

PAPER



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Mono and dimetallic pyrene-imidazolylidene complexes of iridium(III) for the deuteration of organic substrates and the C–C coupling of alcohols†

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Three different Ir(III) complexes with pyrene-containing N-heterocyclic carbenes have been prepared and characterized. Two complexes contain a monodentate pyrene-imidazolylidene ligand, and have the formulae $[\text{IrCp}^*\text{Cl}_2(\text{pyrene-NHC})]$ and $[\text{IrCp}^*(\text{CO}_3)(\text{pyrene-NHC})]$. The third complex is a dimetallic complex with a pyrene-di-imidazolylidene bridging ligand, with the formula $[\text{IrCp}^*(\text{CO}_3)_2(\mu\text{-pyrene-di-NHC})]$. The catalytic activity of the three complexes was tested in the H/D exchange of organic substrates, and in the β -alkylation of 1-phenylethanol with primary alcohols. In the deuteration of organic substrates, the carbonate complexes are active even in the absence of additives. The dimetallic complex is the most active one in the catalytic coupling of alcohols, a result that may be interpreted as a consequence of the cooperativity between the two metal centres.

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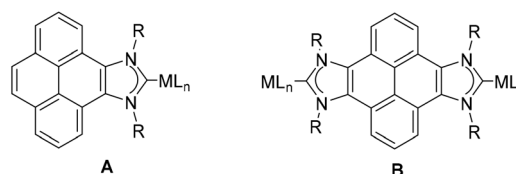
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Introduction

Despite great efforts to create high levels of mechanistic understanding, the development of highly effective homogeneous catalysts remains mainly empirical. Catalytic cooperativity by the action of multiple metal centres¹ or the use of multifunctional ligands^{1h,2} continue to be used by many researchers as valuable strategies for the improvement of catalytic performance. Some authors are starting to merge the benefits produced by the parallel development of homogeneous catalysis and supramolecular catalysis, and for this reason supramolecular catalysis is an expanding discipline that can stimulate the development of innovative catalysts with properties that differ from already known classical catalytic systems.³ We have been recently exploring the design of multitopic N-heterocyclic carbene ligands (NHCs) for the design of multimetallic catalysts.¹ⁱ In the course of our research, we observed that the presence of two metal fragments attached to a unique ligand framework produced clear benefits on the catalytic properties of the complex compared to their related monometallic analogues.¹ⁱ We also observed that some metal complexes with NHC

ligands decorated with polyaromatic functionalities displayed better catalytic activities than other systems lacking these polyaromatic fragments.⁴ The presence of rigid polyaromatic systems plays a role in magnifying the π -stacking interactions between aromatic substrates and our catalysts, and this clearly adds an effect to the catalytic performance of the catalysts. Among the NHC ligands with polyaromatic backbones that we used, those decorated with pyrene allowed us to obtain a series of dimetallic⁵ and monometallic^{5a,6} complexes whose catalytic activities were studied (Scheme 1).

Some years ago, we developed a series of $[\text{IrCp}^*\text{Cl}_2(\text{NHC})]$ catalysts that we used in a number of catalytic transformations.⁷ Based on this experience, we now describe a new set of mono- and di-iridium complexes bearing the pyrene-containing ligands depicted in Scheme 1. These new complexes were studied in two well-known C–H activation processes, the selective deuteration of C–H bonds in organic molecules, and the β -alkylation of secondary alcohols with primary alcohols. Our initial aim was to study if the presence of the two metals in the dimetallic complex may provide any benefits compared



Scheme 1

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† Electronic supplementary information (ESI) available: NMR spectra of new compounds, CIF file of the molecular structures of complexes 3, 4, and 6 and a summary of the crystal data, data collection and refinement details. CCDC 1495410, 1495411 and 1495845. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt02942f

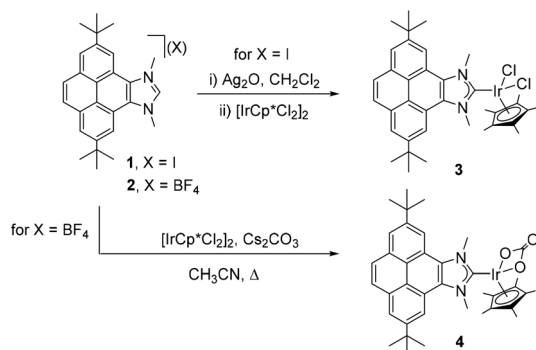
to those with only one metal, and also to determine if the presence of the pyrene fragment may add any further benefits compared to other well-known related systems.

