation between the α angle and the distance C(5)—C(6) (distance F in Figure S1a). When the angle is higher (complexes **[1]** and **[4]**), this distance is longer (1.45–1.46 Å) whereas for the more planar ligands, the distance is shorter (two molecules of **[2]**, 1.44 Å) (the value expected for a C_{sp2}–C_{sp2} distance is 1.47 Å) reflecting in these last cases a higher degree of delocalization (Figure S1b). On the other hand, the β angle (see Table 1 and Chart 1) that reflects the orientation of the *N^N′* ligand with respect the N–M–N plane depends essentially on the metal with the highest values for the Ir compounds (33.8° for **[1]** and 34.1° for **[4]**) and lower values for the Ru complex **[2]** (6.3° and 11.6°), a fact that reflects a possible steric hindrance between both the C(1)—H(1) and mainly the O(2) groups and the methyl groups of the Cp* ring. In the case of the two molecules of **[2]**, the *p*-cymene ring is rotated in such a way that the C(16)—C(17) axis is oriented to reduce the steric interaction with the stated H and O atoms. The value of the bite angle also depends on the metal (around 84° for Ir derivatives and 87° to 88° for the two independent Ru molecules). The reported values for the Ni and Cu complexes with the pyhy ligand are higher (92° to 93°).[44,45]

The 3D architecture in the crystal structures of these complexes is sustained by hydrogen bonding interactions and by other weak interactions such as π–π stacking contacts. In particular, the structure of **[1]** features dimeric entities consisting of two molecules of **[1]** that interact with each other through double, strong, and identical hydrogen bonds, N(3)—H(3A)···O(2) (Figure S2). The 3D structure of **[2]** exhibits dimeric entities as well, but in this case, they are the result of double hydrogen bonding interactions, N(3)—H(3A)···Cl(1), and π–π stacking contacts between the hydantoin rings (Molecule 1, Figure S3). In the crystal structure of **[4]** one of the main motifs is a double chain based on the hydrogen bonding interactions N(3)—H(3A)···O(1) and C(4)—H(4)···O(2) (Figure S4).

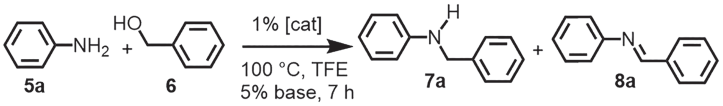
2.2 | Catalytic activity

2.2.1 | Optimization of the reaction conditions

As previously stated, in this work, we decided to test the catalytic potential of our complexes in BH reactions. Thus, we chose the *N*-alkylation of aniline, **5a**, with benzyl alcohol, **6**, as the model reaction (Scheme 3) and performed the initial trials with **[1]** as the precatalyst, using conditions similar to those recently reported by some of us.[13]

To our delight, complex **[1]** was active in the process and provided a moderate conversion (33%) along with a high selectivity for benzylamine **7a** (30%) versus imine **8a** (3%) when the reaction was carried out in 2,2,2-TFE at 100 °C in the presence of K_2CO_3 (5% mol) and using a 20% excess of aniline in a sealed reaction tube under N_2 during 7 h (Entry 1, Table 2). The beneficial role of TFE was demonstrated when this reaction was carried out in the absence of solvent (Entry 2). Both conversion and benzylamine production decreased notably (Entry 2 vs. Entry 1). After that, we analyzed the influence of several factors over the performance of precatalyst **[1]** in this transformation, aiming to optimize the yield of **7a**.

First, we probed different carbonates, hydroxides, and alkoxides as alternative bases in TFE (Entries 2–14;



SCHEME 3 Catalytic borrowing hydrogen reaction studied for the *N*-alkylation of aniline using benzyl alcohol

TABLE 2 Base optimization for the *N*-alkylation of aniline using benzyl alcohol in TFE

Entry	Base	%Conversion	%Amine (product)	%Imine
1	K_2CO_3	33	30	3
2[a]	K_2CO_3	16	13	3
3	Cs_2CO_3	37	34	3
4[b]	Cs_2CO_3	37	34	3
5	Na_2CO_3	6	4	2
6	$CaCO_3$	0	-	-
7	$(NH_4)_2CO_3$	0	-	-
8	$(Fe_3)_2CO_3{\cdot}FeCO_3$	0	-	-
9	$CdCO_3$	0	-	-
10	KOH	11	8	2
11	NaOH	21	18	2
12	NH_4HCO_3	0	-	-
13	^{t}BuOK	8	5	3
14	^{t}BuONa	13	10	3

Note: Aniline (0.6 mmol), benzyl alcohol (0.5 mmol), **[1]** (1 mol%, 5 μmol), base (5 mol%, 0,025 mmol), TFE (2.6 mL), 100 °C, 7 h.
[a]In the absence of any solvent (neat conditions); with identical ratio of the different components but starting with 18 μmol of **[1]**.
[b]120 °C; conversions were determined by ^{1}H NMR spectroscopy.

Table 2). Unfortunately, we only made a small improvement in this study by replacing K_2CO_3 with Cs_2CO_3 (37% conversion, Entry 3, Table 2). In addition, we established that an excess of base is beneficial for both the conversion and the selectivity of the prototype reaction (Table S2). Specifically, the use of two equivalents of either K_2CO_3 or Cs_2CO_3 increased the conversion up to 68% and 67%, respectively (Entries 1–2, Table 3). In conclusion, we decided to use K_2CO_3 in a 2:1 molar ratio (base/limiting substrate), as the ideal additive due to its lower price compared to Cs_2CO_3.

Then, the model reaction was tested in the presence of **[1]** in several protic (ethanol) and aprotic (toluene and DMF) solvents, apart from TFE, using K_2CO_3 as the base (Table 3, Entries 3–5). However, no reaction was observed in these alternative media. The use of other bases in water was neither satisfactory (Entries 6 and 7, Table 3), although a small conversion was obtained when using the combination water/Cs_2CO_3 (Entry 8, Table 3).

Hence, we concluded that TFE is essential to promote the catalytic activity of **[1]** in this reaction and anticipated that it could play a multiple role in the

TABLE 3 Optimization of conditions (solvent and base).

Entry	Base	Solvent	%Conversion	%Amine (product)	%Imine
1	Cs_2CO_3	TFE	67	62	4
2	K_2CO_3	TFE	68	65	1
3	K_2CO_3	Toluene	0	-	-
4	K_2CO_3	EtOH	1	-	-
5[a]	K_2CO_3	DMF	0	-	-
6	NaOH	H_2O	0	-	-
7	KOH	H_2O	0	-	-
8	Cs_2CO_3	H_2O	9	3	6
9[b]	K_2CO_3	TFE	50	48	1

Note: Aniline (0.6 mmol), benzyl alcohol (0.5 mmol), **[1]** (1 mol%, 5 μmol), base (2 equiv., referred to the amount of benzyl alcohol, 1 mmol), solvent (2.6 mL), 100 °C, 7 h; conversion were determined by ^{1}H NMR spectroscopy.
[a]In DMF, the result was analyzed using thin-layer chromatography (TLC) and compared with a product of another reaction.
[b]80 °C.

corresponding catalytic cycle, as discussed below in the mechanistic proposal. The crucial role of TFE has been previously observed by some of us in the alkylation of amines with alcohols or in the synthesis of nitrogen heterocycles when using complexes of the type [Cp*IrCl(*C*^*N*)] as precatalysts.[13]

The effect of the temperature on the production of **7a** was examined as well. Indeed, we determined that a decrease in the reaction temperature from 100 °C to 80 °C is detrimental for the conversion (Entries 2 and 9, Table 3). However, a rise in this parameter up to 120 °C was neither satisfying (Entries 3 and 4, Table 2). Therefore, the ideal temperature for this transformation was established as 100 °C.

