Iridium(I) Complexes with Hemilabile *N*-Heterocyclic Carbenes: Efficient and Versatile Transfer Hydrogenation Catalysts.

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Abstract

A series of neutral and cationic rhodium and iridium(I) complexes based on hemilabile O-donor and N-donor functionalized NHC ligands having methoxy, dimethylamino and pyridine as donor functions have been synthesized. The hemilabile fragment is coordinated to the iridium center in the cationic complexes $[Ir(cod)(MeImR)]^+$ (R = pyridin-2-ylmethyl, 3-dimethylaminopropyl) but remains uncoordinated in the complexes [MBr(cod)(MeImR)], $[M(NCCH_3)(cod)(MeImR)]^+$ (M = Rh, Ir; R = 2-methoxyethyl and 2-methoxybenzyl) and [IrX(cod)(MeImR)] (X = Br, R = pyridin-2-ylmethyl; X = Cl, R = 2-dimethylaminoethyl, 3-dimethylaminopropyl). The structure of [IrBr(cod)(MeIm(2-methoxybenzyl))] has been determined by X-ray diffraction. The iridium complexes are efficient precatalysts for the transfer hydrogenation of cyclohexanone in 2-propanol/KOH. A comparative study has shown that cationic complexes are more efficient than the neutral, and also that complexes having O-functionalized NHC ligands provide much more active systems that the corresponding N-functionalized ligands with TOFs up to 4600 h^{-1}. The complexes $[Ir(NCCH_3)(cod)(MeImR)]^+$ (R = 2-methoxyethyl and 2-methoxybenzyl) have been successfully applied to the reduction of several unsaturated substrates as ketones, aldehydes, α,β-unsaturated ketones and imines. The investigation of the reaction mechanism by NMR and MS has allowed the identification of relevant alkoxo intermediates [Ir(OR)(cod)(MeImR)] and the unsaturated hydride species [IrH(cod)(MeImR)]. The β-H elimination in the alkoxo complex [Ir(O*i*Pr)(cod)(MeIm(2-methoxybenzyl))] leading to hydrido species has been studied by DFT calculations. An interaction between the β-H on the alkoxo ligand and the oxygen atom of the methoxy fragment of the NHC ligand, which results in a net destabilization of the alkoxo intermediate by a free energy of +1.0 kcal/mol, has been identified. This destabilization facilitates the β-H elimination step in the catalytic process and could explain the positive effect of the methoxy group of the functionalized NHC ligands on the catalytic activity.

Introduction

N-Heterocyclic carbenes (NHCs) have attracted much interest as ligands for homogeneous catalysis. NHC ligands have proved to be efficient ancillary ligands because of their strong coordination ability that imparts to the metal complexes an adequate balance between stability and activity, and their tunable character that allows for the control of the sterical and electronic properties on the metal center.[1] These ligands are easily accessible from imidazolium salts[2] and a large number of NHCs precursors: simple, functionalized, bis- or tris-NHC, with different topologies have been prepared that, in combination with well established coordination methodologies, has led to the preparation of a range of transition metal complexes with different geometries and potential catalytic applications.[3]

Hemilabile ligands can play a dual role in a catalyst since they can easily enable coordinative sites at the metal center and, at the same time, protect the coordination sites by a dynamic "on and off" chelating effect.[4] Although the most studied hemilabile ligands are functionalized phosphines containing O and N donor sets, functionalized NHC ligands can also exhibit hemilability[5] and represent a good alternative for the preparation of new compounds with application in homogenous catalysis.[6] In this context, a number of complexes containing functionalized NHCs ligands in which a labile donor function (ether, thioether, alkoxy, pyridine, amine, amido, etc.) is attached to a strongly bonded carbene moiety have been synthesized. In fact, the hemilabile character of several O, N or S-functionalized NHCs ligands have been demonstrated[7] and in some cases, an active role of the hemilabile fragment has been identified in several catalytic processes.[8]

Transfer hydrogenation is a powerful strategy for the reduction of unsaturated C=O and C=N compounds and a range of alcohols and amines are accessible by transfer hydrogenation under mild reaction conditions.[9] Transfer hydrogenation is a valuable and atom efficient reaction with evident

economic and environmental advantages, as it avoids the use of dihydrogen pressure or hazardous reducing agents by using nontoxic hydrogen donors as alcohols, formic acid, hydrazine, etc.[10]

The most active and selective hydrogen transfer catalysts, particularly in enantioselective reductions, are ruthenium, rhodium and iridium complexes. In particular, it is noteworthy to mention Noyori's ruthenium catalysts with chiral tetradentate ligands, and those arene complexes based on chiral *β*-aminoalcohol or *N*-tosyl-ethylenediamine ligands operating through a bifunctional metal-ligand mechanism.[11] Efficient rhodium and iridium hydrogen transfer catalysts are mainly based both on phosphine and N-donor ligands,[10] although NHC ligands have also been applied to the design of hydrogen transfer catalysts. It has been found that, in contrast to phosphine based catalysts, iridium-NHC complexes are more active than their Rh-NHC analogues and accordingly, a number of highly efficient iridium catalyst have been recently reported.[12] In particular, air-stable iridium(III) bis-carbene complexes were found to be active catalysts for transfer hydrogenation of ketones, aldehydes and imines at low catalyst loading.[13]

Our interest is focused on the synthesis and catalytic applications of transition metal complexes containing heteroditopic ligands of hemilabile character that incorporate strong electron donors, such as phosphines and carbenes. We have recently reported the application of cationic rhodium(I) complexes containing flexible hemilabile functionalized phosphine ligands of the type $Ph_2P(CH_2)_nZ$ (Z = OR, NR_2, SR)[14] for the stereoregular polymerization of phenylacetylene,[8a] and the regioselective anti-Markovnikov oxidative amination of olefins.[15] Mechanistic studies led to discover the active role of the hemilabile fragment of the ligands in the initiation process of the polymerization reactions leading to high average molecular weights.[8a,16] In addition, remarkable catalyst efficiency in hydroamination was observed with those catalytic systems based on the ligand (3-ethoxypropyl)diphenylphosphine, $Ph_2P(CH_2)_3OEt$.

It has come to our attention that the catalyst efficiency in transfer hydrogenation of ketones by sterically demanding unsymmetrically *N,N'*-substituted benzimidazol-2-ylidene iridium(I)

[IrBr(cod)(NHC)] complexes was improved when using NHC ligands having a 2-methoxyethyl substituent.[17] In same way, highly effective iridium(I) hydrogen transfer catalysts based on unsymmetrical 2-methoxyphenyl donor-functionalized expanded ring NHCs have been recently reported.[18] It becomes evident that the presence of a hemilabile fragment on the catalyst structure has a considerable impact on hydrogen transfer catalytic activity. Although a possible hemilabile chelating effect at the metal center for the stabilization of coordinatively unsaturated catalytic intermediates could account for the enhanced activity, the promotion of directing effects with the substrate or the stabilization of polar catalytic intermediates through weak interactions can not be ruled out.

In order to investigate further this hemilabile effect we report herein on the synthesis and catalytic activity in hydrogen transfer of a series of rhodium and iridium complexes containing hemilabile O- and N- donor functionalized NHCs ligands. Interestingly, a relationship between the donor function, the flexibility of the backbone and the length of the linker in the ligands, with the catalytic activity has been observed.

Results and Discussion

Synthesis of Precursors for Hemilabile NHC Ligands. The imidazolium salts precursors for selected O- and N-donor functionalized N-heterocyclic carbene ligands were prepared by alkylation of 1-methylimidazole with the corresponding functionalized alkyl bromide or chloride (Chart 1). The imidazolium salts precursors for flexible hemilabile NHC ligands, [MeImH$(CH_2)_2$OMe]Br (**1**)[19] and [MeImH$(CH_2)_n$NHMe$_2$)]Cl_2 (n = 2, **4**; n = 3, **5**),[6a] were prepared by alkylation with 1-bromo-2-methoxyethane and the corresponding chloro-alkyl-dimethylamine hydrochloride derivatives, respectively, following the reported methods. In the same way, [MeImH(pyridin-2-ylmethyl)]Br (**3**), a precursor for a rigid N-functionalized NHC ligand, was prepared using 2-(bromomethyl)pyridine as alkylating reagent.[20] The new salt 1-(2-methoxybenzyl)-3-methyl-1*H*-imidazol-3-ium bromide (**2**)

precursor of a related rigid O-functionalized NHC ligand, was synthesized by alkylation of 1-methylimidazole with 2-methoxybenzyl bromide, prepared by bromination of 2-methoxybenzyl alcohol,[21] in toluene following the procedure described for the *N-tert*-butyl derivative.[22]

[MeImH(2-methoxybenzyl)]Br (**2**) was isolated as a white hygroscopic solid in good yield and characterized by elemental analysis, mass spectrometry (ESI-MS), and ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy. The characteristic downfield shifted resonances of the N*CH*N imidazolium fragment were observed in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra at δ 10.37 and 137.41 ppm, respectively.

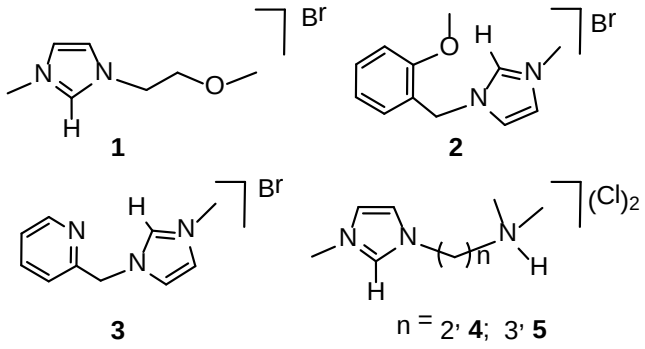


Chart 1. Imidazolium salt precursors for functionalized NHC ligands.

Synthesis of Neutral Iridium(I) and Rhodium(I) Complexes with Functionalized NHC Ligands. The attempts to prepare iridium and rhodium (I) complexes using the free NHC ligands generated *in situ* by deprotonation of the imidazolium salts were unsuccessful, probably due to the acidity of the methylene protons. However, the direct deprotonation of the methoxo ligands in the dinuclear complexes $[\{M(\mu\text{-OMe})(cod)\}_2]$ provide access to neutral mononuclear complexes containing the functionalized NHC ligands. In fact, reaction of the imidazolum salts with 0.5 equiv. of $[\{M(\mu\text{-OMe})(cod)\}_2]$ (M = Rh, Ir) in tetrahydrofuran gave orange solutions from which the bromo complexes [MBr(cod)(MeIm$(CH_2)_2$OMe)] (M = Ir, **6**; M = Rh, **8**) and [MBr(cod)(MeIm(2-methoxybenzyl))] (M = Ir, **7**; M = Rh, **9**) were isolated as orange solids in good yield (Chart 2). This methodology is also applicable for the synthesis of [IrBr(cod)(MeIm(pyridin-2-ylmethyl))] (**10**). The

synthesis of iridium complexes [IrCl(cod)(MeIm$(CH_2)_n$$NMe_2$)] (n = 2, **11**; n = 3, **12**) containing dimethylamino-functionalized NHC ligands was carried out in two steps, through the intermediate cyclooctadienedichloroiridate(I) [MeImH$(CH_2)_n$$NMe_2$][$IrCl_2$(cod)] salts, following the same strategy used for the preparation of analogue rhodium compounds.[6a] Reaction of the ammonium-imidazolium salts [MeImH$(CH_2)_n$$NMe_2$]Cl·HCl with [{Ir(μ-OMe)(cod)}$_2$] resulted in the formation of the amino-imidazolium salts [MeImH$(CH_2)_n$$NMe_2$][$IrCl_2$(cod)], which were further deprotonated by using NaH/H_2O to give the corresponding neutral compounds.

The complexes **6**–**12** have been fully characterized by spectroscopic means. In addition, their neutral character was confirmed by conductivity measurements in acetone and the MALDI-TOF mass spectra that showed peaks at *m/z* corresponding to the molecular ion and the cations resulting from the lost of the halide ligand.