Results and discussion

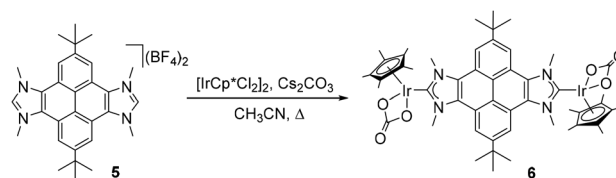
Scheme 2 displays the synthetic procedure to prepare the pyrene-imidazolylidene Ir(III) complexes **3** and **4**. Complex **3**, was obtained by the sequential reaction of pyrene-imidazolium iodide **1**, with silver oxide, to generate the related pyrene-NHC–Ag complex, which was then used to transmetallate the NHC ligand to $[\text{IrCp}^*\text{Cl}_2]_2$. The resulting bright yellow complex with the general formula $[\text{IrCp}^*\text{Cl}_2(\text{NHC})]$ was isolated in 85% yield. The coordination of the NHC ligand can also be performed by reacting pyrene-imidazolium tetrafluoroborate **2**, with $[\text{IrCp}^*\text{Cl}_2]_2$ in the presence of Cs_2CO_3 , although in this case the resulting Ir(III) product (**4**) contained the coordinated pyrene-imidazolylidene ligand along with a coordinated carbonate. Complex **4** was obtained in 92% yield.

Complexes **3** and **4** were characterized by NMR spectroscopy and mass spectrometry, and both complexes gave satisfactory elemental analyses. The ^1H NMR spectra of **3** and **4** were consistent with their twofold symmetries, and clearly showed well-defined signals due to the cyclopentadienyl and pyrene-based ligands. The ^{13}C NMR spectrum of **3** displayed the diagnostic signal due to the carbene carbon at 167.8 ppm. The ^{13}C NMR spectrum of **4** showed the signal due to the metallated carbene carbon at 167.9 ppm, and a signal at 172.2 ppm, which we attributed to the carbon of the carbonate ligand. The presence of the carbonate ligand was also confirmed by the absorption of a single strong infrared band at 1610 cm^{-1} , similar to the spectral data shown for other $[\text{IrCp}^*(\text{CO}_3)(\text{NHC})]$ complexes.⁸

The dimetallic complex **6** was obtained from the reaction of pyrene-bisimidazolium tetrafluoroborate salt **5** with $[\text{IrCp}^*\text{Cl}_2]_2$ in the presence of Cs_2CO_3 in refluxing acetonitrile (Scheme 3). The product was obtained in 77% yield. The ^1H NMR spectrum of the complex was consistent with the pseudo- C_{2v} symmetry of the complex. The ^{13}C NMR spectrum showed the signal due to the carbene carbon atoms at 167.7 ppm, and the resonance due to the carbon of the carbonate ligands at 174.3 ppm. The



Scheme 2



Scheme 3

infrared spectrum of **6** revealed a strong band at 1613 cm^{-1} , which confirmed the presence of the coordinated carbonate ligand. We also tried to obtain the tetrachloride Ir(III) complex with the pyrene-bisimidazolylidene ligand by using the same synthetic protocol that we used for the preparation of **3**, but under these reaction conditions we did not manage to coordinate the ligand. We also tried to coordinate the ligand by using non-carbonate bases (potassium *tert*-butoxide or potassium bis(trimethylsilyl)amide), but all our attempts were unsuccessful.

The molecular structures of complexes **3**, **4** and **6** were confirmed by single crystal X-ray diffraction studies.