Further improvements were achieved using an excess of benzyl alcohol. Thus, we obtained a conversion of 97% with a high selectivity (94% of **7a**) when using a benzyl alcohol/aniline molar ratio of (2:1) (Entry 3, Table 4). This conversion dropped down when 10 mol% of NaCl (NaCl/**[1]** molar ratio = 10/1) was added to the reaction mixture (Entry 4), reflecting that substitution of the chloride ligand is important in the triggering of the catalytic reaction.

The conditions established in the last experiment (Entry 3, Table 4) seem to be optimal for the *N*-benzylation of aniline in the presence of **[1]**. In consequence, we used those conditions for additional experiments aiming to compare the catalytic activity of complexes **[1]**–**[4]** and to explore the substrate scope. A blank experiment without catalyst (24 h) using these conditions was performed, and the unreacted substrates were recovered from the reaction crude after 7 h (Table 4, Entry 5).

As some authors[38,39] have reported that an aldehyde can substitute a metal complex as catalyst in TM-free *N*-alkylation reactions in basic media, two additional catalytic experiments were performed replacing the metal precatalyst with benzaldehyde (10 mol%) both in the presence (Entry 10, Table 4) and in the absence of base (Entry 11). The conversion in both cases was 0%, and minor amounts or imine were observed in both tests.

2.2.2 | Catalyst screening

All the new complexes were tested in the benzylation of aniline using the optimized conditions (Table 4). The catalytic activities of complexes **[2]** and **[3]** in the model reaction were disappointing compared with that of **[1]**. In fact, **[2]** and **[3]** gave conversion values of 13% and 15%, respectively (Entries 7 and 8 in Table 4). However, the Ir(III) hydride species **[4]** exhibited quantitative conversion with ideal selectivity towards the monoalkylated amine (Entry 9), indicating that **[4]** could be the active catalytic intermediate when using **[1]**. The same result in terms of activity and selectivity was also found in the presence of **[1]** after 12 h (Entry 6, Table 4). Consequently, the Ir(III) precatalyst **[1]** was chosen for the subsequent studies because it is more stable and more easily prepared than **[4]**.

TABLE 4 Optimization of alcohol/aniline ratio and precatalyts screening.

Entry	Precatalyts	Benzyl alcohol (mmol)	Aniline (mmol)	%Conversion	%Amine (product)	%Imine
1	**[1]**	0.5	0.6	68	65	1
2	**[1]**	0.5	1	64	61	2
3	**[1]**	1	0.5	97	94	3
4[a]	**[1]**	1	0.5	35	35	0
5[b]	-	1	0.5	0	0	0
6[c]	**[1]**	1	0.5	>99	>99	-
7	**[2]**	1	0.5	13	9	4
8	**[3]**	1	0.5	15	11	4
9	**[4]**	1	0.5	>99	>99	-
10[d]	-	1	0.5	0	-	4
11[e]	-	1	0.5	0	-	8

Note: Precatalyst (1 mol%, with respect to the starting material in default, 5 μmol), K_2CO_3 (2 equiv. with respect the limiting substrate, 1 mmol), TFE (2.6 mL), 7 h, 100 °C; conversion were determined by ^{1}H NMR spectroscopy.

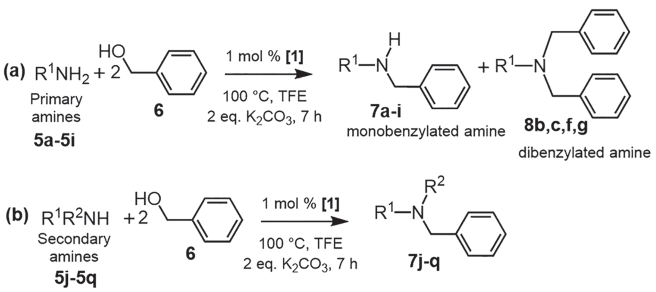
[a]Identical conditions of Entry 3 but adding 10 mol % of NaCl.

[b]24 h. Identical conditions as in "Note" but without precatalyst.

[c]12 h.

[d]Conditions as in "Note" but without a metallic precatalyst and using benzaldehyde (10 mol%).

[e]Conditions as in "Note" but without a metallic precatalyst and without base and using benzaldehyde (10 mol%).



SCHEME 4 Amine scope: general conditions and products for the *N*-benzylation of amines using benzyl alcohol

2.2.3 | Substrate scope

The potential of this protocol for the *N*-benzylation of amines was demonstrated by reacting several types of amines with benzyl alcohol in the presence of **[1]** under the previously established optimized conditions, unless otherwise stated (see Scheme 4 and Table 5).

First, we tested diverse anilines (**5b**–**5f** in Table 5) and obtained excellent conversion values for those with electron-donating groups in the *para* position of the phenyl group, **5b** (—OMe) and **5c** (—Me), or those with moderate electron effects, **5d** (—Cl) (Entries 2–4 in Table 5). Nevertheless, the chemoselectivity of the transformations with **5b** and **5c** was not as good as that observed for aniline, **5a**, because dibenzylated products were formed in significant yields for both substrates (compare Entry 1 with Entries 2 and 3 in Table 5). Aniline **5e** with an electron-withdrawing group (—NO_2) in the *para* position of the phenyl ring gave a low conversion (30%) of the monoalkylated product (Entry 5 in Table 5) as previously reported for other catalytic systems.[13] The bulky aniline **5f** with a methyl group in the *ortho* position of the phenyl ring provided also a low conversion value (compare Entries 3 and 6 in Table 5).

On the other hand, it is worth emphasizing that formation of dialkylated amines is favored for anilines with electron-donating groups (Entries 2 and 3), whereas it is not observed for anilines with electron-withdrawing groups or for aniline (Entries 1, 4 and 5). This tendency can be rationalized as a result of the high nucleophilic nature of the amines resulting from the first benzylation, **7b** and **7c**, which facilitates the second benzylation reaction.

Then, we probed several aliphatic primary amines such as **5g**–**5i** (Entries 7–9 in Table 5). These experiments provided full conversion values with good or excellent selectivity for the monobenzyl product. The less hampered amines **5g** and **5h** allowed the formation of small amounts of dibenzyl products while this is not the case for **5i**, probably due to the steric bulk of two Me groups in the benzyl position of the starting amine that precludes the easy formation of the iminium intermediate.

Finally, we tried some aliphatic secondary amines, **5j**–**5q**, with contrasting results. For instance, amines **5j**–**5l** afforded the expected monobenzyl derivatives with excellent yields (Entries 10–12 in Table 5), and pyrrolidine, **5m**, gave the monoalkylated product in a 57% yield (Entry 13, Table 5). It is remarkable the case of the reaction with **5k** that shows, in addition to high selectivity, a performance that exceeds those obtained with the highly active iridacycles in comparable experimental conditions.[13] On the contrary, amine **5n** and other sterically hampered secondary amines, such as **5o**–**5q**, did not undergo any degree of transformation (Entries 14–17 in Table 5).