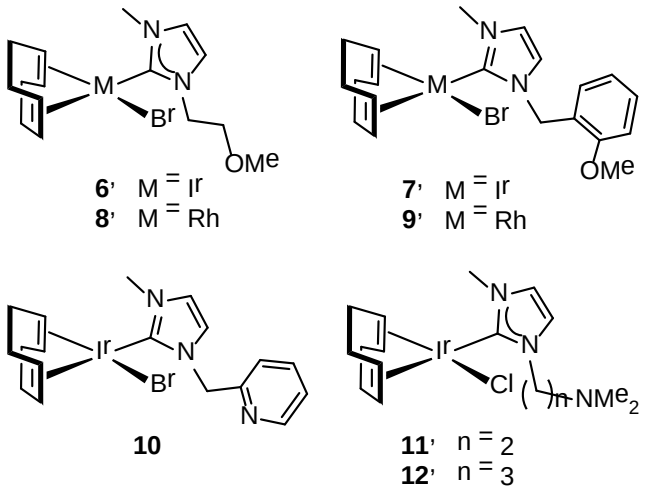


Chart 2. Neutral rhodium and iridium(I) complexes with functionalized NHC ligands.

The ^{1}H NMR spectra of the new iridium/rhodium(I) complexes **6**–**12** showed no low-field signals attributable to the acidic NC*H*N protons, which confirm the deprotonation of the imidazolium fragment. Noteworthy, the coordination of the functionalized-NHC ligands to the metal center becomes evident as low-field resonances around δ 180 ppm (doublet for rhodium complexes **8**-**9**,

$J_{Rh-C} \approx 50$ Hz) were observed in the $^{13}C\{^1H\}$ NMR spectra. Most of the complexes showed two resonances for the vinylic protons of the cod ligand in the ^1H NMR spectra at $\delta \approx 4.5$ and ≈ 3.0 ppm (complex **8** exhibits four resonances), the upfield resonance corresponding to the =CH protons *trans* to the NHC ligand. This effect has also been observed in Ir(I)-cod-phosphine complexes[23] although the chemical shift difference between the vinylic protons is smaller than in related Ir(I)/Rh(I)-cod-NHC complexes.[12e, 24] However, the $^{13}C\{^1H\}$ NMR spectra of the complexes featured four resonances for the olefinic carbons of the cod ligand which is indicative of the lack of an effective symmetry plane in the molecules, probably as a result of the hindered rotation about the carbene-metal bond enforced by the presence of the sidearm in the hemilabile NHC ligands *cis* to large halide and cod ligands. As a consequence, the methylenic protons of the sidearm of NHC ligands were found to be diastereotopic and two distinct resonances for the =CH protons and carbons of the imidazole fragment were observed in the NMR of the complexes.

In order to get detailed information on the structural parameters in these complexes, the X-ray determination of the molecular structure of [IrBr(cod)(MeIm(2-methoxybenzyl))] (**7**) was carried out. The molecular structure of **7** and the more significant bond distances and angles are shown in Figure 1. The coordination geometry around the iridium center,- formed by the coordination to the metal of the two olefinic bonds of the cyclooctadiene ligand, the carbon atom of the NHC ligand and the bromide atom,- is slightly distorted square-planar, as evidenced by the *trans* bond angles Br–Ir–C(17)/C(18) 178.72(12) and C(1)–Ir(1)–C(13)/C(14) 176.11(18)º. The most remarkable structural feature involves the different olefinic bond distances observed (Ir–M(1) 2.072(5), C(13)–C(14) 1.376(6) Å *versus* Ir–M(2) 1.980(4), C(17)–C(18) 1.409(6) Å, M(1) and M(2) represent the midpoints of the olefinic bonds C(13)-C(14) and C(17)-C(18), respectively), most likely as a clear consequence of the high structural *trans* effect of the NHC ligand.

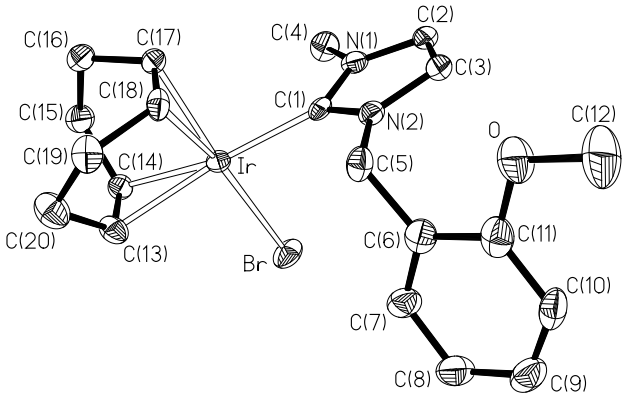


Figure 1. Molecular structure of complex [IrBr(cod)(MeIm(2-methoxybenzyl))] (**7**) (Hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (º): Ir–Br 2.4904(6), Ir–C(1) 2.035(4), Ir–C(13) 2.192(4), Ir–C(17) 2.105(4), Ir–C(14) 2.174(4), Ir–C(18) 2.098(4), N(1)–C(1) 1.357(5), N(2)–C(1) 1.351(5), N(1)–C(2) 1.385(6), N(2)–C(3) 1.390(5), N(1)–C(4) 1.452(5), N(2)–C(5) 1.463(5), C(13)–C(14) 1.376(6), C(17)–C(18) 1.409(6), Br–Ir–C(1) 89.03(10), M(1)–Ir–M(2) 87.26(19), Ir–C(1)–N(1) 125.4(3), Ir–C(1)–N(2) 130.4(3), N(1)–C(1) –N(2) 104.2(3).

Synthesis of Cationic Rhodium(I) and Iridium(I) Complexes with Functionalized NHC Ligands. The coordination of the amino/pyridine donor set of the functionalized NHC ligands can be accomplished, between other methods, by abstraction of the halide ligand in the neutral complexes.[25] However, the coordination of the methoxy fragment by abstraction of the bromo ligand in the complexes containing O-functionalized NHC ligands was unsuccessful and the presence of acetonitrile is required for the stabilization of the cationic complexes.

Reaction of the bromo complexes [MBr(cod)(MeIm$(CH_2)_2$OMe)] (**6**, **8**) and [MBr(cod)(MeIm(2-methoxybenzyl))] (**7**, **9**) with $AgBF_4$ in acetone in the presence of 1 equiv. of CH_3CN at room temperature resulted in the precipitation of AgBr and the formation of yellow solutions of the cationic complexes [M($NCCH_3$)(cod)(MeIm$(CH_2)_2$OMe)][BF_4] (M = Ir, **13**; M = Rh, **15**) and [M($NCCH_3$)(cod)(MeIm(2-methoxybenzyl))][BF_4] (M = Ir, **14**; M = Rh, **16**) which were isolated as

microcrystalline yellow solids in good yield (Chart 3). The more convenient synthesis of complexes [Ir(cod)(MeIm(pyridin-2-ylmethyl))][BF_4] (**17**) and [Ir(cod)(MeIm(CH_2)$_3$$NMe_2$)][$BF_4$] (**18**) relies on the NHC transfer from the silver complexes [AgCl(NHC)]$_x$, generated *in situ*, to the cyclooctadiene solvato [Ir(cod)($OCMe_2$)$_2$]$^+$ species containing labile acetone ligands.

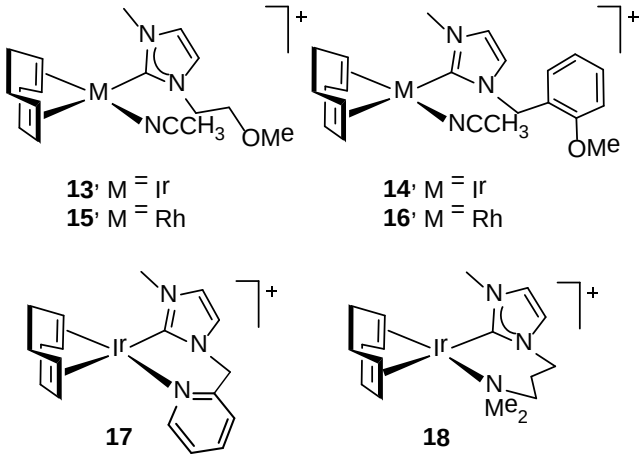
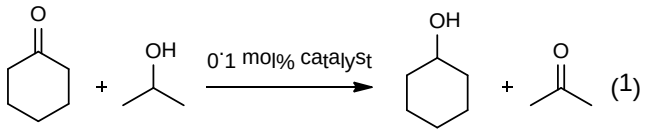


Chart 3. Cationic rhodium and iridium(I) complexes with functionalized NHC ligands.

The conductivity measurements in acetone solutions were in agreement with the presence of 1:1 electrolytes and the MALDI-TOF mass spectra showed the molecular ion (compounds **17** and **18**) or the ion resulting from the lost of the acetonitrile ligand. The presence of an acetonitrile ligand in complexes **13-16**, which was observed at $\delta \approx 2.4$ ppm in the ^{1}H and at $\delta \approx 130$ and 3 ppm in the ^{13}C{^{1}H} NMR spectra, suggests an uncoordinated methoxy moiety in the complexes. In contrast, no coordinated solvents were observed in the NMR spectra of complexes **17** and **18**, even when the reaction was conducted in the presence of acetonitrile, from which the coordination of the pyridine and dimethyl amino moieties was inferred. On the other hand, the large downfield shift observed for the resonance of the >CH_2 attached to the NHC ring compared to the neutral precursor in the ^{13}C{^{1}H} NMR spectra (*ca.* 9 and 14 ppm, respectively) is a diagnostic for the coordination of the hemilabile fragment in the complexes.[15]

Transfer Hydrogenation Catalysis: Preliminary Screening. The neutral and cationic rhodium and iridium complexes with N- and O-functionalized NHCs have been tested as catalysts for transfer hydrogenation of unsaturated substrates. The reduction of cyclohexanone to cyclohexanol was chosen as model reaction to explore the catalytic performance of the different compounds (Equation 1) and the reaction conditions were optimized using [IrBr(cod)(MeIm(2-methoxybenzyl))] (**7**) as catalyst precursor. 2-Propanol was used as hydrogen source because of its favorable properties, particularly a stable, non toxic solvent with a moderate boiling point. Standard catalyst loading of 0.1 mol % and KOH (0.5 mol %) were routinely used. Other inorganic bases as Cs_2CO_3 or K*t*-BuO were found to provide less active catalytic systems with reaction times over 25% higher for the same level of conversion under the same experimental conditions. On the other hand, although $KN(Si(CH_3)_3)_2$ reduces the reaction time more or less in the same proportion, the cheaper KOH was selected as base because there is more reported data in the literature. The reaction times required to reach conversions over 90% (determined by GC using mesitylene as internal standard) and the average turnover frequencies (TOF) for all the examined catalysts are shown in Table 1. The temperature has a strong influence on the catalyst performance and a sharp decrease in the catalytic activity was observed when the temperature was lowered from 80 to 40 ^oC under the standard conditions using **7** as catalyst precursor (Table 1, entries 2–4).



(1)

The neutral iridium complexes with N-functionalized NHCs **10**-**12** were found to be moderately active in the transfer hydrogenation of cyclohexanone to cyclohexanol with compound [IrCl(cod)(MeIm$(CH_2)_2NMe_2$)] (**11**), having a NHC ligand with a flexible arm, the more active (entries 5-7). It is noteworthy that a notable increase in the catalytic activity was observed with the

corresponding cationic complexes **17** and **18**, having NHC ligands κ^2-C,N coordinated, which exhibited a TOF of *ca.* 240 h^{-1} (entries 10-11).

Table 1. Catalytic Hydrogen Transfer from 2-Propanol to Cyclohexanone with Iridium and Rhodium Complexes having N- and O-functionalized NHC ligands.[a, b]

entry	catalyst		time (min)	conversion(%)	TON	TOF[c]/ h^{-1}
1	M = Ir	**6**	110	90	900	490
2		**7**	72	98	989	824
3		**7**[d]	320	96	961	180
4		**7**[e]	1500	97	972	39
5		**10**	1730	90	904	31
6		**11**	408	94	941	138
7		**12**	1360	91	910	40
8		**13**	35	90	907	1555
9		**14**	12	92	924	4622
10		**17**	220	91	910	248
11		**18**	240	93	934	234
12	M = Rh	**8**[f]	90	98	50	33
13		**9**[f]	180	97	49	16
14		**15**[f]	120	98	50	25
15		**16**[f]	210	98	50	14

[a] Reaction conditions: catalyst/substrate/KOH ratio of 1/1000/5, $[catalyst]_o$ = 1 x 10^{-3} M in 2-propanol at 80 °C. [b] The reactions were monitored by GC using mesitylene as internal standard. [c] Average turnover frequency (mol of product/mol of catalyst per hour) determined at the reaction time. [d] T = 60 ºC. [e] T = 40 ºC. [f] Catalyst/subtract/base ratio of 1/100/5.