The molecular structure of complex **3** (Fig. 1) consists of a pyrene-imidazolylidene ligand bound to a Cp^*IrCl_2 fragment. The distance between the iridium centre and the centroid of the Cp^* ligand is 1.810 \AA , and the Ir–C(carbene) bond distance is $2.060(5)\text{ \AA}$. The angle established between the plane formed by the iridium atom and the two chloride ligands, and the plane of the imidazolylidene is 106.63° . Interestingly, the pyrene-imidazolylidene ligand deviates from planarity, as observed by the angle between the plane of the imidazole ring and the plane formed by the tetracyclic pyrene moiety, which is 9.31° . The geometry of the molecule can be compared to that of complex **4**, which is displayed in Fig. 2. Complex **4** is formed by a pyrene-imidazolylidene ligand bound to a $\text{Cp}^*\text{Ir}(\text{CO}_3)$ fragment, and the Ir–C(carbene) bond distance is $2.038(5)\text{ \AA}$, thus very similar to the related distance in **3**. The molecule has a mirror plane that is defined by the C(1)–Ir(1) axis and is

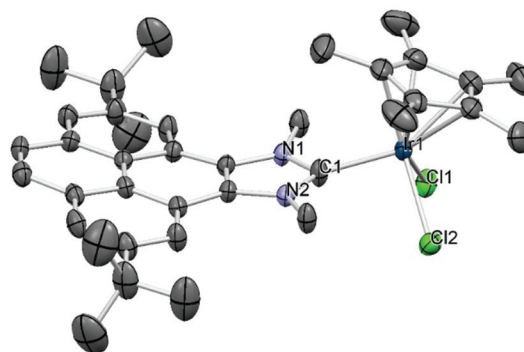


Fig. 1 Molecular diagram of complex **3**. Ellipsoids at 50% probability. Hydrogen atoms and solvent (hexane) are omitted for clarity. Selected bond distances (\AA) and angles ($^\circ$): Ir(1)–C(1) $2.060(5)$, Ir(1)–Cl(1) $2.4274(14)$, Ir(1)–Cl(2) $2.4031(14)$, C(1)–N(1) $1.351(7)$, C(1)–N(2) $1.361(7)$, C(1)–Ir(1)–Cl(1) $92.86(18)$, Cl(2)–Ir(1)–Cl(1) $85.76(5)$.

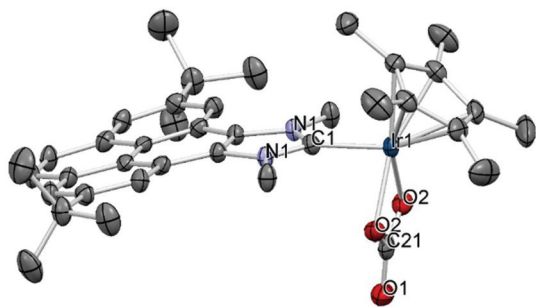


Fig. 2 Molecular diagram of complex **4**. Ellipsoids at 50% probability. Hydrogen atoms and solvent (chloroform) are omitted for clarity. Selected bond distances (Å) and angles (°): Ir(1)–C(1) 2.038(5), Ir(1)–O(2) 2.100(3), C(1)–N(1) 1.354(4), C(21)–O(2) 1.324(4), O(1)–C(21) 1.220(7), C(1)–Ir(1)–O(2) 84.90(14), O(2)–Ir(1)–O(2) 62.16(16), O(2)–C(21)–O(2) 109.7(5).

perpendicular to the pyrene-based ligand. The bite angle of the chelate carbonate ligand is 109.7(5)°. The angle between the plane formed by the iridium atom and the carbonate ligand and the imidazolyliene ring is 83.28°. For this complex, the deviation between the plane of the imidazole ring and the pyrene fragment is 7.78°.