Moreover, the reaction between 1,2,3,4-tetrahydroisoquinoline (**5k**) and benzyl alcohol was carried out in the optimal conditions for the *N*-benzylation of the amine, but in the presence of air instead of N_2, resulting in a conversion > 99%. Therefore, we concluded that the use of inert atmosphere is dispensable in this protocol.

Furthermore, the synthetic viability of the established protocol was demonstrated by isolating benzyl amines, **7a**, **7g**, **8g**, **7j**, **7k**, **7l**, and **7i** from the respective reactions with amines **5a**, **5g**, **5j**, **5k**, **5l**, and **5i** (Table 5) as the ammonium chloride salts.* In all the cases, the isolated yields were higher than 80% except for the products obtained from **5g** (Entry 7).

2.2.4 | Optimization of selectivity

First at all, we decided to extend the reaction time to 24 h, using the standard conditions established in Table 5, in order to increase the selectivity towards the dialkylation of some of our amines. Amines **5b**, **5c**, **5g**, and **5h** were selected for this study since the selectivity after 7 h was moderate or low and hence improvable. As expected, the relative ratio of the dialkylated amine increased up to certain extend, although the selectivity towards the dialkylated products remained far from optimal (Table 6, Entries 1–4).

With the goal of refining the selectivity towards the monoalkylated amines of this methodology, we decided to monitor the benzylation of *p*-anisidine (**5b**) and *p*-toluidine (**5c**) using short reaction times. The results for times of 1, 2, 4, 7, and 24 h can be found in Tables S3

*The substrates chosen have been those with almost a total conversion and among them those that present the best chemoselectivity towards the formation of the monoalkylated amine.

TABLE 5 *N*-Alkylation of amines using benzyl alcohol (substrate scope).

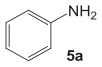
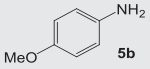
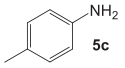
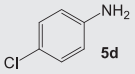
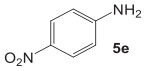
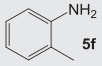
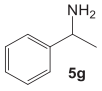
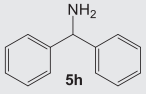
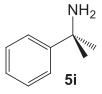
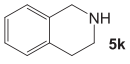
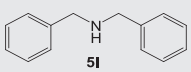
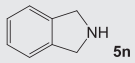
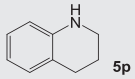
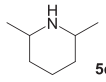
Entry	Amine	% Conversion	% Amine product monoalkylated/dialkylated	Isolated yield (%)[a]
1	 5a	97[b]	94/0	84
2	 5b	>99	58/42	-
3	 5c	>99	70/30	-
4	 5d	70	70/0	-
5	 5e	30	30/0	-
6	 5f	58	50/8	-
7	 5g	>99	84/16	75/15
8	 5h	>99	89/11	-
9	 5i	>99	>99/0	92
10	 5j	>99	>99/0	80
11	 5k	>99	>99/0	84
12	 5l	>99	>99/0	90
13	 5m	57	57/0	-

TABLE 5 (Continued)

Entry	Amine	% Conversion	% Amine product monoalkylated/dialkylated	Isolated yield (%)[a]
14	 5n	0	-	-
15	 5o	0	-	-
16	 5p	0	-	-
17	 5q	0	-	-

Note: Amine (0.5 mmol), benzyl alcohol (1 mmol), K_2CO_3 (2 equiv.), **[1]** (1 mol%), TFE (2.6 ml), $T = 100$ °C, 7 h; conversion values were determined by ^{1}H NMR spectroscopy. Conversions are referred to the starting amine. All the experiments that gave dialkylated amines were checked by mass spectrometry.

[a]Isolated yields were calculated for the hydrochloride salts.

[b]3% of imine was detected in solution for this substrate.

and S4 for **5b** and **5c**, respectively. The corresponding data are depicted in Figure S6 for **5b** and Figure 4 for **5c**.

In the case of **5b** (Entry 1 of Tables 6 and S3), the highest amount of monoalkylated amine is achieved after 2 h (86%). At this time, only 6% of dialkylated amine and an 8% of the starting *p*-anisidine are present in solution. Better results were obtained for *p*-toluidine **5c** (Entry 2 of Tables 6 and S4 and Figure 4) with a 94/6 ratio (monoalkylated/dialkylated amine) upon 2 h of reaction and a 100% of monoalkyaled amine after 1 h, in both cases with a quantitative conversion of the amine.

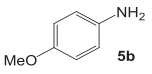
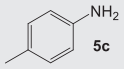
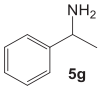
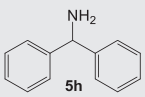
For the bulky amines **5g** and **5h**, the products ratio at 2 h was also determined (Entries 3 and 4, Table 6). The selectivity towards the monalkylated amine was improved relative to that obtained upon 7 h for **5g** but not for **5h**. In any case, quantitative conversions and good selectivity were already obtained for these substrates at 7 h.

Besides, in the case of **5b**, an increase in the initial alcohol:amine ratio to a 10:1 value was also assayed to achieve a better conversion to the dibenzylamine. A ratio of 4.6:1 of the dialkylated/monoalkylated amines was obtained, although benzaldehyde (17%) was also found in the reaction mixture (see Entry 7 of Table S3) due to the use of an excess of alcohol.

2.3 | Mechanistic proposal

In order to delve into the mechanism of the benzylation process, we performed some additional experiments. The ^{1}H NMR spectrum of complex **[1]** in TFE-d_3 exhibited resonances that did not change their position when five equivalents of NBu_4Cl were added, and therefore, they were assigned to the chlorido complex **[1]**. The addition

TABLE 6 Time dependence of the ratio of monoalkylated/dialkylated amine products obtained from **5b**, **5c**, **5g**, and **5h** at different reaction times.

Entry	Amine	2 h	7 h	24 h
1	 5b	86/6[a]	58/42	32/68
2	 5c	94/6	70/30	47/63
3	 5g	90/10	84/16	68/32
4	 5h	89/11	89/11	80/20

Note: Amine (0.5 mmol), benzyl alcohol (1 mmol), K_2CO_3 (2 equiv.), **[1]** (1 mol%), TFE (2.6 ml), $T = 100$°C. Reaction time 2, 7, or 24 h; conversion values were determined by ^{1}H NMR spectroscopy. Conversions were determined with respect to the starting amine.

[a]8% of *p*-anisidine remains unreactive.