The neutral bromo iridium complexes with O-functionalized NHCs, **6** and **7**, are far more active than the related neutral N-functionalized precursors (entries 1 and 2), with compound [IrBr(cod)(MeIm(2-methoxybenzyl))] (**7**), having a NHC with a less flexible arm, the more active with a TOF of 824 h^{-1}. Interestingly, the corresponding cationic complexes having a labile

acetonitrile ligand and methoxy functionalized free arms, $[Ir(NCCH_3)(cod)(MeIm(CH_2)_2OMe)]^+$ (**13**) and $[Ir(NCCH_3)(cod)(MeIm(2\text{-methoxybenzyl}))]^+$ (**14**), were highly efficient catalyst precursors giving TOFs of 1555 and 4622 h^{-1} (entries 8 and 9), respectively. These results points out the superior catalytic performance of cationic complexes and highlights the positive influence of O-functionalized NHC ligands having a donor set with weak coordination ability. In addition, the outstanding catalytic activity of **14**, with a 2-methoxybenzyl substituent, suggests that the flexibility of the functionalized arm of the NHC ligand also influences the catalytic activity.

The related rhodium complexes having *O*-functionalized NHCs were poor catalysts, even using 1 mol % catalyst loading, which is agreement with the general observed trend that, opposite to the phosphine-based catalysts,[10] iridium-carbene complexes are more active in transfer hydrogenation than their rhodium analogues.[26,13c] In sharp contrast with the iridium precursors, the neutral complexes **8** and **9** are slightly more active than the corresponding cationic complexes **15** and **16** (entries 12-15) with the flexible ligands giving a somewhat superior activity.

The catalytic activity exhibited by **13** and **14** is significantly higher than the observed for related iridium(I)/unfunctionalized-NHC complexes, as for example $[Ir(cod)py(ICy)]^+$ (ICy = 1,3-dicyclohexylimidazol-2-ylidene),[12e] that gave a TOF of 300 h^{-1} for the transfer hydrogenation of cyclohexanone at the same catalyst loading, benzannulated-NHC iridium(I) complexes (TOFs from 70 to 250 h^{-1}) or $[Ir(OSiMe_3)(cod)(IMes)]$ (TOF = 125 h^{-1}) transfer hydrogenation catalysts previously reported.[12,17,26] On the other hand, the catalytic activity of both precursors is even higher that the shown by a number of Ir(I) complexes having unsymmetrical 2-methoxyphenyl donor functionalized NHC ligands which exhibited turnover frequencies up to 400 h^{-1} for the transfer hydrogenation of 4-bromoacetophenone.[18]

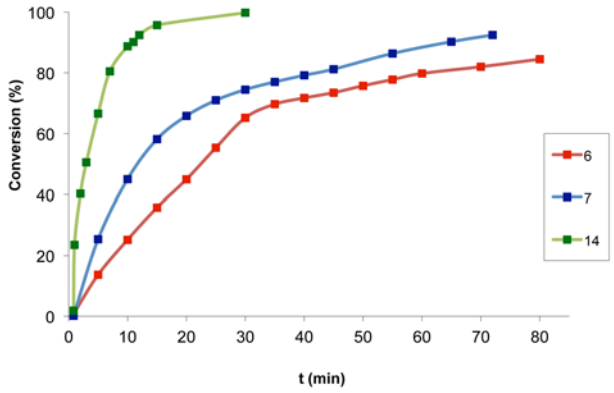


Figure 2. Time dependence of the catalytic transfer hydrogenation of cyclohexanone using 0.1 mol % catalyst (**6**, **7** and **14**) in 2-propanol at 80 ^{o}C with KOH as base.

The transfer hydrogenation of cyclohexanone with the catalyst precursors **6**, **7** and **14**, under standard conditions, was monitored by GC analysis taking 0.1 mL aliquots of the reaction mixture at intervals of 5 min. As can be observed in the conversion *vs* time plots no induction period was detected as cyclohexanone reduction was observed immediately after thermal equilibration of the reactant mixture (Figure 2). Interestingly, quantitative conversion was achieved in less than 15 minutes for compound **14**, the more efficient catalyst precursor in this series. A plot of the ln[cyclohexanone] *vs* time gave a linear fit that is representative of a pseudo-first-order kinetic behavior with the slope of the line corresponding to the observed first-order rate constant k(min^{-1}) (Table 2 and Supporting information). The TOF_{50} (turnover frequency at 50% of conversion) calculated from the kinetic data for this catalyst is as high as 8750 h^{-1}. The catalyst reaction order for the transfer hydrogenation of cyclohexanone with 2-propanol at 80 ^{o}C has been determined using catalyst precursor **14**. Thus, several catalytic runs were carried out at different catalyst concentrations using substrate/catalyst ratios of 1000:1, 2500:1, 5000:1 and 7500:1 in order to determine the corresponding first-order rate constants (Table 2). The representation of ln$k$ *vs* ln[Ir] gave a straight line with slope 1.10 (R^2 = 0.993) in agreement with the expected first-order

dependence on the catalyst indicating no loss of catalytic activity due to catalyst deactivation (see Supporting information).[27]

Table 2. Calculated Rate Constants for the Transfer Hydrogenation of Cyclohexanone with Catalyst **6**, **7** and **14**. [a, b]

Catalyst	Catalyst loading (mol%)	[Ir] (mol L^{-1})	k (min^{-1})	R^2
6	0.1	1.0×10^{-3}	$2.38 \pm 0.06 \times 10^{-2}$	0.991
7	0.1	1.0×10^{-3}	$3.31 \pm 0.08 \times 10^{-2}$	0.994
14	0.1	1.0×10^{-3}	$2.08 \pm 0.02 \times 10^{-1}$	0.999
14	0.04	4.0×10^{-4}	$8.6 \pm 0.2 \times 10^{-2}$	0.996
14	0.02	2.0×10^{-4}	$3.95 \pm 0.08 \times 10^{-2}$	0.999
14	0.013	1.33×10^{-4}	$2.19 \pm 0.06 \times 10^{-2}$	0.993

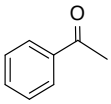
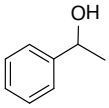
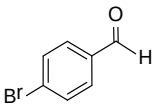
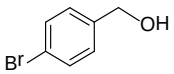
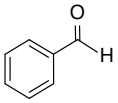
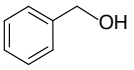
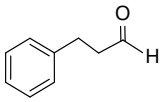
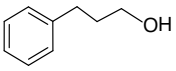
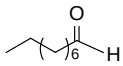
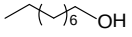
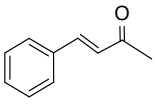
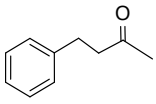
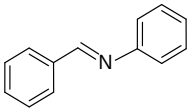
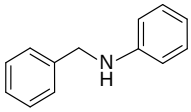
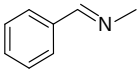
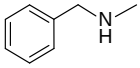
[a] Reaction conditions: cyclohexanone 5 mmol, catalyst/KOH ratio of 1/5 in 2-propanol at 80 °C.
[b] The reactions were monitored by GC using mesitylene as internal standard.

Catalytic Transfer Hydrogenation of Unsaturated Substrates Catalyzed by Iridium Complexes with O-donor functionalized NHC Ligands. Following these initial studies, we have examined the performance of the efficient cationic iridium catalysts containing O-donor functionalized NHC ligands, $[Ir(NCCH_3)(cod)(MeIm(CH_2)_2OMe]^+$ (**13**) and $[Ir(NCCH_3)(cod)(MeIm(2\text{-methoxybenzyl}))]^+$ (**14**), for the transfer hydrogenation of several unsaturated substrates, and the results are summarized in Table 3. In addition, the catalytic activity of the neutral bromo complexes **6** and **7** has been also studied in some cases for comparative purposes.

Acetophenone was efficiently reduced although at moderate rates compared to the observed with the smaller and geometry constrained substrate cyclohexanone (entries 1–3). Interestingly, the same activity trend **7** < **13** < **14** was also observed in the transfer hydrogenation of acetophenone, being the catalyst having a 2-methoxybenzyl functionalized NHC ligand the more active with a TOF of

683 h^{-1}. 4-Bromacetophenone was reduced to 1-(4-bromophenyl)ethanol by **14** at similar rate with no observable dehalogenation due to Ar-X activation (entry 4).

Table 3. Catalytic Transfer Hydrogenation of Unsaturated Substrates Catalyzed by Iridium Complexes with O-donor-functionalized NHC Ligands.[a, b]

entry	substrate	product	catalyst	time (min)	conversion (%)	TOF[c]/ h^{-1}
1			**7**	180	91	303
2			**13**	110	91	497
3			**14**	80	90	683
4			**14**	85	91	645
5[d]			**7**	35	95	1635
6[d]			**14**	25	96	2318
7[d]			**14**	130	95	438
8[d]			**14**	80	96	720[f]
9			**6**	120	94	471
10			**7**	340	45	80
11			**14**	2470	63	15
12			**6**	180	96	320
13			**7**	30	90	1817
14			**14**	50	96	1163
15			**13**	200	94	281
16			**14**	60	93	931
17[e]			**14**	345	93	161

[a] Reaction conditions: catalyst/substrate/KOH ratio of 1/1000/5, $[catalyst]_o$ = 1 x 10^{-3} M in 2-propanol at 80 °C. [b] The reactions were monitored by GC using mesitylene as internal standard. [c] Average turnover frequency (mol of product/mol of catalyst per hour) determined at the reaction time. [d] Catalyst/substrate/KOH ratio of 1:1000:10. [e] Catalyst/substrate/KOH ratio of 1:100:5.

In general, aldehydes are hard to reduce by hydrogen transfer catalysis. The reduction of aldehydes to primary alcohols via transfer hydrogenation can be problematic due to the possible substrate decarbonylation resulting in deactivation of the catalysts. In addition, the CH α to the carbonyl are susceptible to deprotonation under the required basic conditions to give aldol and related products resulting from condensation. In any case, beyond the activity and chemoselectivity issues the higher redox potentials of aldehydes compared to ketones shifts the transfer hydrogenation equilibrium towards the formation of the primary alcohol products. Benzaldehyde was successfully reduced to phenylmethanol by the neutral complex **7** with no detectable aldol product in spite of using a strongest basic media (entry 5). The cationic complex **14** showed an outstanding catalytic activity with a TOF of 2318 h^{-1}, calculated at 96% of conversion, under the same conditions (entry 6). Standard activities for most transition metal catalysts are around a few hundred turnovers per hour, however, the remarkable activity of **14** is of the same order that the exhibited by bis-NHC -Ir(III)[13a] or NHC-hidroxo-Os(II)[28] complexes but lower than for example, [RuCl(CNN)(dppb)] (HCNN = 6-(4′-methylphenyl)-2-pyridylmethylamine; dppb = $Ph_2P(CH_2)_4PPh_2$)[29] or $[Cp^*IrCl(\mu\text{-}Cl)]_2$ in the presence of diamines[30] in aqueous media which show TOFs up to 10^5 h^{-1}.

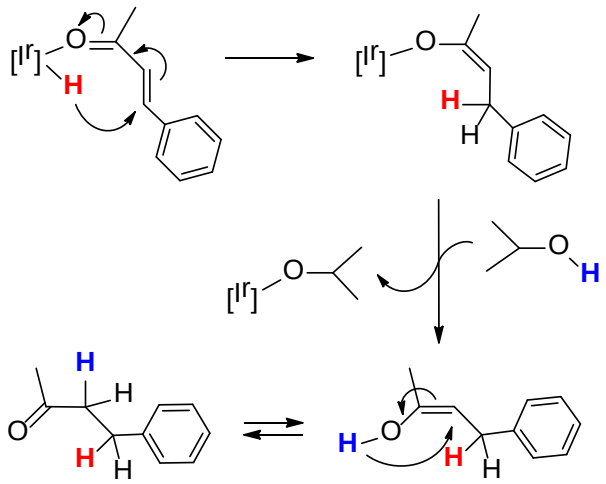
Transfer hydrogenation of aliphatic aldehydes by **14** took place at lower rates. 3-Phenylpropanal, an enolizable aldehyde, was quantitative and selectively reduced to 3-phenylpropan-1-ol in 130 min under the standard conditions with a TOF of 438 h^{-1} (entry 7). In the same line, the reduction of nonanal, a long chain aliphatic aldehyde, by **14** resulted in selective and quantitative formation of nonan-1-ol in *ca*. 85 min (entry 8).