The molecular structure of complex **6** is displayed in Fig. 3. The molecule contains a pyrene-bisimidazolyliene ligand connecting two iridium fragments, which complete their coordination spheres with a Cp* ligand and a carbonate. The molecule has a twofold symmetry axis defined by the two central carbon atoms of the two *tert*-butyl groups. The metal-to-metal distance is 13.23 Å, similar to those established by the same ligand bound to other metals.⁵ The two metal fragments are in a relative *anti* orientation. The iridium–C(carbene) bond distance is 2.0286(4) Å, very similar to that found for the monometallic analogue **4**. The angle between the plane of the imidazolyliene ligand and the plane formed by the carbonate iridium atom and the carbonate ligand is 85.61°. Contrary to what we observed for complexes **3** and **4**, the polycyclic dicarbene in complex **6** is essentially coplanar.

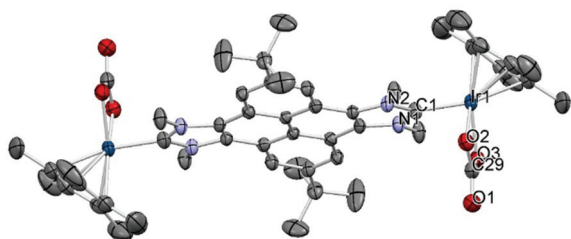


Fig. 3 Molecular diagram of complex **6**. Ellipsoids at 50% probability. Hydrogen atoms and solvent (3 molecules of chloroform) are omitted for clarity. Selected bond distances (Å) and angles (°): Ir(1)–C(1) 2.0286(4), Ir(1)–O(2) 2.096(3), Ir(1)–O(3) 2.113(3), C(1)–N(1) 1.358(6), C(1)–N(2) 1.364(5), O(3)–C(29) 1.301(4), O(2)–C(29) 1.328(6), C(1)–Ir(1)–O(2) 85.65(16), O(2)–C(29)–O(3) 11.7(4), O(2)–Ir(1)–O(3) 62.25(13).

As previously published, the σ -donating properties of the pyrene-imidazolyliene ligand in **3** and **4**,^{6b} and the pyrene-bisimidazolyliene ligand in **6**,^{5b} are quasi-identical. The determination of the molecular structures of **4** and **6** also provided us with a very useful tool for evaluating the steric bulk of both ligands. By using the corresponding CIF files, we estimated the percent of buried volumes (%V) of the two ligands in **4** and **6** as 27.2 and 27.3%, respectively.⁹ These results indicate that both mono- and dicarbene ligands have virtually the same steric and electronic properties, and therefore, they should provide similar reactivity patterns for their related metal complexes.

Because we have been recently interested in determining if dimetallic complexes connected by polyconjugated linkers may benefit from the catalytic cooperativity between the two metal fragments,¹ⁱ and also in studying the supramolecular effects in catalysis produced by the use of catalysts with polyaromatic ligands,⁴ we thought that the comparison of the catalytic behaviour of **3**, **4** and **6** should be worthy of evaluation.

We first studied the deuteration of several organic fragments by H/D exchange. This type of study is an easy method to determine the potential of a catalyst to cleave and form C–H bonds,¹⁰ and we have already provided some effective catalysts for this type of process.^{7g,11} Table 1 shows the extent of deuteration incorporation on a series of substrates, using **3**, **4** and **6** as catalysts. The reactions were carried out in a sealed tube in CD₃OD at 100 °C, using 2 mol% catalyst loading based on