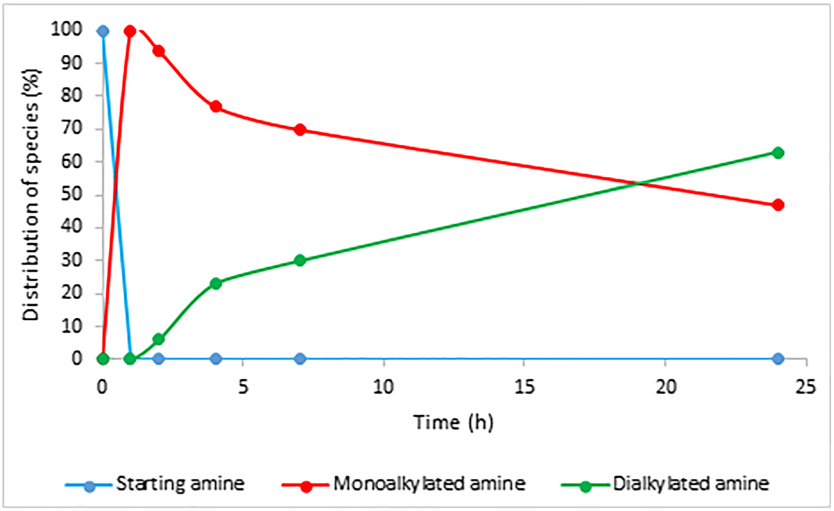


FIGURE 4 *N*-Alkylation of *p*-toluidine (**5c**) using benzyl alcohol (1:2 ratio)

of the salt only produced a broadening of two of these resonances, a fact that could be due to equilibria involving hydrogen bonds, either intermolecular or with the chloride anions of NBu_4Cl (Figure S7). In contrast, the addition of five equivalents of $AgBF_4$ to the initial solution of **[1]** led to the disappearance of the stated resonances and the appearance of new signals for a species labeled as **1A** (see Figure S8) that could be a TFE-solvato derivative or an unsaturated complex stabilized by the presence of the Ir—N (hydantoin) amido bond.

Complex **[1]** in TFE-d_3 reacts with K_2CO_3 (the base used in our catalytic processes). When 10 equiv. of the base were added to a solution of the precatalyst in an NMR tube, an equilibrium was established between **[1]** and a major species that putatively was assigned to the carbonato compound $[Cp^*Ir(OCO_2)(pyhy)]^-$ (**1B**) (Figure S5). A 2/8 ratio between the chlorido and the carbonato species was found after 2 days of reaction. Attempts to isolate this new species in its pure form failed due to its insolubility in conventional solvents such as $CHCl_3$, acetone, or methanol and its lability in others, such as DMSO, in which the formation of two major species was observed.

In another NMR experiment (see Figures S9 and S10 for the different regions of the spectra), benzyl alcohol (5 equiv.) was added to a TFE-d_3 solution of **[1]**, and no changes were observed in the ^1H NMR spectrum of the Ir complex. When K_2CO_3 (5 equiv.) was added, the stated equilibrium between the chlorido and the carbonato species was observed. Additionally, three other minor Ir species appeared in the spectrum (**x**, **y**, and **z**) that can be due to the reaction of the carbonato-complex with benzyl alcohol. They were clearly observed, at room temperature, in the spectrum regions corresponding to the methine-bridge protons of the pyhy ligand and the Cp* (Figure S10), although in this last region resonances of **x** and **y** exhibit the same chemical shift. Besides, the incipient formation of benzaldehyde was also observed (1.4% relative to the concentration of all the Ir species). Heating at 60 °C for 5 min produced an increase in the signals of the aldehyde (3%) and mainly in those of the carbonato-complex **1B** that represented 55% of the Ir mixture. The resonances of **[1]** were small at this moment. At 60 °C, the resonances of the three minor products (**x**–**z**) broadened, together with the residual resonances of **[1]**. We tentatively assigned these resonances as due to species resulting from the substitution of the chloride or the carbonate ligand by $CF_3CH_2O^-$ or $PhCH_2O^-$ (**1D**) and the adduct with benzyl alcohol (**1C**), that could be, all together, in dynamic interchange with **[1]** at 60 °C.

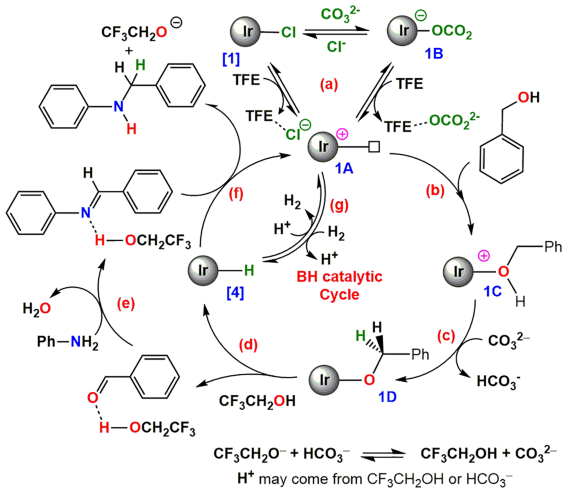
Then, aniline (2.5 equiv.) was subsequently added. At room temperature, although **1B** was the major component, other four Ir compounds were visible in the spectrum (labeled as **h**–**k** in Figure S10). After an increase in temperature to 60 °C for 5 min, the resonances of **1B** almost disappeared while the intensity of resonances of **i**–**k** species increased, achieving the respective **h**–**k** species a ratio of 3/29/38/30.

The resonances for the hydrido complex **[4]** were not observed along these experiments, reflecting a fast evolution of this species in the presence of the amine, which indicates that when the imine intermediate is present, **[4]** acts as a good nucleophile.

In an independent experiment, we proved that the benzyl alcohol undergoes dehydrogenation to produce benzaldehyde (6%) under the optimal catalytic conditions in the presence of complex **[1]** (**[1]** 1 mol %, TFE, 100 °C, K_2CO_3, 7 h) but in the absence of aniline. Consequently, we proved that this reaction may well be the first step of the alkylation process, even though from a thermodynamic point of view it is likely that subsequent steps push the dehydrogenation equilibrium forward.

A mechanistic interesting point is to know if the condensation step of the starting amine and the aldehyde intermediate occur with or without the assistance of the catalyst. On one side, this condensation has been considered rapid and easily accomplished without the intervention of the catalyst by some authors.[53–55] Other authors have reported that this process is more favored by water[56] or alcohols[57] than by some metallic species. In contrast, other theoretical[21,58,59] and experimental[21] studies indicate that the condensation step takes place in the coordination sphere of the catalyst. In order to delve this question, we monitored by ^{1}H NMR the reaction of benzaldehyde and *p*-toluidine in a molar ratio 2:1 in TFE media in the absence of catalyst, and we found that this reaction was completed at room temperature in 5 min (see Figure S11). Therefore, the condensation of benzaldehyde and an arylamine seems to take place quickly in TFE and without the need of either the catalyst or the base. Interestingly, it has been observed in our catalytic amine alkylation experiments that as long as the starting arylamine is not completely consumed, benzaldehyde is not present.