Deactivated olefins were also subjected to transfer hydrogenation under the optimized standard conditions. In contrast with the above described results for carbonyl compounds, the catalytic activity for the transfer hydrogenation of cyclohexene follows the order **14** < **7** < **6** (entries 9–11). Unexpectedly, the neutral bromo complex [IrBr(cod)(MeIm$(CH_2)_2$OMe)] (**6**) having a functionalized NHC ligand with a flexible 2-methoxyethyl substituent exhibited good activity giving a 94% of

conversion in 120 min with a TOF of 471 h^{-1} (entry 9). This result improves those obtained for the transfer hydrogenation of alkenes with related NHC-iridium complexes.[12e]

The selectivity commonly observed in competitive hydrogen transfer reduction of mixtures of alkenes and ketones or aldehydes often implies the selective reduction of C=O over the C=C bonds.[31] However, in the case of α,β-unsaturated ketones the general observed trend in hydrogen transfer catalysis is the preferential reduction of the activated double bond over the C=O reduction.[10] In agreement with this, mixtures of saturated ketone[32,33] and saturated alcohol[12e,13c,34] (major component) are generally obtained although a limited number of transition-metal complexes produce the chemoselective reduction to allylic alcohols.[35]

Transfer hydrogenation of benzylideneacetone by O-functionalized NHC iridium complexes produces 4-phenylbutan-2-one as a result of the selective reduction of the C=C bond (entries 12-14). The more active catalysts were those containing NHC ligands with a rigid 2-methoxybenzyl free arm. Interestingly, the neutral complex **7** is more active than the cationic complex **14** giving a 90 % conversion in 30 min with a TOF of 1817 h^{-1} (entry 13). In order to confirm the selective formation of 4-phenylbutan-2-one, the catalytic reaction was monitored by GC/MS and ^{1}H NMR. Thus, the resonances at δ 7.47 and 6.66 ppm of the benzylideneacetone olefinic protons progressively disappeared and two new multiplets at δ 2.78 and 2.66 ppm, corresponding to the methylenic protons of the 4-phenylbutan-2-one, were observed. In addition, no evidence for the formation of the allylic alcohol product, 4-phenylbutan-2-ol, was obtained even heating at prolonged reaction times as it was observed with other transfer hydrogenation catalysts.[36,37] The mechanism for the selective formation of 4-phenylbutan-2-one probably involves the 1,4-reduction of benzylideneacetone through a keto-enol tautomerization (Scheme 1).[38]



Scheme 1. Hydrogen transfer mechanism for the selective reduction of benzylideneacetone.

Imines are harder to reduce by transfer hydrogenation catalysis than aldehydes and ketones and relatively few examples are known.[39] Imine hydrogenation has several important drawbacks such as the imine nitrogen lone pair coordination to the metal center, that inhibit the η^2–(C=N) coordination required for the insertion into metal–hydride bonds, or the poisoning effect of the resultant amines on the catalyst. However, recent progress in the field has led to the discovery of new catalytic systems with high activities for the hydrogenation of imines.[40]

We have found that cationic complexes **13** and **14** are also efficient catalysts for transfer hydrogenation of imines being **14** considerably more active (entries 15 and 16). Thus, (*E*)-*N*-benzylideneaniline was reduced to *N*-benzylaniline under the standard conditions reaching a 93% of conversion in 1h with a TOF of 931 h^{-1} (entry 16). To the best of our knowledge, the most active catalytic system described is the bis-NHC-Ir(III) complex $[(NHC)CH_2(NHC)IrI_2(OAc)]$,[13b] having triazole NHCs with neopentyl wingtip groups, with a TOF of 6000 h^{-1}. The activity of **14** is similar to the Shvo's catalyst (TOF = 800 h^{-1}),[41] and better than triazole-NHC iridium(I) complexes (TOF = 333 h^{-1}),[42] $[RhI_2(OAc)(n\text{-BuIm}(o\text{-}C_6H_4)Imn\text{-Bu})]$ (TOF of 100 h^{-1})[12d] or $[RuCl_2(PPh_3)(IPr(2,6\text{-py})IPr]$ (TOF = 213 h^{-1}).[43] Additionally, the reduction of (*E*)-*N*-benzylidenemethanamine by **14**, a

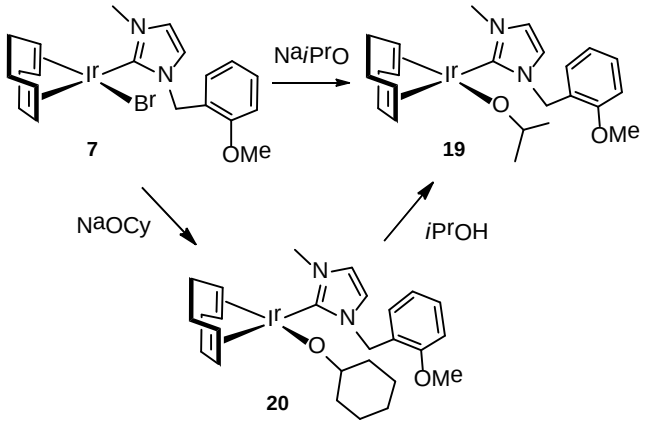
harder substrate, took place a moderate rate even at 1 mol % catalyst loading with a TOF of 161 h^{-1} (entry 17).

Mechanistic Studies. The currently accepted putative mechanism for late-transition-metal-catalyzed hydrogen transfer involves the participation of metal hydride species. H-transfer to the unsaturated substrate can take place through an outer sphere mechanism with the participation of a ligand in the catalytic reaction, metal–ligand bifunctional catalysis,[10,44] or an inner sphere mechanism depending if the substrate coordinates to the metallic center during the catalytic process. In the later case, different mechanisms involving monohydride or dihydride species have been proposed.[45] Studies on the mechanism of metal-catalyzed hydrogen transfer from alcohols to ketones by monitoring the racemization of (*S*)-α-deutero-α-phenylethanol have established that most iridium and rhodium catalysts follow a monohydride pathway.[46] In the same way, Crabtree *et al* have observed the specificity of deuterium incorporation in the hydrogen transfer catalyzed by bis-NHC-Ir(III) complexes using cyclohexanol-d_1, which also support a monohydride mechanism.[13c]

The rhodium and iridium catalysts featuring hemilabile O- and N-donor-functionalized NHC ligands required the presence of a base for catalytic activity and, according with the above observations, most likely follow a monohydride pathway with a neutral hydride/NHC as the catalytically active species. In order to gain insight into the mechanism of hydrogen transfer using O-functionalized-NHC iridium(I) complexes, we have tried to identify the key intermediates likely involved in the process.

The relevant neutral alkoxo intermediates have been identified by NMR. Thus, when a suspension of [IrBr(cod)(MeIm(2-methoxybenzyl))] (**7**) in tetrahydrofurane-d_8 was treated with 1 equiv. of Na*i*PrO a yellow-orange solution of [Ir(O*i*Pr)(cod)(MeIm(2-methoxybenzyl))] (**19**) was immediately formed. The most significant features in the ^{1}H NMR of **19** were the *i*-PrO^- ligand, that was observed at δ 3.67 (-CH) and 0.95 ($–CH_3$) ppm, the downfield shift of $>CH_2$ resonance of the 2-

methoxybenzyl fragment and the highfield shift of the olefin resonances of the cod ligand compared to **7**. The ESI+ mass spectra of solutions of **19** in 2-propanol do not exhibit the molecular ion although the specie [**19** - O*i*Pr]$^+$ was detected at m/z 503.1 (100%). When a 2-propanol solution of **19** was heated at 65 ºC for a couple of minutes the formation of several unidentified hydride species was observed by NMR together with free cyclooctene, also detected by GC/MS, resulting from the hydrogen transfer to coordinated 1,5-cyclooctadiene. Interestingly, when compound **19** was heated in the presence of cyclohexanone, an external hydride acceptor, cyclohexanol and acetone were identified in the reaction mixture. In the same way, the formation of the alkoxo compound [Ir(OCy)(cod)(MeIm(2-methoxybenzyl))] (**20**) was observed in the reaction of **7** with NaOCy in TDF-d_8. Solutions of **20** slowly decomposed at room temperature to give cyclooctene (NMR and GC/MS evidence). However, we have observed that **20** reacts quickly with 2-propanol in TDF-d_8 to give **19** and HOCy in an alkoxide exchange reaction that is a key step in most of the inner-sphere mechanistic proposals.



Scheme 2. Synthesis and reactivity of complexes [Ir(OR)(cod)(MeIm(2-methoxybenzyl))].

The stability of the O-functionalized-NHC iridium(I) catalytic systems has been established by consecutive hydrogen transfer reactions. Thus, to the solution obtained from a catalytic run using **14** /cyclohexanone/KOH in 2-propanol under the standard conditions (>90% conversion was attained in 12 min) an additional 5 mmol of cyclohexanone were added subsequently. Monitoring of the

reaction by GC showed similar conversion after the same reaction time what is an indication of the catalyst stability. Interestingly, the ^{1}H NMR of the solid residue at the end of the reaction allowed the identification of compound **19** as the resting state of the iridium catalyst. In addition, there was no evidence for the loss of imidazolium salt by reductive elimination in the likely [IrH(cod)(O-NHC)] (**21**) (O-NHC = MeIm(2-methoxybenzyl)) intermediate.

We have studied the *in situ* generation of the active species under catalytic hydrogen transfer conditions by ESI and MALDI-TOF mass spectrometry.[47] The ESI mass spectrum of a $1x10^{-3}$ M solution of complex [IrBr(cod)(O-NHC)] (**7**) in 2-propanol under argon atmosphere (diluted with acetonitrile to $1x10^{-6}$ M, manual injection) showed the molecular ion protonated at m/z 583.1 (41%), and the peaks at m/z 203.0 (74 %) and 705.1 (57%) that correspond to the imidazolium cation [H-O-NHC]$^{+}$ and the bis-carbene species [Ir(O-NHC)$_2$]$^{+}$ probably generated under the operating conditions. The ESI mass spectrum after the addition of a solution of KOH (1:5), at room temperature or after heating at 80 ºC, was basically identical although a tiny peak at m/z 504.8 (10%) with the right isotopic distribution for the species [IrH(cod)(O-NHC)] (**21**) was observed (see Supporting Information).

The excessive fragmentation observed under ESI conditions suggests the presence of metastable species. In order to get further information on the catalytic intermediates MALDI-TOF mass spectra were recorded in linear mode[48] (Figure 3). The mass spectra of a 2-propanol solution of **7** showed the molecular ion at m/z 582.0 and the ion resulting from the loss of the bromo ligand [Ir(cod)(O-NHC)]$^{+}$, [**7** – Br]$^{+}$, at m/z 502.9. In addition, a peak at m/z 585.3 (overlapped with the first one) which isotopic distribution corresponds to [Ir(O*i*Pr)(cod)(O-NHC)Na]$^{+}$, [**19** + Na]$^{+}$, was also observed (Figure 3a). The mass spectra immediately after the addition of a solution of KOH (1:5) shows both overlapping ions and a tiny peak at m/z 526.0 that might correspond to the species [IrH(cod)(O-NHC)Na]$^{+}$ ([**21** + Na]$^{+}$, Figure 3b). Interestingly, the spectrum recorded after 30 min of

the addition of the base shows exclusively the presence of $[\mathbf{7} - Br]^+$ and $[\mathbf{19} + Na]^+$ due to the complete transformation of **7** into the catalytic intermediates.