Table 1 H/D exchange using complexes **3**, **4** and **6**^a

Entry	Substrate	Cat.	%D _{inc.}	Time (h)
1	Acetophenone	3 ^b	<i>o</i> : 20; <i>m</i> : 17; <i>p</i> : 25, CH ₃ > 99	3
2			<i>o</i> : 51; <i>m</i> : 45; <i>p</i> : 46, CH ₃ > 99	12
3			<i>o</i> : 43; <i>m</i> : 41; <i>p</i> : 39, CH ₃ > 99	3
4		4	<i>o</i> : 53; <i>m</i> : 52; <i>p</i> : 51, CH ₃ > 99	12
5			<i>o</i> : 0; <i>m</i> : 0; <i>p</i> : 0, CH ₃ > 99	3
6			<i>o</i> : 33; <i>m</i> : 33; <i>p</i> : 30, CH ₃ > 99	12
7	Styrene	3 ^b	<i>o</i> : 0; <i>m</i> , <i>p</i> : 0, vinyl > 99	3
8			<i>o</i> : 0; <i>m</i> , <i>p</i> : 0, vinyl > 99	12
9			<i>o</i> : 0, <i>m</i> , <i>p</i> : 0, vinyl: 0	3
10		4	<i>o</i> : 0, <i>m</i> , <i>p</i> : 0, vinyl: 16	12
11			<i>o</i> : 0, <i>m</i> , <i>p</i> : 0, vinyl: 20	3
12			<i>o</i> : 0, <i>m</i> , <i>p</i> : 0, vinyl: 29	12
13	THF	3 ^b	α -CH ₂ : 24, β -CH ₂ : 28	12
14			α -CH ₂ : 86, β -CH ₂ : 87	12
15			α -CH ₂ : 85, β -CH ₂ : 85	12
16	Benzo[<i>h</i>]quinoline	3 ^b	H9: 20	5
17			H9: 50	5
18			H9: 80	5
19	<i>trans</i> -Stilbene	3 ^b	Alkene: 67	12
20			Alkene: 81	24
21			Alkene: 9	12
22		4	Alkene: 24	24
23			Alkene: 20	12
24			Alkene: 21	24

^a General reaction conditions: substrate (0.22 mmol), catalyst **3**, **4** (4.4×10^{-3} mmol) or **6** (2.2×10^{-3} mmol) in CD₃OD (2 mL), 100 °C. Reaction progress measured by ¹H NMR spectroscopy. ^b With addition of AgOTf (8.8×10^{-3} mmol).

the metal. In the case of catalyst **3**, addition of AgOTf was needed as a chloride scavenger. For catalysts **4** and **6** no additives were needed. The results show that the activity of catalyst **3** is comparable, although slightly lower, than that of our previously reported catalyst [IrCp*Cl₂(InBu)] (InBu = *N,N'*-di-*n*-butyl-imidazolylidene),^{7g} probably due to the lower electron-donating strength of the pyrene-NHC ligand. Catalyst **3** shows higher activity than complexes **4** and **6** in the deuteration of the olefinic protons of styrene and *trans*-stilbene. All three catalysts are very active in the deuteration of the protons of the methyl group of acetophenone, and **3** and **4** were also active in the deuteration of the aromatic ring, as observed by a level of deuteration of about 50% in all aromatic positions. In the deuteration of tetrahydrofuran, both **4** and the dimetallic complex **6**, are highly active, as observed by the incorporation of 85% deuterium on both methylene groups of the molecule (entries 14 and 15), while **3** is only capable of incorporating less than 30% of deuterium (entry 13). For the deuteration of the C(9)-H proton of benzo[*h*]quinoline, **3** is less active than the other two complexes, with **6** being the most active one (yields up to 80%, entry 18). With these results in hand, it is important to point out that both carbonate complexes **4** and **6** do not need to be activated by any external additive, as in the case of **3** or other related Ir(III)-NHC-based catalysts.^{7g} It is also noteworthy mentioning that all three catalysts are significantly more active than the phosphine complex [IrCp*Cl(PMe₃)],¹² whose activities in the same type of substrates were explored by us.^{7g}

We were also interested in evaluating how the differences in the nature of the ligands may have some influence on the outcome of the catalytic behaviour of these three complexes in the β -alkylation of secondary alcohols with primary alcohols.¹³ The reactions were carried out in 0.5 mL of toluene, at 100 °C, using 0.5 mol% catalyst loading in the case of the monometallic complexes, and 0.25 mol% for the case of the dimetallic complex **6**. This ensured that all three different catalysts were used with the same concentration of iridium. We decided to couple 1-phenylethanol with a series of benzyl alcohols (benzyl alcohol, 3-chlorobenzyl alcohol and 4-chlorobenzyl alcohols) and *n*-butanol, using an equimolecular amount of both alcohols. As can be seen from the results shown in Table 2, all three catalysts were active in the reaction, but the carbonate complexes **4** and **6** were more active than the complex bearing two chloride ligands (**3**). Among the two carbonate complexes, the dimetallic complex **6** was significantly more active than its monometallic analogue (**4**). This result is particularly interesting, especially if we take into account that the ligand in both complexes displays virtually identical stereoelectronic properties. It is important to recall that the catalytic experiments were carried out with the same concentration of Ir, therefore suggesting that in the case of the dimetallic complex **6**, the two iridium fragments act independently in the reaction and, furthermore, the dimetallic nature of the complex affords an extra benefit compared to the monometallic complex. Regardless of the nature of such a benefit, we believe that this behaviour may be assigned to the catalytic cooperativity between the two metal fragments.