Finally, considering that the catalytic experiments were performed in sealed reaction vessels and in order to get information about the possible participation of released H_2 in the process, a catalytic experiment of the *N*-alkylation of *p*-anisidine using benzyl alcohol in an open reaction vessel (coupled to a condenser) was performed (2 h, 100 °C, see Table S3, Entry 3). If the results are compared with the similar experiment in a sealed reaction vessel (Entry 2), a clear reduction in the amine conversion (from 92% to 58%) was observed. Thus, it is concluded that hydrogen gas may be released and reused when the catalytic process is performed in close vessels, a fact that although has been previously pointed out, is not usually studied.[13]



SCHEME 5 Proposed mechanism for the *N*-benzylation of aniline with benzyl alcohol through borrowing hydrogen (BH) methodology

With all this experimental information in mind, we tentatively formulate a mechanistic proposal for this one-pot catalytic process with the following steps (Scheme 5): (a) activation of the Ir–Cl precatalyst **[1]** by dissociation of the chloride anion to form intermediate **1A** that could be a TFE-solvato species or to have a vacant site. The formation of the carbonato-complex **1B** is also reasonable from our experimental data and can act as a resting state of the precatalyst **[1]**; (b) coordination of the benzyl alcohol to the metal ion to produce the Ir-OHR species **1C**; (c) deprotonation of the coordinated benzyl alcohol which affords the Ir-alkoxide intermediate **1D**; (d) formation of the Ir-hydride intermediate, **[4]**, together with benzaldehyde, through β-elimination; (e) condensation between the benzaldehyde and the aniline, assisted by TFE, to form an imine; and (f) activation of the imine through the formation of a hydrogen bonding imine-TFE adduct and hydride transfer from the Ir–H intermediate, **[4]**, to produce the final amine and regenerate the active Ir species **1A**. The result of the aforementioned catalytic test performed in an open vessel indicates that the hydrido intermediate, **[4]**, can alternatively react with protons from the media (CF_3COOH or HCO_3^-) to generate species **1A** and H_2. From our view, this unproductive pathway is disfavored in close vessels due to the reversibility of reaction (step g in Scheme 5) but can really compete with the productive pathway in open vessels.

As aforementioned, the crucial role of TFE in this process could stem from its participation in several steps of the mechanism. First, it could intercede in the activation of the Ir—Cl bond of **[1]** and the carbonato-complex **1B** through hydrogen bonding interactions.[13,60] In other words, we postulate that the polarity and hydrogen bonding ability of TFE could promote the dissociation of the chloride or carbonate anions to afford the coordination of benzyl alcohol due to the assumed high solvation energy of Cl^- and CO_3^{2-} in this solvent (step a in Scheme 5). Second, we speculate that the acidic nature of TFE could also catalyze the condensation reaction (step e). In third place, TFE could activate the imine bond (C═N) through hydrogen bonding (step f), facilitating the hydride transfer from the Ir—H intermediate. The activation of the imine intermediate has been previously considered as a necessary step for an effective hydride transfer to imines.[61–63] In Scheme 5, we also assume that TFE is presumably the proton donor in the amine formation (step f), based on its pK_a value (11.4) lower than that of benzyl alcohol (15.4). The participation of the HCO_3^- anion as proton donor (pK_a = 10.33) cannot be ruled out, although its concentration in the medium is lower than

that of TFE. Finally, TFE can also participate as the proton transfer agent in step g.

It is interesting to note that in the catalytic tests, the presence of imine is only observed in one case (Entry 1, Table 5) suggesting that the hydrogen transfer to the imine is also a fast process.

3 | CONCLUSIONS

To conclude, we have synthesized and characterized four new half-sandwich complexes of Ru(II), Rh(III), and Ir(III) with the deprotonated form of the proligand 5-(pyridin-2-ylmethylene)hydantoin. In addition, we have demonstrated that this kind of *N^N′* anionic ligand, never used previously in homogeneous catalysis, leads to iridium(III) derivatives (chloride and hydride) which are active catalysts in the one-pot monobenzylation or dibenzylation of amines using benzyl alcohol as the alkylating agent. It has been verified that the chlorido precatalyst [Cp*IrCl(pyhy)] is stable in the presence of air under catalytic conditions. The optimized conditions for this protocol included the use of K_2CO_3 and TFE as base and solvent, respectively. In general, with primary or secondary amines, good to excellent yields were obtained for the monoalkylated amines although the presence of electron-withdrawing or ortho-substituted groups in anilines or steric hindrance in secondary amines reduced the conversions. The selectivity towards the monoalkylated amines was good in general and it was improved using short reaction times reaching to selectivity values between 90% and 100% even with quantitative conversion in one case. It was verified that the presence of donor groups in anilines, longer reaction times or higher alcohol:amine ratios increased the ratio of the dialkylated amines. Different NMR and catalytic experiments gave information about the mechanism of the process that includes the detection of some iridium intermediates and of the aldehyde formed by dehydrogenation of the alcohol. It is demonstrated that the condensation of benzaldehyde and *p*-toluidine in TFE even at room temperature is a fast process that takes place in the absence of catalyst. The potential release of H_2 from the reaction between the Ir—H species and protons under open vessel conditions seems to be deleterious for the alkylation reaction. However, under pressure, this unproductive process is in some way reversed or hampered. The demonstration of the activity in BH of the iridium compounds with the anionic pyhy ligand opens the way to the formation of new complexes with modified ligands including substituents either in the pyridine ring or in the NH group that could lead to complexes with improved catalytic performance.

4 | EXPERIMENTAL SECTION

4.1 | General methods

All manipulations were carried out under an atmosphere of dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents and degassed before use. Elemental analyses were performed with a Thermo Quest FlashEA 1112 microanalyzer and IR spectra on a Shimadzu IRPrestige-21 IR spectrometer equipped with a Pike Technologies ATR. The FAB^+ mass spectrometry measurements were made with a Thermo MAT95XP mass spectrophotometer with magnetic sector. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Varian Innova 500, Varian Unity 300, and Varian Gemini 400. Chemical shifts (ppm) are relative to TMS (^1H, ^{13}C NMR). The atom numbering is reflected in Scheme 2. Coupling constants (J) are in Hertz. ^1H–^1H COSY spectra: standard pulse sequence with an acquisition time of 0.214 s, pulse width of 10 ms, relaxation delay of 1 s, 16 scans, 512 increments. For ^1H–^{13}C g–HMBC and g–HMQC spectra, the standard Varian pulse sequences were used (VNMR 6.1 C software). The spectra were acquired using 16,096 (^1H) and 25,133.5 Hz (^{13}C) widths; 16 transits of 2048 data points were collected for each of the 256 increments. NOESY spectra were acquired using 8000 Hz width, and 16 transits of 2048 data points were collected for each of the 256 increments, with a pulse time of 1 s and mixing time of 1 s. In the NMR analysis, s, d, and bs denote singlet, doublet and broad signal, respectively. Unless otherwise stated, the $^{13}C\{^1H\}$ NMR signals are singlets. For mass spectrometry, a GC-EI Varian 3800 GC coupled with a Varian Triple Quad 1200L detector was used; 20 and 70 eV were tested as power source for the electronic ionization of the sample, and representative changes in the analyzed signals and in the ionization level of the sample were not observed. The experimental conditions for GC were as follows: column factor IV (30 m × 0.25 mm × 0.25 μm). Helium flux: 1 mL min^{-1}; injector. All the ammonium chloride salts resulting as reaction products were vacuum dried for several hours prior to being weighed and analyzed. The metal complexes $[(p\text{-cymene})RuCl_2]_2$,[64] $[Cp^*RhCl_2]_2$,[65] $[Cp^*IrCl_2]_2$,[65] and 5-(pyridin-2-ylmethylene)hydantoin[46] were prepared following published procedures.