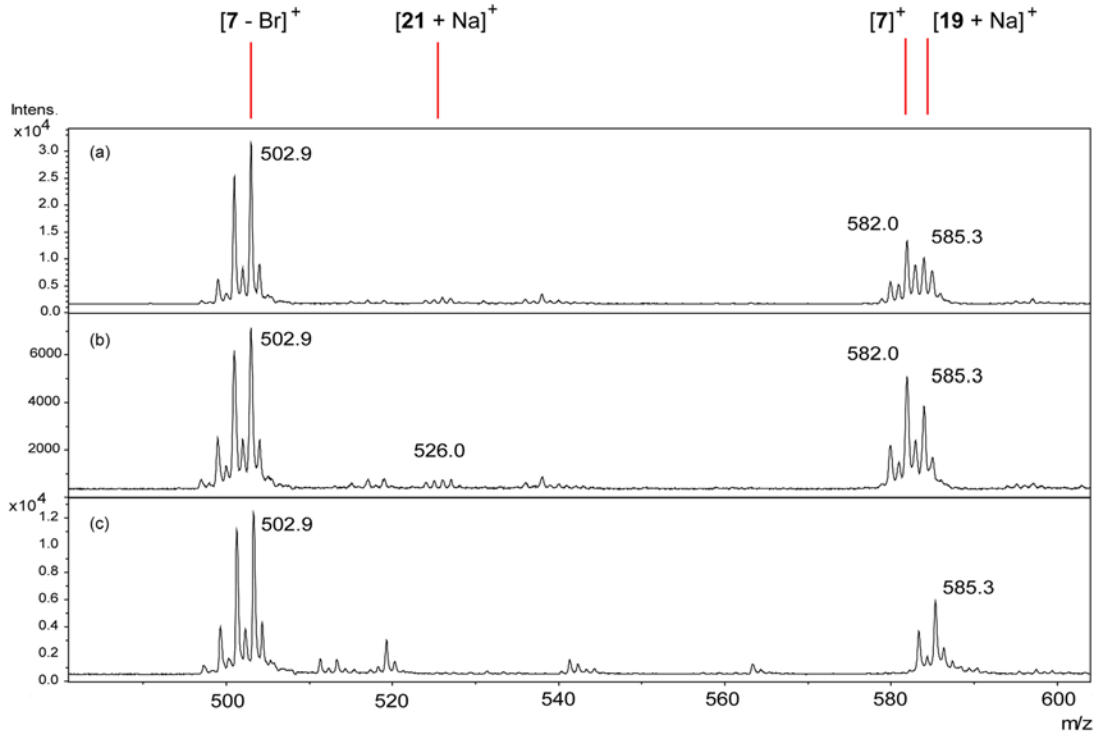
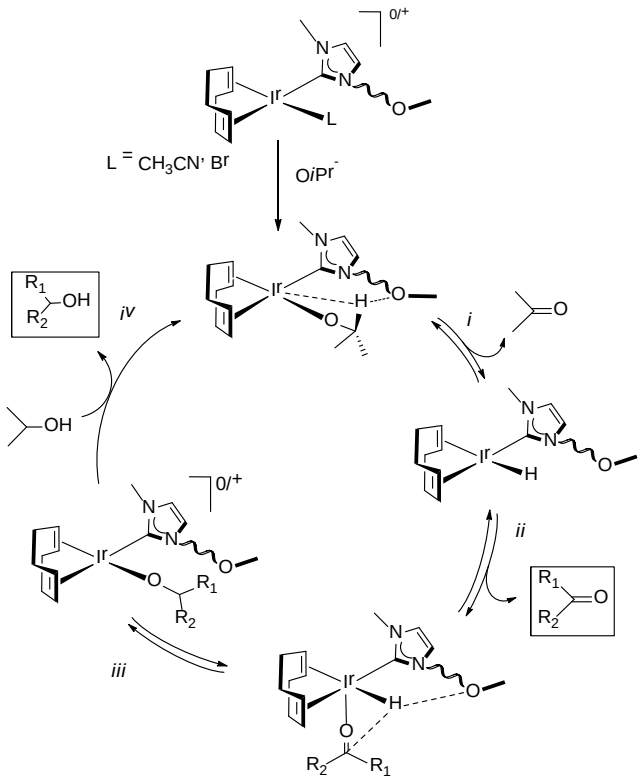


Figure 3. Iridium species detected in the MALDI-TOF MS (linear mode) of an 2-propanol solution of: a) [IrBr(cod)(MeIm(2-methoxybenzyl))] (**7**); b) **7** plus KOH, 1:5 ratio, registered immediately at room temperature; c) **7** plus KOH, 1:5 ratio, registered after 30 min at room temperature.

The detection of the hydride species **21** and the remarkable stability shown by complex **19**, which was generated from **7** and 2-propanol under MALDI conditions, strongly support an inner-sphere transfer hydrogenation mechanism with a monohydride complex as the active catalytic species. The proposed mechanism compatible with the information obtained from the different performed experiments is depicted in Scheme 3. The first step is the β-H elimination from the alkoxo complex [Ir(O*i*Pr)(cod)(O-NHC)] (**19**) to generate the neutral hydride intermediate [IrH(cod)(O-NHC)] (**21**) with the concomitant formation of acetone (step i). The coordination of the ketone substrate to the

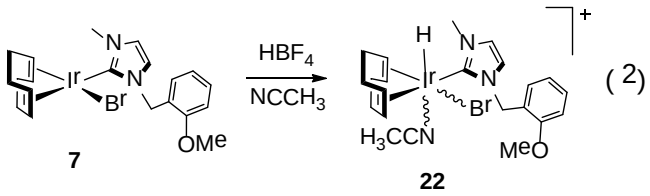
unsaturated hydride complex (step ii) and the migratory insertion into the Ir-H bond (step iii) results in the formation of a new alkoxo complex. Finally, the protonation of the alkoxo ligand by 2-propanol (solvent) results in the formation of the reduced substrate regenerating the starting alkoxo complex in an alkoxide exchange reaction (step iv).



Scheme 3. Proposed mechanism for the catalytic transfer hydrogenation of ketones.

In order to investigate the potential participation of iridium(III) species in the mechanism we have synthesized the cationic hydride complex $[IrHBr(NCCH_3)(cod)(MeIm(2\text{-methoxybenzyl}))]^+$ (**22**) by reaction of **7** with 1 equiv. of HBF_4 in acetone in the presence of 1 equiv. of acetonitrile (Equation 2). The molecular structure of one cation of **22** together to the more significant bond distances and angles are presented in Figure 4. Although two crystallographically independent molecules were observed in the crystal structure, both were chemically identical with minor torsion angle differences. The whole cationic complexes resemble the structure of **7** where a hydride and an

acetonitrile ligand have been added below and above the metal coordination plane. Thus, the cationic complexes in **22** could be described as octahedral with significant distortions associated to the different steric ligand requirements and the chelate behavior of the cod molecule (C(1)–Ir–M(1) 170.50(11), Br–Ir–M(2) 171.26(8), N(3)–Ir–H 164(2)º, mean values, (M(1) and M(2) represent the midpoints of the olefinic bonds C(13)-C(14) and C(17)-C(18), respectively). If compared with **7**, the new ligands in the metal environment, together with the oxidation of the metal centre, originate slightly longer bonding distances for all ligands, particularly evidenced in the Ir-olefinic bonds (Ir–M(1) 2.072(5) in **7** *vs.* 2.161(2) Å in **22**, or Ir–M(2) 1.980(4) in **7** *vs.* 2.072(3) Å in **22**). This relative elongation is not particularly significant for the NHC ligand (2.035(4) in **7** *vs.* 2.049(3) Å in **22**) which maintains identical symmetric bonding distances within the imidazole moiety. Complex **22** features a very long Ir–N(3) bond distance *trans* to hydride, 2.156(3) Å, significantly longer than values found in other related acetonitrile-dihydride NHC-Ir(III) complexes (range 2.098–2.135(5) Å), where readily dissociable acetonitriles have been observed.[3e]



7 **22** (2)

The ^{1}H NMR of **22** in CD_2Cl_2 evidenced that the compound exists in solution as two non interconvertible isomers, **22a** and **22b**, in a 28/72 ratio. The major isomer **22b** showed a somewhat broad resonance for the hydride ligand at δ -14.30 ppm and a labile acetonitrile ligand at δ 2.75 ppm that was found to undergo exchange with CD_3CN. This dynamic behavior is probably due to the strong *trans* effect of the hydride ligand having an acetonitrile ligand in *trans* and consequently, **22b** is the isomer characterized by X-ray diffraction. In contrast, the minor isomer **22a** is not dynamic and displayed sharp resonances both for the hydride and acetonitrile ligands at δ -14.51

and 1.24 ppm, and probably corresponds to the isomer having the bromo ligand *trans* to the hydride ligand.

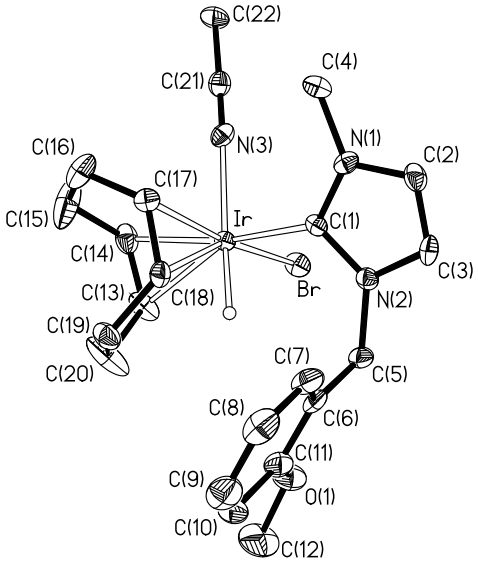


Figure 4. Molecular structure of one independent cation of [IrHBr($NCCH_3$)(cod)(MeIm(2-methoxybenzyl))] [BF_4] complex (**22**). (Organic hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (º) for the two independent cations: Ir–Br 2.5040(8), 2.5068(8); Ir–C(1) 2.052(5), 2.046(4); Ir–N(3) 2.162(4), 2.151(4); Ir–H(1) 1.596(10), 1.583(10); Ir–C(13) 2.261(5), 2.253(5); Ir–C(14) 2.277(5), 2.281(5); Ir–C(17) 2.183(5), 2.183(5); Ir–C(18) 2.182(6), 2.192(5); N(1)–C(1) 1.359(6), 1.357(6); N(2)–C(1) 1.366(6), 1.368(6); C(13)–C(14) 1.376(7), 1.384(7); C(17)–C(18) 1.381(7), 1.391(8); Br–Ir–N(3) 85.85(11), 84.35(12); N(3)–Ir–C(1) 94.07(18), 94.16(16); Br–Ir–C(1) 89.81(14), 89.37(14); N(3)–Ir–H(1) 166(3), 162(2); Br–Ir–H(1) 104(3), 79(2); C(1)–Ir–H(1) 76(3), 78.1(17); C(1)–N(1)–C(2) 110.8(4), 111.1(4); Ir–C(1)–N(1) 131.4(4), 131.5(3); Ir–C(1)–N(2) 124.4(3), 124.8(3); Ir–N(3)–C(21) 174.1(4), 174.6(4).

Interestingly, the formation of **22** is reversible and the reaction with one equiv. of KOH, or even with water, gave the precursor iridium (I) compound **7**. In full agreement with this, both compounds

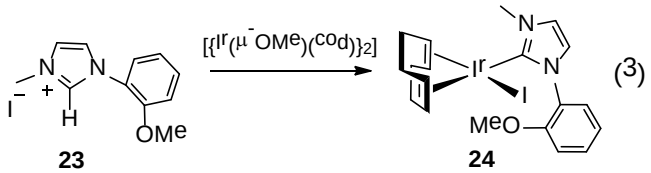
7 and **22** exhibited identical catalytic activity for the transfer hydrogenation of cyclohexanone, which supports the participation of iridium (I) intermediates.

The Influence of the Hemilabile Ligand on the Catalytic Activity. The hydrogen transfer catalytic activity exhibited by iridium complexes with donor functionalized NHC ligands of hemilabile character evidence that O-donor functionalized NHC ligands provide much more active systems that the corresponding N-functionalized ligands. Although the interplay of several factors could be responsible for the activity differences, the chelating effect of the ligands probably plays an important role.

The greater coordination ability of the donor set in the N-functionalized NHC ligands became evident in the synthesis of the cationic complexes **17** and **18** where the NHC ligand is κ^2-C,N coordinated trough the pyridine and dimethylamino fragments, respectively. In contrast, the methoxy fragment in the cationic complexes **13** and **14** remained uncoordinated, in spite of their potential for bidentate coordination, and the complexes were stabilized by the coordination of an acetonitrile ligand. As a mechanism through 18-electron pentacoordinated iridium (I) species is unlikely due to required coordination of the substrate, the dissociation of the hemilabile fragment of the NHC ligand could be a requisite for catalytic activity in order to drive the reaction through square-planar iridium (I) intermediates (Scheme 3).[49] The easier dissociation of the coordinated acetonitrile ligand and the strong coordination ability of the N-donor functionalized NHC ligands for the iridium center could account for the different catalytic activity of both types of complexes. However, the modest catalytic activity of complexes **17** and **18** contrast with the exhibited by related iridium complexes containing quinoline-functionalized NHC ligands.[50] On the other hand, the higher catalytic activity of the cationic complexes, $[Ir(NCCH_3)(cod)(O\text{-}NHC)]^+$, compared to the neutral bromo complexes, [IrBr(cod)(O-NHC)], is probably a consequence of the easier generation of the alkoxy intermediate species [Ir(O*i*Pr)(cod)(O-NHC)] from the cationic acetonitrile complexes.