Table 2 β -Alkylation of 1-phenylethanol with primary alcohols using complexes **3**, **4** and **6**^a

Entry	R	Catalyst	Yield ^b	Conversion ^b
1	Ph	3	40	40
2		4	40	40
3		6	90	90
4	3-Cl(C ₆ H ₄)	3	35	35
5		4	48	48
6		6	75	75
7	4-Cl(C ₆ H ₄)	3	51	52
8		4	57	57
9		6	67	67
10	<i>n</i> Pr	3	41 ^c	42 ^c
11		4	45 ^c	45 ^c
12		6	61 ^c	61 ^c

^a General reaction conditions: 1-phenylethanol (1 mmol), primary alcohol (1 mmol), KOH (1 mmol) and catalyst (0.5 mol%, based on the metal) in dry toluene (0.5 mL), 100 °C. ^b Yields and conversions determined by GC using anisole (1 mmol) as an internal standard. ^c Reaction time: 24 h.

Conclusions

In summary, we have prepared three different complexes with two pyrene-based imidazolylidene ligands. Two of the complexes contain a mono-NHC ligand, and the third one is a dimetallic complex with a bridging pyrene-di-NHC ligand. All three complexes were spectroscopically and crystallographically characterized. The catalytic properties of these complexes were tested in the H/D exchange of a series of organic substrates and in the β -alkylation of 1-phenylethanol with primary alcohols. The results of the deuteration of organic substrates indicate that the dichloride monometallic complex **3** is more active than the carbonate complexes **4** and **6** in the deuteration of *trans*-stilbene, although it needs the addition of AgOTf for showing activity. The two carbonate complexes **4** and **6** are active even in the absence of additives. The activity of these two complexes in the deuteration of THF is remarkable, and the dimetallic complex **6** is very active in the mono-deuteration of benzo[*h*]quinoline.

The catalytic activity shown by all three complexes in the β -alkylation of 1-phenylethanol may be more conclusive, in the sense that the dimetallic complex **6** is unambiguously the most active catalyst for all the combinations of alcohols used. This result may be interpreted as a consequence of some kind of cooperativity between the metals in the dimetallic unit, a conclusion that can be extracted by comparison of the activity shown by **6**, with the activity exhibited by **4**, a monometallic complex with a ligand with virtually identical stereoelectronic properties.

Experimental

General procedures

Pyrene-based imidazolium salts **1**^{6b} and **5**^{5b} were prepared according to literature methods. All other reagents were used

as received from commercial suppliers. NMR spectra were recorded on a Bruker 400 MHz, using CDCl₃ as solvent. Electrospray ionization mass spectra (ESI-MS) were recorded on a Micromass Quattro LC instrument; nitrogen was employed as drying and nebulizing gas. Elemental analyses were carried out on a TruSpec Micro Series. Fourier Transform Infrared (FT-IR) spectra were recorded on a Bruker EQUINOX 55 spectrometer with a spectral window of 4000–600 cm⁻¹. Liquid samples were placed between KBr windows.