4.2 | X-ray crystallography

A summary of crystal data collection and refinement parameters for all compounds are given in Table S1. The single crystals for **[1]·CHCl$_3$**, **[2]·0.5 EtOH**, and **[4]** were

mounted on a glass fiber and used for data collection on a Bruker X8 APEX II CCD-based diffractometer equipped with a graphite monochromated MoKα radiation source (λ = 0.71073 Å). The data reduction was performed with the APEX3 software,[66] and an absorption correction was performed with the program SADABS.[67] Crystal structures were solved by direct methods using the SIR97 program[68] and refined by full-matrix least squares on F^2 including all reflections using anisotropic displacement parameters by means of the WINGX crystallographic package.[69,70] All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model except H(1a) of **[4]**, which was taken from the Fourier difference map and refined freely. CCDC 1,868,126–1,868,128, respectively, for complexes **[1]**, **[2]**, and **[4]** contain the supplementary crystallographic data for this paper.

4.3 | Synthesis of the new complexes

4.3.1 | Synthesis of [Cp*IrCl(pyhy)] ([1])

To a solution of Hpyhy (491.9 mg, 2.6 mmol) in 40 mL of acetone:ethanol (40:60) mixture, $[Cp^*IrCl_2]_2$ (868.4 mg, 1.09 mmol) was added, and the reaction mixture was stirred for 24 h at room temperature. The yellow precipitate obtained was filtered and washed with an acetone: ethanol mixture (40:60) (2 × 10 mL) and dried in vacuum. **[1]** was obtained as a yellow solid (1100 mg, 92%). Anal. Calcd. for $C_{19}H_{21}ClIrN_3O_2$: C, 41.41; H, 3.84; N, 7.63. Found: C, 41.56; H, 3.79; N, 7.61. The ^{1}H and $^{13}C\{^1H\}$ NMR spectra in DMSO-d_6 reflect the presence of two compounds: **[1]** and a DMSO adduct. When tetrabutylammonium chloride is added, only the resonances of **[1]** are observed. ^{1}H NMR of **[1]** (400 MHz, DMSO-d_6, 25°C): δ = 10.83 (s, 1*H*, NH_{Hyd}), 8.61 (dd, ^{3}J(H,H) = 5.9 Hz, ^{4}J(H,H) = 1.4 Hz, 1*H*, $H^{6'}{}_{Pyr}$), 7.89 (td, ^{3}J(H,H) = 7.6 Hz, ^{4}J(H,H) = 1.5 Hz, 1*H*, $H^{4'}{}_{Pyr}$), 7.48 (dd, ^{3}J(H,H) = 7.8 Hz, ^{4}J(H,H) = 1.4 Hz, 1*H*, $H^{3'}{}_{Pyr}$), 7.20 (ddd, ^{3}J(H,H) = 7.4 Hz, ^{3}J(H,H) = 5.9 Hz, ^{4}J(H,H) = 1.5 Hz, 1*H*, $H^{5'}{}_{Pyr}$), 5.91 (s, 1*H*, =CH^6), 1.42 (s, 15*H*, 5 × Me_{Cp^*}) ppm. ^{1}H NMR of the DMSO adduct of **[1]** (400 MHz, DMSO-d_6, 25°C): δ = 11.31 (s, 1*H*, N*H*), 8.71 (dd, ^{3}J(H,H) = 6.0 Hz, ^{4}J(H,H) = 1.5 Hz, 1*H*, $H^{6'}{}_{Pyr}$), 8.14 (td, ^{3}J(H,H) = 7.8 Hz, ^{4}J(H,H) = 1.6 Hz, 1*H*, $H^{4'}{}_{Pyr}$), 7.82 (dd, ^{3}J(H,H) = 7.9 Hz, ^{4}J(H,H) = 1.2 Hz, 1*H*, $H^{3'}{}_{Pyr}$), 7.41 (ddd, ^{3}J(H,H) = 7.6 Hz, ^{3}J(H,H) = 5.7 Hz, ^{4}J(H,H) = 1.6 Hz, 1*H*, $H^{5'}{}_{Pyr}$), 6.22 (s, 1*H*, =CH^6), 1.55 (s, 15*H*, 5 × Me_{Cp^*}) ppm. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 8.70 (dd, ^{3}J(H,H) = 5.8 Hz, ^{4}J(H,H) = 1.3 Hz, 1*H*, $H^{6'}{}_{Pyr}$), 7.68 (td, ^{3}J(H,H) = 7.6 Hz, ^{4}J(H,H) = 1.8 Hz, 1*H*, $H^{4'}{}_{Pyr}$), 7.42 (s, 1*H*, NH_{Hyd}), 7.16 (dd, ^{3}J(H,H) = 8.0 Hz, ^{4}J(H,H) = 1.5 Hz, 1*H*, $H^{3'}{}_{Pyr}$), 7.03 (ddd, ^{3}J(H,H) = 7.7 Hz, ^{3}J(H,H) = 5.8 Hz, ^{4}J(H,H) = 1.4 Hz, 1*H*, $H^{5'}{}_{Pyr}$), 5.97 (s, 1*H*, =CH^6), 1.54 (s, 15*H*, 5 × Me_{Cp^*}) ppm. ^{1}H NMR (500 MHz, TFE-d_3, 25°C): δ = 8.73 (d, ^{3}J(H,H) = 5.5 Hz, 1*H*, $H^{6'}{}_{Pyr}$), 7.80 (t, ^{3}J(H,H) = 6.8 Hz, 1*H*, $H^{4'}{}_{Pyr}$), 7.37 (d, ^{3}J(H,H) = 8.4 Hz, 1*H*, $H^{3'}{}_{Pyr}$), 7.21 (t, ^{3}J(H,H) = 6.8 Hz, 1*H*, $H^{5'}{}_{Pyr}$), 6.20 (s, 1*H*, =CH^6), 1.50 (s, 15*H*, 5 × Me_{Cp^*}) ppm. $^{13}C\{^1H\}$ NMR of **[1]** (101 MHz, DMSO-d_6, 25°C): δ = 167.75 ($C^5{}_{Hyd}$), 159.76 ($C^4{}_{Hyd}$), 157.53 ($C^{6'}{}_{Pyr}$), 151.90 ($C^{2'}{}_{Pyr}$), 140.41 ($C^2{}_{Hyd}$), 138.15 ($C^{4'}{}_{Pyr}$), 125.06 ($C^{3'}{}_{Pyr}$), 123.30 ($C^{5'}{}_{Pyr}$), 100.08 (=CH—), 86.70 ($C_{q\text{-}Cp^*}$), 9.18 (Me_{Cp^*}) ppm. $^{13}C\{^1H\}$ NMR, DMSO adduct of **[1]** (101 MHz, DMSO-d_6, 25°C): δ = 166.89 ($C^5{}_{Hyd}$), 161.25 ($C^4{}_{Hyd}$), 157.70 ($C^{6'}{}_{Pyr}$), 151.79 ($C^{2'}{}_{Pyr}$), 140.69 ($C^2{}_{Hyd}$ or $C^{4'}{}_{Pyr}$), 139.46 ($C^2{}_{Hyd}$ or $C^{4'}{}_{Pyr}$), 127.86 ($C^{3'}{}_{Pyr}$ or $C^{5'}{}_{Pyr}$), 125.34 ($C^{3'}{}_{Pyr}$ or $C^{5'}{}_{Pyr}$), 102.36 (=C^6H—), 95.29 ($C_{q\text{-}Cp^*}$), 9.13 (Me_{Cp^*}) ppm. IR (ν_{max}/cm^{-1}): 3159, (br), ν(N—H); 3061, (br), ν(CH_{Cp^*}); 1695, (s), ν(C(4)=O(4)); 1624, (s), ν(C(2)=O(2)); 1595, (s), ν(C=C); 1340, (vs), δ(N—H); 1122, (s), ν(C—N—C); 763, (s), δ(C—H)ip; 640, (s), δ(C—H)oop. MS (FAB$^+$): *m/z* (assign., rel. int. %): 516 [(M − Cl)$^+$, 100.0], 363 [(M − L)$^+$,7.2]. Crystals suitable for X-ray diffraction were obtained by slow evaporation from a saturated chloroform solution of **[4]** at 20°C. **[1]** is soluble in TFE, DMSO, $CDCl_3$, and MeOH. It is insoluble in toluene, water, and acetone.