It became evident that the presence of a methoxy group with weak coordination ability on the functionalized NHC ligands has a considerable impact on the catalytic activity. However, this effect could be more probably associated to weak interactions in the forward and backward hydrogen transfer from the hydride intermediate [IrH(cod)(O-NHC)] (**21**) (hydride migration and β-H transfer, steps ii and i, respectively, Scheme 3) rather than to the interaction with the iridium center. The enhanced catalytic activity of complex **14** compared to **13** should be ascribed to the different flexibility of the O-functionalized NHC ligand. Then, the rigid 2-methoxybenzyl substituent in **14** probably brings about the -OMe group close to the external coordination sphere of the iridium center more effectively than the highly flexible 2-methoxyethyl substituent (compound **13**) as a consequence of a proximity effect. In order to test this hypothesis, we speculate about the catalytic performance of complexes having more rigid O-functionalized NHC ligands, as for example a 2-methoxyphenyl substituted NHC ligand.

The imidazolium salt 1-(2-methoxyphenyl)-3-methyl-1*H*-imidazol-3-ium iodide (**23**) was obtained as a white hygroscopic solid in excellent yield following the general method of synthesis for arylimidazole derivatives.[51] The reaction of **23** with [{Ir(μ-OMe)(cod)}$_2$] (0.5 equiv.) in tetrahydrofurane gave the iridium(I) complex [IrI(cod)(MeIm(2-methoxyphenyl))] (**24**) which was isolated as a yellow microcrystalline solid in good yield (Equation 3). Unfortunately, the attempts to prepare the cationic complex [Ir(NCCH$_3$)$_x$(cod)(MeIm(2-methoxyphenyl))]$^+$ from **23** or using the silver-NHC complex were unsuccessful because of the compound was frequently obtained together with minor unidentified hydride species.



23 **24** (3)

In line with our expectations, compound **24** is an efficient catalyst precursor for transfer hydrogenation of cyclohexanone with 2-propanol. A conversion of 92% was attained in 50 min,

under the standard conditions (catalyst:substrate:KOH ratio of 1:1000:5 in 2-propanol at 80 ºC), with an average TOF 1100 h^{-1}. The catalytic activity of **24** is in the same range as the found for the related neutral complexes but, interestingly, slightly more active than **7** (TOF 824 h^{-1}). Nevertheless, in addition to the expected ligand effect, the presence of a better leaving ligand (iodo *vs* bromo) could also contribute to the increase of the activity. In fact, a catalytic test with the system **24**/$AgBF_4$ (1 equiv.), in order to generate the cationic complex *in situ*, gave a 92% conversion in 23 min under the standard conditions with a TOF of 2200 h^{-1}, just a half-fold reduction in catalytic activity compared with **14** under the same conditions.

The Role of the O-donor Hemilabile Fragment: DFT Calculations. In order to understand the superior catalytic activity of the complexes having O-donor functionalized NHC ligands we have studied the key steps of the proposed mechanism by DFT calculations. The unsaturated hydride intermediate [IrH(cod)(O-NHC)] (**21**) (O-NHC = MeIm(2-methoxybenzyl)) plays a crucial role in the catalytic cycle and thus, their generation from the alkoxo complex [Ir(O*i*Pr)(cod)(O-NHC)] (**19**) by β-H elimination has been investigated in detail (step i, Scheme 3). It is worth of notice that the reduction of the substrate by this species (steps ii and iii) results in the formation of an alkoxo intermediate and thus it can be considered as the reverse process.

β-H elimination from transition metal alkoxides is believed to occur via a mechanism analogous to that established for transition metal alkyls that involved the initial β-H transfer to an unsaturated metal center followed by elimination of the unsaturated organic compound.[52] An alternative two-step mechanism involving σ-bond metathesis followed by oxidative addition has been proposed in palladium chemistry.[53] β-H elimination studies on ruthenium, rhodium and palladium alkoxide complexes have shown that the formation a metal vacant site prior β-H transfer is generally required.[49,53,54] In the same way, β-H elimination in the octahedral *mer-cis*-[Ir(Cl)(H)(OMe)(PMe_3)$_3$]

compound is promoted by the solvent-assisted dissociation of the chloro ligand, followed by irreversible β-H transfer and dissociative substitution of formaldehyde by chloride.[55]

The β-H elimination in square planar iridium(I) alkoxides has been studied recently by Macgregor and Vadivelu[56] with regard to the reactions of *trans*-[Ir(OR)(CO)(PPh_3)$_2$] observed by Atwood[57] and the related mechanistic studies by Hartwig and co-workers.[58] The detailed mechanistic studies by Hartwig evidenced the involvement of 14-electron unsaturated species generated by phosphine dissociation. Calculations by Macgregor and Vadivelu on this mechanism have shown that the reaction proceeds via an agostic in-plane intermediate that leads to the rate limiting β-elimination process. Theoretical analysis on the alkoxo complex [Ir(O*i*Pr)(cod)(O-NHC)] (**19**) have revealed that β-H elimination process is possible without the need of ligand dissociation. The analysis has been performed by DFT using the B3LYP functional and a 6-31G** basis set for all atoms but Ir for which the LANL2DZ basis and associated pseudopotential was used. The complex was not modelized and instead its full composition was used in the calculations.

The geometry of the two isomers of the square planar alkoxo intermediate **19** is shown in Figure 5. Both isomers are virtually of the same energy being **19b**, the isomer having the β-H of the alkoxo ligand directed towards the NHC ligand, only ΔG = +0.8 kcal/mol less stable than isomer **19a**, with the β-H directed to the cod ligand. The possibility of some interaction between the β-H on the alkoxo ligand and the oxygen atom of the 2-methoxybenzyl substituent on the NHC ligand was analyzed by approaching this group and fully optimizing the resulting structure. This leads to a third isomer **19c**, a rotamer in fact, which shows a close O···H interaction (2.98 Å) and a free energy of just +1.0 kcal above **19a** and 0.2 above **19b**.

By approaching the H atom to the iridium center, in order to modelize the β-H elimination process, the intermediate **19'** was found. This intermediate shows a significant agostic interaction of the β-H with the iridium center with distances of Ir···H = 1.86 Å and C···H = 1.19 Å. The formation of **19'**

requires the anticlockwise rotation about the Ir–O bond in **19c** to facilitate the η^2-CH interaction (Ir···C = 2.49 Å) which results in a constrained geometry of the alkoxo ligand (Ir–O–C = 84.7 °). The intermediate **19'** has a free energy of +26.6 kcal/mol relative to **19a**, which is comparable to the found (ca. 30 kcal/mol) for agostic intermediates derived from iridium unsaturated species generated by ligand dissociation.[56] Finally, the β-elimination process proceeds leading to the square planar hydrido complex [IrH(cod)(O-NHC)] (**21**), with a Ir-H bond distance of 1.64 Å, and the prompt elimination of ketone, this process releases a free energy of -6.5 kcal/mol relative to **19a**.

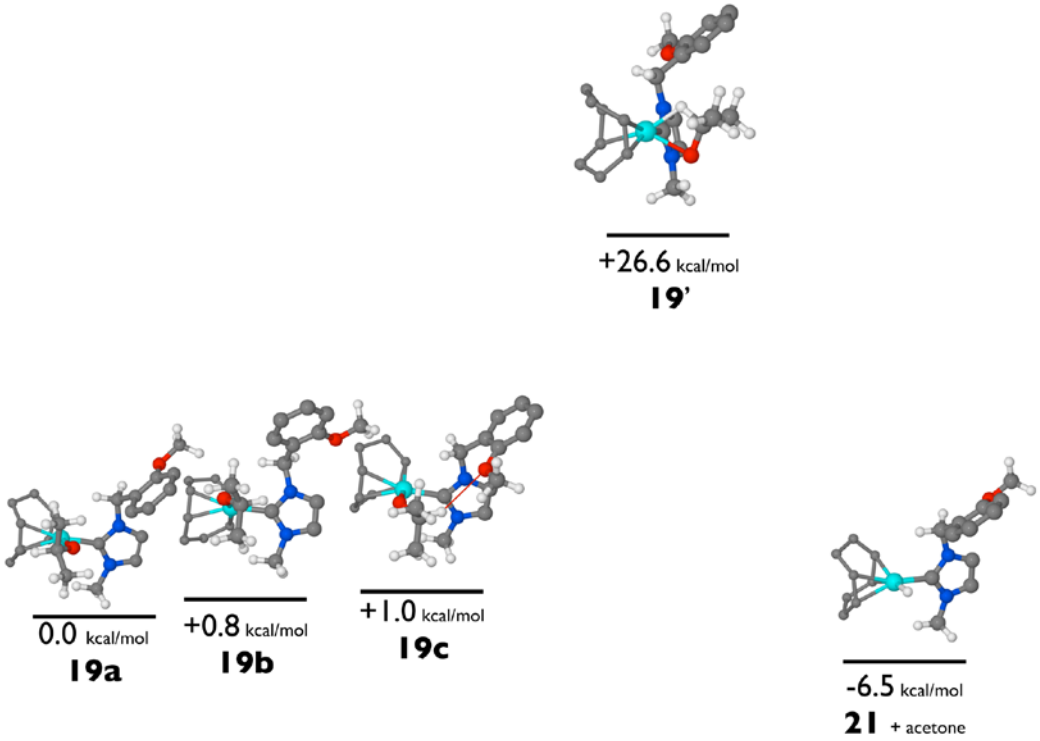


Figure 5. Relative free energies (ΔG, kcal/mol) in the gas phase and geometries of the intermediate species for the β-H elimination in [Ir(O*i*Pr)(cod)(MeIm(2-methoxybenzyl))] (**19**).

The described results outline the role of the methoxy fragment of the substituent in the NHC ligand and its influence on the catalytic activity. The interaction between the β-H on the alkoxo ligand and the oxygen atom of the methoxy fragment results in a net destabilization of the alkoxo intermediate by a free energy of 1.0 kcal/mol, probably due to the induced steric effects. Thus, the

destabilization of **19** reduces the activation barrier leading to the intermediate **19'** facilitating the β-H elimination step in the catalytic process. This fact could explain the positive effect of the methoxy group of the functionalized NHC ligands on the catalytic activity.

Conclusions

Iridium(I) complexes having hemilabile O- and N-donor functionalized NHC ligands are efficient catalyst precursor for the transfer hydrogenation of unsaturated compounds in 2-propanol/KOH. The catalytic activity is strongly dependent on the donor function and flexibility of the backbone in the NHC ligands, as well as the charge of the complexes. Iridium complexes based on O-donor functionalized NHC ligands were found to be much more active than the corresponding N-functionalized ligands which is related to the strong coordination ability of the dimethylamino donor set compared to methoxy, because of the dissociation of the hemilabile fragment is required for the formation of square-planar alkoxo iridium (I) intermediates. In fact, the higher catalytic activity of the cationic complexes compared to the neutral ones is also a consequence of the easier generation of the alkoxo intermediate species. Investigation of the reaction mechanism in combination with DFT calculations have allowed to disclose a potential role of the hemilabile fragment on the NHC ligands that could be responsible for the observed positive effect on the catalytic activity. The interaction between the β-H on the alkoxo ligand and the oxygen atom of the methoxy fragment of the NHC ligand, results in a net destabilization of the alkoxo intermediate that facilitates the β-H elimination step in route to the key hydrido intermediate species.

Experimental Section

Scientific Equipment. C, H and N analyses were carried out in a Perkin-Elmer 2400 Series II CHNS/O analyzer. Infrared spectra were recorded on a FT-Perkin-Elmer Spectrum One spectrophotometer using Nujol mulls between polyethylene sheets. NMR spectra were recorded on a

Bruker Avance 300, or a Bruker Avance 400 spectrometers. ^{1}H (300.1276 MHz, 400.1625 MHz) and ^{13}C (75.4792 MHz, 100.6127 MHz) NMR chemical shifts are reported in ppm relative to tetramethylsilane and referenced to partially deuterated solvent resonances. Coupling constants (*J*) are given in Hertz. Spectral assignments were achieved by combination of ^{1}H-^{1}H COSY, ^{13}C APT and ^{1}H-^{13}C HSQC experiments. MALDI-TOF mass spectra were obtained on a Bruker MICROFLEX spectrometer using DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix.[59] Electrospray mass spectra (ESI-MS) were recorded on a Bruker MicroTof-Q using sodium formiate as reference. Conductivities were measured in *ca.* 5 10^{-4} M acetone solutions of the complexes using a Philips PW 9501/01 conductimeter.