Synthesis of 2. Under aerobic conditions, a solution of **1** (200 mg, 0.39 mmol) in anhydrous CH₂Cl₂ (20 mL) was treated with [Me₃O](BF₄) (63.7 mg, 0.43 mmol). The mixture was stirred at room temperature for 1 h. The solution was concentrated and Et₂O (5 mL) was added to induce precipitation. The yellow solid so formed was filtered and washed with diethyl ether (5 mL). Yield: 134.0 mg, 73%. ¹H NMR (400 MHz, CDCl₃): δ = 9.58 (s, 1H, NCHN), 8.77 (s, 2H, CH_{pyr}), 8.35 (s, 2H, CH_{pyr}), 8.12 (s, 2H, CH_{pyr}), 4.75 (s, 6H, NCH₃), 1.62 (s, 18H, C(CH₃)₃). ¹⁹F NMR (376.5 MHz, CDCl₃): δ = -151.3. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 150.2 (C_{q pyr}), 141.9 (NCHN), 132.1 (C_{q pyr}), 128.7 (CH_{pyr}), 127.9 (C_{q pyr}), 124.9 (CH_{pyr}), 122.3 (C_{q pyr}), 120.2 (C_{q pyr}), 116.5 (CH_{pyr}), 38.8 (NCH₃), 35.7 (C(CH₃)₃), 31.9 (C(CH₃)₃). Electrospray MS (20 V, *m/z*): 383.4 [M - BF₄]⁺. Electrospray MS negative mode (20 V, *m/z*): 87.1 [BF₄]⁻. Anal. Calcd for C₂₇H₃₁N₂BF₄ (470.25): C, 68.90; H, 6.64; N, 5.95. Found C, 68.93; H, 6.64; N, 5.96.

Synthesis of complex 3. A suspension of **1** (150 mg, 0.3 mmol) and Ag₂O (35.1 mg, 0.15 mmol) in dry dichloromethane (15 mL) was stirred at room temperature for 2 h without light. Then, [IrCp*Cl₂]₂ (119.4 mg, 0.15 mmol) was added and the resulting mixture was stirred at room temperature overnight. The suspension was filtered through a pad of Celite and the solvent was removed under vacuum. The desired solid was isolated as a bright yellow crystalline solid. Yield: 200 mg, 85%. ¹H NMR (500 MHz, CDCl₃): δ = 8.83 (d, *J*_{H-H} = 3 Hz, 2H, CH_{pyr}), 8.13 (d, *J*_{H-H} = 3 Hz, 2H, CH_{pyr}), 7.99 (s, 2H, CH_{pyr}), 4.78 (s, 6H, NCH₃), 1.67 (s, 15H, C₅(CH₃)₅), 1.53 (s, 18H, C(CH₃)₃). ¹³C{¹H} NMR: δ = 167.8 (Ir-C_{carbene}), 148.8 (C_{q pyr}), 131.7 (C_{q pyr}), 129.9 (C_{q pyr}), 128.2 (CH_{pyr}), 122.4 (CH_{pyr}), 121.3 (C_{q pyr}), 121.1 (C_{q pyr}), 116.9 (CH_{pyr}), 89.2 (C₅(CH₃)₅), 41.9 (NCH₃), 35.4 (C(CH₃)₃), 31.8 (C(CH₃)₃), 9.3 (C₅(CH₃)₅). Electrospray MS (20 V, *m/z*): 745.3 [M - Cl]⁺. Anal. Calcd for C₃₇H₄₅IrN₂Cl₂ (780.90): C, 56.91; H, 5.81; N, 3.59. Found: C, 56.26; H, 5.70; N, 3.29.

Synthesis of complex 4. A mixture of imidazolium salt **2** (100 mg, 0.21 mmol), [IrCp*Cl₂]₂ (84.7 mg, 0.11 mmol), and Cs₂CO₃ (349.8 mg, 1.06 mmol) in dry acetonitrile (20 mL) was stirred at reflux overnight. After removal of the volatiles, the crude solid was suspended in CH₂Cl₂ and filtered through a pad of Celite to remove insoluble salts. The solvent was removed nearly to dryness and diethyl ether (5 mL) was added, yielding a brown solid that was collected by filtration. Yield: 149.6 mg, 92%. IR (CH₂Cl₂): 1610.3 cm⁻¹ (ν_{C=O}). ¹H NMR (400 MHz, CDCl₃): δ = 8.86 (s, 2H, CH_{pyr}), 8.22 (s, 2H, CH_{pyr}), 8.07 (s, 2H, CH_{pyr}), 4.67 (s, 6H, NCH₃), 1.85 (s, 15H, C₅(CH₃)₅), 1.61 (s, 18H, C(CH₃)₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ =

172.2 (CO₃), 167.9 (Ir-C_{carbene}), 149.0 (C_{q pyr}), 131.9 (C_{q pyr}), 129.4 (C_{q pyr}), 128.4 (CH_{pyr}), 122.8 (CH_{pyr}), 121.5 (C_{q pyr}), 121.3 (C_{q pyr}), 116.6 (CH_{pyr}), 86.5 (C₅(CH₃)₅), 40.2 (NCH₃), 35.6 (C(CH₃)₃), 32.0 (C(CH₃)₃), 9.7 (C₅(CH₃)₅). Electrospray MS (20 V, *m/z*): 745.3 [M - CO₃ + Cl]⁺. Anal. Calcd for C₃₈H₄₅N₂O₃Ir (770.30): C, 59.19; H, 5.89; N, 3.63. Found: C, 59.41; H, 5.78; N, 3.52.

Synthesis of complex 6. A mixture of **5** (100 mg, 0.16 mmol), [IrCp*Cl₂]₂ (127.2 mg, 0.16 mmol) and Cs₂CO₃ (420.4 mg, 1.28 mmol) in dry acetonitrile (20 mL) was stirred at reflux overnight. Once at room temperature, the solvent was removed under vacuum. The crude solid was dissolved in CH₂Cl₂ and filtered through a pad of Celite in order to remove insoluble salts. After removal of the volatiles, complex **6** was precipitated in Et₂O as a beige solid. Yield: 150.2 mg, 77%. IR (CH₂Cl₂): 1613.2 (ν_{C=O}) cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ = 8.94 (s, 4H, CH_{pyr}), 4.70 (s, 12H, NCH₃), 1.88 ppm (s, 30H, C₅(CH₃)₅), 1.64 (s, 18H, C(CH₃)₃). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 174.3 (CO₃), 167.7 (Ir-C_{carbene}), 149.2 (C_{q pyr}), 129.3 (C_{q pyr}), 121.9 (C_{q pyr}), 119.4 (C_{q pyr}), 116.5 (CH_{pyr}), 86.6 (C₅(CH₃)₅), 40.4 (NCH₃), 35.7 (C(CH₃)₃), 31.7 (C(CH₃)₃), 9.6 (C₅(CH₃)₅). Electrospray MS (20 V, *m/z*): 582.3 [M - CO₃]²⁺. Anal. Calcd for C₅₂H₆₄N₄O₆Ir₂ (1225.54): C, 50.88; H, 5.26; N, 4.57. Found: C, 50.75; H, 5.37; N, 4.52.

Catalytic experiments

General procedure for the deuteration in CD₃OD. A mixture of the substrate (0.22 mmol) and catalyst (2 mol% based on the metal) in CD₃OD was heated at 100 °C in a Schlenk tube fitted with a Teflon cap. AgOTf (8.8 × 10⁻³ mmol) was added to the solution in the reactions performed by catalyst **3**. At the desired reaction times, aliquots of 50 μL were extracted from the reaction vessel and added to an NMR tube with 0.6 mL of CDCl₃. Deuteration levels were monitored by ¹H NMR using a standard capillary consisting of a solution of ferrocene in CDCl₃ (0.025 mg μL⁻¹).

General procedure for the β-alkylation of secondary alcohols with primary alcohols. The corresponding catalyst (0.5 mol% based on the metal) and KOH (1 mmol) were placed in a Schlenk tube fitted with a Teflon cap. The tube was then degassed and filled with nitrogen three times. Dry toluene (0.5 mL), 1-phenylethanol (1 mmol) and the corresponding primary alcohol (1 mmol) were subsequently added, and the mixture was stirred at 100 °C for 8 h. Yields and conversions were determined by GC analyses using anisole (1 mmol) as an internal standard.

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