4.3.2 | Synthesis of [(*p*-cym)RuCl(pyhy)] ([2])

To a solution of Hpyhy (491.9 mg, 2.6 mmol) in a CH_2Cl_2:ethanol (40:60) mixture (40 mL), $[(p\text{-cym})RuCl_2]_2$ (667.5 mg, 1.09 mmol) was added, and the reaction mixture was stirred for 24 h at room temperature. A yellow precipitate was formed in a red solution. This solution was filtered and evaporated in vacuum to 10 ml to precipitate a solid that was filtered, washed with CH_2Cl_2 (5 mL), and vacuum dried. A red solid was obtained (636.7 mg, 64%). Anal. Calcd. for $C_{19}H_{20}ClN_3O_2Ru$: C, 49.53; H, 4.39; N, 9.16. Found: C, 49.55; H, 4.32; N, 9.12. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 9.16 (dd, ^{3}J(H,H) = 5.9 Hz, ^{4}J(H,H) = 1.4 Hz, 1*H*, $H^{6'}{}_{Pyr}$), 8.17 (bs, 1*H*, NH_{Hyd}), 7.61 (ddd, ^{3}J(H,H) = 7.7 Hz, ^{4}J(H,H) = 1.5 Hz, 1*H*, $H^{4'}{}_{Pyr}$), 7.10 (dd, ^{3}J(H,H) = 7.9 Hz, ^{4}J(H,H) = 1.3 Hz, 1*H*, $H^{3'}{}_{Pyr}$), 7.00 (ddd, ^{3}J(H,H) = 7.4 Hz, ^{3}J(H,H) = 5.9 Hz, ^{4}J(H,H) = 1.5 Hz, 1*H*, $H^{5'}{}_{Pyr}$), 5.97 (s, 1*H*, =CH^6), 5.69 (d, J = 6.0 Hz, 1*H*, H(*p*-cym)), 5.60 (d, J = 6.0 Hz, 1*H*, H(*p*-cym)), 5.37 (d, J = 6.0 Hz, 1*H*, H(*p*-cym)), 5.29 (d, J = 6.0 Hz, 1*H*, H(*p*-cym)), 2.56 (sept, 1*H*, CH^{iPr}(*p*-cym)), 2.33 (s, 3*H*, Me^{Tol}(*p*-cym)), 1.18 (d, J = 6.9 Hz, 3*H*, Me^{iPr}(*p*-cym), 1.13

(d, J = 6.9 Hz, 3*H*, Me^{iPr}(*p*-cym) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25°C): δ = 167.1 (C^5_{Hyd}), 161.5 (C^4_{Hyd}), 158.4 ($C^{6'}_{Pyr}$), 154.0 ($C^{2'}_{Pyr}$), 141.8 (C^2_{Hyd}), 137.5 ($C^{4'}_{Pyr}$), 125.6 ($C^{3'}_{Pyr}$), 121.2 ($C^{5'}_{Pyr}$), 103.0 ($C^{1''}$ or $C^{4''}$(*p*-cym)), 101.8 ($C^{1''}$ or $C^{4''}$(*p*-cym)), 100.7 (=C^6H—), 85.4 (CH(*p*-cym)), 85.0 (CH(*p*-cym)), 84.7(CH(*p*-cym)), 81.7 (CH(*p*-cym)), 31.0 (CH^{iPr}(*p*-cym)), 22.5 (Me^{iPr}(*p*-cym)), 19.0 (Me^{Tol}(*p*-cym)) ppm. IR (ν_{max}/cm^{-1}): 3366 (br), ν(N—H); 3128, ν(C=C—H); 3074, ν(C_{arom}—H); 2962, ν(C—H); 1709 (s), ν(C(4)=O(4)); 1630 (s), ν(C(2)=O(2)); 1599, ν(C=C) (s); 1333(s), δ(N—H); 1130 (s), ν(C—N—C); 786, δ(C—H)ip; 650, δ(C—H)oop. MS (FAB^+): *m/z* (assign., rel. int. %): 459 [$(M)^+$, 18.4], 424 [$(M - Cl)^+$, 100.0]. Crystals suitable for X-ray diffraction were obtained by a saturated chloroform solution of **[2]** at 20°C. **[2]** is soluble in $CHCl_3$ and insoluble in CH_2Cl_2.

4.3.3 | Synthesis of [Cp*RhCl(pyhy)] ([3])

To a solution of Hpyhy (141.6 mg, 0.75 mmol) in 8 mL of CH_2Cl_2:ethanol (40:60) mixture, $[Cp^*RhCl_2]_2$ (193.2, 0.31 mmol) was added, and the reaction mixture was stirred for 24 h at room temperature. The yellow precipitate obtained was filtered and washed with aCH_2Cl_2:ethanol mixture (40:60) (1 mL) and dried in vacuum. A yellow solid was obtained (192 mg, 99%). Anal. Calcd. for $C_{19}H_{21}ClN_3O_2Rh$: C, 49.42; H, 4.58; N, 9.10. Found: C, 49.24; H, 4.55; N, 9.03. ^1H NMR (500 MHz, $CDCl_3$, 25°C): δ = 8.77 (d, $^3J(H,H)$ = 5.5 Hz, 1*H*, $H^{6'}_{Pyr}$), 7.68 (dd, $^3J(H,H)$ = 7.0 Hz, $^4J(H,H)$ = 1.5 Hz, 1*H*, $H^{4'}_{Pyr}$), 7.40 (s, 1*H*, NH_{Hyd}), 7.20 (d, $^3J(H,H)$ = 7.8 Hz, 1*H*, $H^{3'}_{Pyr}$), 7.14 (dd, $^3J(H,H)$ = 5.5 Hz, $^3J(H,H)$ = 1.5 Hz, 1*H*, $H^{5'}_{Pyr}$), 6.07 (s, 1*H*, =CH^6), 1.55 (s, 15*H*, 5 × Me_{Cp^*}) ppm. This product was not soluble enough in conventional NMR solvents to obtain a $^{13}C\{^1H\}$ NMR spectrum and in DMSO-d_6 indications of a transformation were observed. IR (ν_{max}/cm^{-1}): 3149, (br), ν(N—H); 3096, (br), ν(CH_{Cp^*}); 1744, (s), ν(C(4)=O(4)); 1690, (s), ν(C(2)=O(2)); 1620, (s), ν(C=C); 1340, (s), δ(N—H); 1124, (s), ν(C—N—C); 775, (s), δ(C—H)ip; 648, (s), δ(C—H)oop. MS (FAB^+): *m/z* (assign., rel. int. %): 461 [$(M)^+$, 11.6], 426 [$(M - Cl)^+$, 100.0]. **[3]** is slightly soluble in $CHCl_3$ and CH_3CN. It is insoluble in toluene and acetone. It is soluble but instable in TFE and DMSO.