Organic compounds were identified by Gas Chromatography-Mass Spectrometry (GC/MS) using an Agilent 6890 GC system with an Agilent 5973 MS detector, equipped with a polar capillary column HP-5MS (df = 0.25 μm, 30m x 0.25 mm i.d.). The catalytic reactions were analyzed on an Angilent 4890 D system equipped with an HP-INNOWax capillary column (df = 0.4 μm, 25 m x 0.2 mm i.d.) using mesitylene as internal standard.

Synthesis. All experiments were carried out under an atmosphere of argon using Schlenk techniques. The solvents were distilled immediately prior to use from the appropriate drying agents or obtained from a Solvent Purification System (Innovative Technologies). Oxygen-free solvents were employed throughout. $CDCl_3$, and CD_2Cl_2 were dried using activated molecular sieves, methanol-d_4 (<0.02% D_2O) was purchased from Euriso-top and used as received. MeImH (*N*-methyl-imidazole) was obtained from Sigma-Aldrich and distilled prior to use. The substrates were obtained from common commercial sources and used as received, or re-crystallized or distilled prior to use depending on their purity. The imidazolium salts [MeImH$(CH_2)_2$OMe]Br (**1**),[19] [MeImH(pyridin-2-ylmethyl)]Br (**3**),[20] and [MeImH$(CH_2)_n$NHMe$_2$)]Cl_2 (n = 2, **4**; n = 3, **5**)[6a] and the starting materials [{Ir(μ-Cl)(cod)}$_2$][60] and [{Ir(μ-OMe)(cod)}$_2$][61] were prepared according to literature procedures.

Preparation of 1-(2-methoxybenzyl)-3-methyl-1*H*-imidazol-3-ium bromide (2). *N*-Methylimidazole (1.15 g, 14.0 mmol) was added to a solution of 2-methoxybenzyl bromide (14.0 mmol, obtained *in situ* from 2-methoxybenzyl alcohol, 1.93 g, and PBr_3, 1.33 g)[21] in toluene (15 mL) and the mixture refluxed for 12 h. The white solid formed was separated by decantation, washed with hot *n*-hexane and dried in vacuum. Yield: 97%. Anal. Calcd for $C_{12}H_{15}BrN_2O$: C, 50.90; H, 5.34; N, 9.89. Found: C, 51.23; H 6.01; N, 9.93. ^{1}H NMR (298 K, CD_3OD): δ 10.37 (s, 1H, NCHN), 7.59 (dd, *J* = 7.4, 1.4, 1H, CH Ar), 7.51, 7.35 (m, 1H, 1H, CH Ar), 6.95 (td, *J* = 7.4, 1.0, 1H, CH Ar), 6.91 (s, 1H, CH Im), 6.88 (s, 1H, CH Im), 5.47 (s, 2H, NCH_2), 4.08 (s, 3H, OMe), 3.89 (s, 3H, MeIm). $^{13}C\{^1H\}$ NMR (298 K, $CDCl_3$): δ 157.45 (C Ar), 137.41 (NCHN), 131.49, 131.48 (CH Ar), 123.33, 122.13 (CH Im), 121.32 (C Ar), 121.24, 110.97 (CH Ar), 55.79 (OMe), 48.79 (CH_2), 36.75 (MeIm). ESI-MS (CH_3OH) *m/z* = 203.2 $[M]^+$.

General Procedure for the Preparation of [MBr(cod)(MeImXOMe)] (M = Rh, Ir; X = $(CH_2)_2$, $CH_2C_6H_4$). The rhodium and iridium complexes containing methoxy-functionalized NHC ligands were synthesized through the following procedure. A mixture of $[\{M(\mu\text{-OMe})(cod)\}_2]$ (M = Rh, Ir) and [MeImHXOMe]Br in THF (10 mL) was stirred overnight at room temperature to give an orange suspension. The solid was removed by filtration and the resulting orange solution was concentrated to evaporated to dryness. Treatment of the yellow residue with pentane rendered a yellowish solid which was separated by decantation, washed with pentane, and dried in vacuum.

[IrBr(cod)(MeIm$(CH_2)_2$OMe)] (6). $[\{Ir(\mu\text{-OMe})(cod)\}_2]$ (270 mg, 0.407 mmol) and [MeImH$(CH_2)_2$OMe)]Br (180 mg, 0.814 mmol). Yield: 74%. Anal. Calcd for $C_{15}H_{24}BrN_2OIr$: C, 34.61; H, 4.65; N, 5.38. Found: C, 34.31; H, 4.59; N, 5.36. ^{1}H NMR (298 K, $CDCl_3$): δ 7.01, (d, *J* = 1.9, 1H, CH Im), 6.77 (d, *J* = 1.9, 1H, CH Im), 4.71 (ddd, *J* = 13.9, 4.8, 3.5, 1H, NCH_2), 4.58 (m, 2H, CH cod), 4.36 (ddd, *J* = 14.1, 7.6, 4.3, 1H, NCH_2), 3.90 (s, 3H, MeIm), 3.76 (m, 2H, CH cod), 3.35 (s, 3H, OMe), 2.95 (ddd, *J* = 7.0, 7.0, 3.2, 1H, CH_2O), 2.84 (ddd, *J* = 7.0, 7.0, 3.2, 1H, CH_2O), 2.17, 1.72, 1.49 (m, 4H, 2H, 2H, CH_2 cod). $^{13}C\{^1H\}$ NMR (298 K, $CDCl_3$): δ 180.16 (NCN),

121.72, 120.60 (CH Im), 84.49, 83.92 (CH cod), 72.12 (CH_2O), 59.50 (OMe), 52.24, 51.99 (CH cod), 50.03 (NCH_2), 37.34 (MeIm), 33.36, 33.24, 29.93, 29.74 (CH_2 cod). MS (MALDI-TOF, DCTB matrix, CH_2Cl_2) *m/z* = 522.5 $[M + H]^+$, 441.0 $[M - Br]^+$. Λ_M (acetone) = 16 $\Omega^{-1}cm^2mol^{-1}$.

[IrBr(cod)(MeIm(2-methoxybenzyl))] (7). [{Ir(μ-OMe)(cod)}$_2$] (125 mg, 0.188 mmol) and [MeImH(2-methoxybenzyl)]Br (107 mg, 0.377 mmol). Yield: 73%. Anal. Calcd for $C_{20}H_{26}BrN_2OIr$: C, 41.23; H, 4.50; N, 4.81. Found: C, 41.38; H, 4.56; N, 4.80. ^{1}H NMR (298 K, $CDCl_3$): δ 7.33−7.18, 6.93−6.80 (m, 2H, 2H, CH Ar), 6.70 (d, *J* = 1.6, 1H, CH Im), 6.65 (d, *J* = 1.6, 1H, CH Im), 5,53 (AB system, δ_A = 5.70, δ_B = 5.42, J_{AB} = 14.7, 2H, NCH_2), 4.61 (m, 2H, CH cod), 3.88 (s, 3H, OMe), 3.80 (s, 3H, MeIm), 2.96 (br, 2H, CH cod), 2.13, 2.01, 1.70, 1.61, 1.48, 1.37 (m, 3H, 1H, 1H, 1H, 1H, CH_2 cod). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 178.37 (NCN), 155.23 (C Ar), 129.12, 127.22 (CH Im), 124.82 (C Ar), 123.25, 121.12, 120.45, 110.25 (CH Ar), 83.85, 82.95 (CH cod), 55.24 (OMe), 52.51, 52.02 (CH cod), 49.12 (NCH_2), 37.51 (MeIm), 33.54, 32.21, 29.58, 28.12 (CH_2 cod). MS (MALDI-TOF, DCTB matrix, CH_2Cl_2) *m/z* = 582.2 $[M]^+$, 503.3 $[M - Br]^+$. Λ_M (acetone) = 14 $\Omega^{-1}cm^2mol^{-1}$.

[RhBr(cod)(MeIm(CH$_2$)$_2$OMe)] (8). [{Rh(μ-OMe)(cod)}$_2$] (370 mg, 0.764 mmol) and [MeImH(CH$_2$)$_2$OMe)]Br (338 mg, 1.53 mmol). Yield: 64%. Anal. Calcd for $C_{15}H_{24}BrN_2ORh$: C, 41.78; H, 5.61; N, 6.49. Found: C, 41.42; H, 5.54; N, 6.30. ^{1}H NMR (298 K, $CDCl_3$): δ 6.95, 6.71 (s, 1H, 1H, CH Im), 4.97 (m, 2H, CH cod), 4.81, 4.40 (m, 1H, 1H, >CH_2), 4.11 (s, 3H, OMe), 3.76 (m, 2H, >CH_2), 3.28 (s, 3H, MeIm), 3.21 (br, 2H, CH cod), 2.26, 1.86 (m, 4H, 4H, CH_2 cod). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 181.99 (d, J_{Rh-C} = 50.5, NCN), 121.96, 121.77 (CH Im), 98.00 (d, J_{Rh-C} = 6.5, CH cod), 97.82 (d, J_{Rh-C} = 6.6, CH cod), 72.13 (CH_2O), 69.06 (d, J_{Rh-C} = 11.1, CH cod), 68.91 (d, J_{Rh-C} = 11.0, CH cod), 58.97 (OMe), 50.48 (NCH_2), 37.69 (MeIm), 32.77, 32.67, 29.15, 29.06 (CH_2 cod). MS (MALDI-TOF, DCTB matrix, CH_2Cl_2) *m/z* = 431.2 $[M]^+$, 351.8 $[M - Br]^+$. Λ_M (acetone) = 0.6 $\Omega^{-1}cm^2mol^{-1}$.

[RhBr(cod)(MeIm(2-methoxybenzyl))] (9). [{Rh(μ-OMe)(cod)}$_2$] (150 mg, 0.310 mmol) and [MeImH(2-methoxybenzyl)]Br (166 mg, 0.620 mmol). Yield: 90%. Anal. Calcd for $C_{20}H_{26}BrN_2ORh$: C, 48.70; H, 5.31; N, 5.68. Found: C, 49.16; H, 5.68; N, 5.50. ^{1}H NMR (298 K, $CDCl_3$): δ 7.32, 6.94 (m, 2H, 2H, CH Ar), 6.78, 6.70 (s, 1H, 1H, CH Im), 5.60 (AB system, δ_A = 5.74, δ_B = 5.46, J_{AB} = 14.7, 2H, NCH_2), 5.12 (m, 2H, CH cod), 4.11 (s, 3H, OMe), 3.88 (s, 3H, MeIm), 3.44 (br, 2H, CH cod), 2.37, 1.91 (m, 4H, 4H, CH_2 cod). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 182.81 (d, J_{Rh-C} = 50.0, NCN), 157.75 (C Ar), 130.78, 129.88 (CH Im), 125.18 (CH Ar), 122.50 (C Ar), 121.12, 121.05, 110.89 (CH Ar), 97.84 (d, J_{Rh-C} = 6.7, CH cod), 97.70 (d, J_{Rh-C} = 6.7, CH cod), 69.65 (d, J_{Rh-C} = 14.6, CH cod), 69.13 (d, J_{Rh-C} = 14.5, CH cod), 55.75 (OMe), 49.41 (NCH_2), 38.06 (MeIm), 33.47, 32.70, 29.75, 29.21 (CH_2 cod). MS (MALDI-TOF, DCTB matrix, CH_2Cl_2) *m/z* = 413.5 $[M - Br]^+$, 203.5 $[MeHIm(CH_2)C_6H_4OMe]^+$. Λ_M (acetone) = 1.4 $\Omega^{-1}cm^2mol^{-1}$.