4.3.4 | Synthesis of [Cp*IrH(pyhy)] ([4])

To a solution of complex **[1]** (30 mg, 0.0544 mmol) in a DMSO:H_2O (1:5) mixture (6 ml), HCOONa (34 mg, 0.50 mmol) was added, and the reaction mixture was stirred for 24 h at room temperature. It was evaporated in vacuum up to 3 ml to precipitate the product and washed with H_2O (3 × 1 mL) affording a pure product as a red solid (11.7 mg, 42%). Anal. Calcd. for $C_{19}H_{22}IrN_3O_2$: C, 44.18; H, 4.29; N, 8.13. Found: C, 43.87; H, 4.34; N, 8.14. ^1H NMR (500 MHz, acetone-d_6, 25°C): δ = 10.42 (br, 1*H*, NH_{Hyd}), 8.71 (dd, $^3J(H,H)$ = 6.0 Hz, $^4J(H,H)$ = 1.1 Hz, 1*H*, $H^{6'}_{Pyr}$), 7.78 (td, $^3J(H,H)$ = 7.6 Hz, $^4J(H,H)$ = 1.6 Hz, 1*H*, $H^{4'}_{Pyr}$), 7.30 (d, $^3J(H,H)$ = 7.8 Hz, 1*H*, $H^{3'}_{Pyr}$), 6.89 (ddd, $^3J(H,H)$ = 7.4 Hz, $^3J(H,H)$ = 6.0 Hz, $^4J(H,H)$ = 1.4 Hz, 1*H*, $H^{5'}_{Pyr}$), 5.83 (s, 1*H*, =CH^6), 1.65 (s, 15*H*, 5 × Me_{Cp^*}), −9.60 (s, 1*H*, Ir—H) ppm. ^1H NMR (500 MHz, $CDCl_3$, 25°C): δ = 8.70 (dd, $^3J(H,H)$ = 5.7 Hz, $^4J(H,H)$ = 1.4 Hz, 1*H*, $H^{6'}_{Pyr}$), 7.60 (td, $^3J(H,H)$ = 8.0 Hz, $^4J(H,H)$ = 1.7 Hz, 1*H*, $H^{4'}_{Pyr}$), 7.52 (br, 1*H*, NH_{Hyd}), 7.06 (dd, $^3J(H,H)$ = 8.2 Hz, $^4J(H,H)$ = 1.1 Hz, 1*H*, $H^{3'}_{Pyr}$), 6.74 (ddd, $^3J(H,H)$ = 7.2 Hz, $^3J(H,H)$ = 5.7 Hz, $^4J(H,H)$ = 1.4 Hz, 1*H*, $H^{5'}_{Pyr}$), 5.96 (s, 1*H*, =CH^6), 1.68 (s, 15*H*, 5 × Me_{Cp^*}), −9.48 (s, 1*H*, Ir—H) ppm. ^1H NMR (500 MHz, TFE-d_3, 25°C): δ = 8.82 (br, 1*H*, $H^{6'}_{Pyr}$), 7.74 (t, $^3J(H,H)$ = 8.6 Hz, 1*H*, $H^{4'}_{Pyr}$), 7.27 (dd, $^3J(H,H)$ = 7.0 Hz, 1*H*, $H^{3'}_{Pyr}$), 6.94 (br, 1*H*, $H^{5'}_{Pyr}$), 6.24 (s, 1*H*, =CH^6), 1.62 (s, 15*H*, 5 × Me_{Cp^*}), −9.48 ppm (s, 1*H*, Ir—H) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6:acetone-d_6 1:2, 25°C): δ = 167.82 (C^5_{Hyd}), 160.33 (C^4_{Hyd}), 159.55 ($C^{6'}_{Pyr}$), 153.86 ($C^{2'}_{Pyr}$), 142.69 (C^2_{Hyd}), 136.81 ($C^{4'}_{Pyr}$), 124.75 ($C^{3'}_{Pyr}$), 121.81 ($C^{5'}_{Pyr}$), 100.35 (=C^6H), 87.01($C_{q\text{-}Cp^*}$), 9.76 (Me_{Cp^*}) ppm. IR (ν_{max}/cm^{-1}): 3318 (br) ν(N—H); 2095, (m), ν(Ir—H(3)); 1726, (s), ν(C(4)=O(4)); 1697, (s), ν(C(2)=O(2)). MS (FAB^+): *m/z* (assign., rel. int. %): 516 [$(M)^+$, 100.0]. Crystals suitable for X-ray diffraction were obtained by slow diffusion of **[1]**, dissolved in dimethylformamide, in a water solution of HCOONa at 20°C. **[4]** is soluble in acetone, TFE, and $CDCl_3$. It is insoluble in MeOH and water.

4.4 | General procedure for the catalytic *N*-alkylation of aniline with benzyl alcohol

All reactions were carried out under nitrogen, using Schlenk–vacuum line techniques in a multireactor carousel 12 plus reaction Station™ Radleys that allow set 12 assays simultaneously. Every pressure tube was loaded with the properly salt, **[1]** (2.8 mg, 5 μmol), the necessary benzyl alcohol, the aniline derivative, and TFE (2.6 mL). The resulting mixtures were degassed and flushed with nitrogen and stirred at 100°C for 7 h. The reactions were stopped on ice and aliquots placed in an NMR tube containing $CDCl_3$ (0.3 mL) after solvent was removed under vacuum. Conversions were determined by ^1H

NMR. Calculations for the conversion values are referred to the reactant in default, that is, benzyl alcohol in Entries 1 and 2 and aniline in Entry 3. Moreover, the aldehyde formed was not taken into account in the calculation of the conversion percentage.

4.5 | General procedure to determine isolated yields

After cooling to room temperature, the reaction solution was adjusted with hydrochloric acid (3 M) to pH = 2 and stirred for 10 min. The solution was then adjusted to pH 10 with saturated NaOH solution and extracted with CH_2Cl_2 (3 × 10 mL). The set of organic layers were washed with brine (20 mL) and dried over Mg_2SO_4. The organic solvent was removed under reduced pressure. The residue was dissolved in diethyl ether and 0.7 ml of a HCl solution 0.8 M in diethyl ether were added to form a precipitate that was filtered in a funnel with fritted disc (pore size: 3 μm).

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AUTHOR CONTRIBUTIONS

Margarita Ruiz-Castañeda: Investigation; methodology. **Ana Rodríguez:** Methodology. **Ahmed Aboo:** Methodology. **Blanca R. Manzano:** Funding acquisition; supervision. **Gustavo Espino:** Conceptualization; formal analysis. **Jianliang Xiao:** Conceptualization; formal analysis; funding acquisition; supervision. **Felix A. Jalon:** Conceptualization; formal analysis; funding acquisition; supervision.

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article.

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