Preparation of [IrBr(cod)(MeIm(pyridin-2-ylmethyl))] (10). A mixture of [{Ir(μ-OMe)(cod)}$_2$] (100 mg, 0.150 mmol) and [MeImH(pyridin-2-ylmethyl)]Br (76.6 mg, 0.302 mmol) in acetone (10 mL) was stirred for 4 hours at room temperature giving an orange suspension. The solid was removed by filtration and the resulting solution was evaporated to dryness. The compound was extracted with diethyl ether and the solution concentrated to *ca.* 1 mL and then treated with *n*-hexane until a solid was formed. The orange solid was isolated by decantation, washed with n-hexane (2 x 2 mL) and dried in vacuum. Yield: 81%. Anal. Calcd for $C_{18}H_{23}BrN_3Ir$: C, 39.06; H, 4.19; N, 7.59. Found: C, 39.21; H, 4.15; N, 8.13. ^{1}H NMR (298 K, $CDCl_3$): δ 8.62 (d, *J* = 5.5 , 1H, CH py), 7.64 (ddd, *J* = 7.9, 7.8, 1.7, 1H, CH py), 7.40 (d, *J* = 7.8, 1H, CH py), 7.17 (dd, *J* = 7.9, 5.5, 1H, CH py), 6.86, (s, *J* = 1.9, 1H, CH Im), 6.75 (d, *J* = 1.9, 1H, CH Im), 5.53 (AB system, δ_A = 5.73, δ_B = 5.32, J_{AB} = 14.6, 2H, NCH_2), 4.65, 4.37 (br, 1H, 1H, CH cod), 3.91 (s, 3H, MeIm), 2.82, 2.69 (br, 1H, 1H, CH cod), 2.22, 2.02, 1.61, 1.50 (m, 2H, 2H, 2H, 2H, CH_2 cod). ^{13}C{^{1}H} NMR (298 K, $CDCl_3$): δ 155.59 (C py), 150.74, 136.88, 123.58, 122.89 (CH py), 122.02, 120.38 (CH Im), 101.32, 99.58

(br, CH cod), 56.00 (NCH_2), 52.75, 51.00 (br, CH cod), 37.65 (MeIm), 32.15, 31.50, 29.67, 28.36 (CH_2 cod). MS (MALDI-TOF, DCTB matrix, CH_2Cl_2) *m/z* = 554.1 $[M + H]^+$, 474.0 $[M - Br]^+$. Λ_M (acetone) = 15 $\Omega^{-1}cm^2mol^{-1}$.

Preparation of [IrCl(cod)(MeIm(CH$_2$)$_n$NMe$_2$)] (n = 2, 3). $[MeImH(CH_2)_nNHMe_2)]Cl_2$ (0.301 mmol) was added to a solution of $[\{Ir(\mu\text{-}OMe)(cod)\}_2]$ (100 mg, 0.150 mmol) in tetrahydrofurane (10 mL) and stirred overnight. The resulting suspension was treated with NaH (7.22 mg, 0.301 mmol) and H_2O (0.1 mL) and stirred for 10 min. The solid was removed by filtration to give a yellow solution that was evaporated until *ca.* 1 mL. The pale yellow solids formed after treatment with *n*-hexane were washed with diethyl ether, separated by decantation and dried in vacuum.

[IrCl(cod)(MeIm(CH$_2$)$_2$NMe$_2$)] (11). Yield**:** 69%. Anal. Calcd for $C_{16}H_{27}ClN_3Ir$: C, 39.29; H, 5.56; N, 8.59. Found: C, 39.11; H, 5.32; N, 8.11. ^{1}H NMR (298 K, $CDCl_3$): δ 6.99 (d, *J* = 2.0, 1H, CH Im), 6.77 (d, *J* = 2.0, 1H, CH Im), 4.51 (m, 2H, CH cod and 1H, NCH_2), 4.31 (m, 1H, NCH_2), 3.88 (s, 3H, MeIm), 2.91, 2.81 (m, 1H, 1H, CH cod), 2.70 (m, 2H, CH_2N), 2.21 (s, 6H, NMe_2), 2.14, 1.72, 1.60, 1.51 (m, 4H, 1H, 2H, 1H, CH_2 cod). $^{13}C\{^1H\}$ NMR (298 K, $CDCl_3$): δ 180.05 (NCN), 121.15, 120.06 (CH Im), 85.58, 84.32 (CH cod), 60.24 (NCH_2), 53.15, 51.58 (CH cod), 49.78 (CH_2N), 44.85 (NMe_2), 39.78 (MeIm), 35.56, 33.11, 29.10, 27.85 (CH_2 cod). MS (MALDI-TOF, DCTB matrix, CH_2Cl_2) *m/z* = 489.0 $[M]^+$, 454.0 $[M - Cl]^+$. Λ_M (acetone) = 14 $\Omega^{-1}cm^2mol^{-1}$.

[IrCl(cod)(MeIm(CH$_2$)$_3$NMe$_2$)] (12). Yield: 72%. Anal. Calcd for $C_{17}H_{29}ClN_3Ir$: C, 40.50; H, 5.81; N, 8.55. Found: C, 39.89; H, 5.76; N, 8.39. ^{1}H NMR (298 K, $CDCl_3$): δ 6.81 (d, *J* = 1.8, 1H, CH Im), 6.73 (d, *J* = 1.8, 1H, CH Im), 4.56−4.44 (m, 2H, CH cod and 1H, NCH_2), 4.19 (ddd, *J* = 15.1, 8.8, 6.6, 1H, NCH_2), 3.88 (s, 3H, MeIm), 2.91, 2.80 (m, 1H, 1H, CH cod), 2.31 (m, 2H, CH_2), 2.21 (s, 6H, NMe_2), 2.14 (m, 4H, CH_2 cod), 1.92 (m, 1H, CH_2), 1.75–1.42 (m, 4H, 4H, CH_2 cod), 0.78 (m, 1H, CH_2). $^{13}C\{^1H\}$ NMR (298 K, $CDCl_3$): δ 121.94, 120.61 (CH Im), 84.81, 84.60 (CH cod), 55.66 (NCH_2), 52.30, 51.38 (CH cod), 47.86 (CH_2N), 45.00 (NMe_2), 37.61 (MeIm), 33.91,

33.17 (CH_2 cod), 32.15 (CH_2), 29.96, 29.11 (CH_2 cod). MS (MALDI-TOF, DCTB matrix, CH_2Cl_2) *m/z* = 504.2 $[M + H]^+$, 468.2 $[M + H - Cl]^+$. Λ_M (acetone) = 10 $\Omega^{-1}cm^2mol^{-1}$.

General procedure for the preparation of [M(NCCH$_3$)(cod)(MeImXOMe)][BF$_4$] (M = Rh, Ir; X = (CH$_2$)$_2$, CH$_2$C$_6$H$_4$). $AgBF_4$ (1 mmol) was added to a solution of the corresponding complex [MBr(cod)(MeImXOMe)] (1 mmol) in acetone (15 mL) and CH_3CN (52 μL, 1 mmol). After 2 h of stirring at room temperature, the AgCl formed was filtered off to give a yellow solution. The solvent was pumped off and the dried oil residue was treated with cold pentane to give orange-yellowish solids which were separated by decantation, washed with pentane (2 x 2 mL) and dried in vacuum.

[Ir(NCCH$_3$)(cod)(MeIm(CH$_2$)$_2$OMe)][BF$_4$] (13). [IrBr(cod)(MeIm(CH_2)$_2$OMe)] (**6**), (100 mg, 0.190 mmol), $AgBF_4$ (37.4 mg, 0.190 mmol). Yield: 67%. Anal. Calcd for $C_{17}H_{27}BF_4N_3OIr$: C, 35.92; H, 4.79; N, 7.39. Found: C, 36.03; H, 4.80; N, 6.99. ^{1}H NMR (acetone-d_6): δ 7.37, 7.31 (s, 1H, 1H, CH Im), 4.66 (br, 2H, CH cod), 4.53 (m, 2H, CH_2O), 4.03 (s, 3H, OMe), 3.84 (m, 2H, NCH_2), 3.70 (br, 2H, CH cod), 3.37 (s, 3H, MeIm), 2.62 (s, 3H, $NCCH_3$), 2.30, 1.90 (m, 4H, 4H, CH_2 cod). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 130.13 (N*C*CH$_3$), 123.12, 121.97 (CH Im), 82.73 (CH cod,), 71.27 (CH_2O), 58.12 (OMe), 50.07 (NCH_2), 36.85 (MeIm), 32.55, 29.27 (CH_2 cod), 2.16 (NC*C*H$_3$). MS (MALDI-TOF, DCTB matrix, CH_2Cl_2) *m/z* = 439.1 $[M - CH_3CN]^+$. Λ_M (acetone) = 73 $\Omega^{-1}cm^2mol^{-1}$.

[Ir(NCCH$_3$)(cod)(MeIm(2-methoxybenzyl))][BF$_4$] (14). [IrBr(cod)(MeIm(2-methoxybenzyl))] (**7**) (100 mg, 0.172 mmol), $AgBF_4$ (33.4 mg, 0.172 mmol). Yield: 61%. Anal. Calcd for $C_{22}H_{29}BF_4N_3OIr$: C, 41.91; H, 4.63; N, 6.66. Found: C, 41.50; H, 4.65; N, 6.40. ^{1}H NMR (298 K, acetone-d_6): δ 7.73−7.22 (m, 3H, CH-Ar), 7.28, 7.09 (s 1H, 1H, CH-Im), 7.03 (dd, *J* = 7.1, 1H, CH Ar), 5.53 (AB system, δ_A = 5.55, δ_B = 5.51, J_{AB} = 14.2, 2H, NCH_2), 4.43 (br, 2H, CH cod), 4.01 (s, 3H, OMe), 3.90 (s, 3H, MeIm), 3.53 (br, 2H, CH cod), 2.44 (s, 3H, $NCCH_3$), 2.31, 1.80 (m, 4H, 4H, CH_2 cod). $^{13}C\{^1H\}$ NMR (298 K, CD_2Cl_2): δ 179.51 (NCN), 157.33 (C Ar), 130.26, 129.91 (CH

Im), 129.56 (N*C*CH$_3$), 123.20, 122.01, 120.00, 110.42 (CH Ar), 120.68 (C Ar), 83.39, 82.98, 65.98, 63.78 (CH cod), 55.39 (OMe), 49.82 (NCH$_2$), 37.59 (MeIm), 33.18, 32.23, 29.91, 29.19 (CH$_2$cod), 3.58 (NC*C*H$_3$). MS (MALDI-TOF, DCTB matrix, CH_2Cl_2) *m/z* = 503.2 [M − CH_3CN] $^+$. Λ_M (acetone) = 69 $\Omega^{-1}cm^2mol^{-1}$.

[Rh(NCCH$_3$)(cod)(MeIm(CH$_2$)$_2$OMe)][BF$_4$] (15). [RhBr(cod)(MeIm(CH$_2$)$_2$OMe)] (**8**), (100 mg, 0.232 mmol), $AgBF_4$ (45.2 mg, 0.232 mmol). Yield: 65%. Anal. Calcd for $C_{17}H_{27}BF_4N_3ORh$: C, 42.62; H, 5.68; N, 8.77. Found: C, 42.99; H, 5.90; N, 8.55. ^{1}H NMR (CD_2Cl_2): δ 7.15, 7.04 (s, 1H, 1H, CH Im), 4.87 (br, 2H, CH cod), 4.64 (m, 2H, CH$_2$O), 4.04 (s, 3H, OMe), 3.81 (m, 4H, NCH$_2$, CH cod), 3.38 (s, 3H, MeIm), 2.47 (m, 4H, CH$_2$ cod), 2.31 (s, 3H, NCCH$_3$), 2.08 (m, 4H, CH$_2$ cod). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 125.06 (N*C*CH$_3$), 123.54, 122.56 (CH Im), 97.78, 77.75 (CH cod,), 71.89 (CH$_2$O), 59.18 (OMe), 50.86 (NCH$_2$), 37.91 (MeIm), 32.46, 29.32 (CH$_2$ cod), 3.41 (NC*C*H$_3$). MS (MALDI-TOF, DCTB matrix, CH_2Cl_2) *m/z* = 351.7 [M − CH_3CN]$^+$. Λ_M (acetone) = 81 $\Omega^{-1}cm^2mol^{-1}$.

[Rh(NCCH$_3$)(cod)(MeIm(*o*-methoxybenzyl))][BF$_4$] (16). [RhBr(cod)(MeIm(2-methoxybenzyl))] (**9**) (100 mg, 0.200 mmol), $AgBF_4$ (38.9 mg, 0.200 mmol). Yield: 85%. Anal. Calcd for $C_{22}H_{29}BF_4N_3ORh$: C, 48.82; H, 5.40; N, 7.76. Found: C, 48.50; H, 5.65; N, 7.40. ^{1}H NMR (298 K, $CDCl_3$): δ 7.34 (m, 2H, CH-Ar), 6.99 (m, 2H, CH-Ar), 6.97, 6.91 (s 1H, 1H, CH-Im), 5.59 (br, 2H, NCH$_2$), 4.67 (br, 2H, CH cod), 4.14 (s, 3H, OMe), 3.88 (s, 3H, MeIm), 3.49 (br, 2H, CH cod), 2.44 (s, 3H, NCCH$_3$), 2.26, 1.82 (m, 4H, 4H, CH$_2$ cod). ^{13}C{^{1}H} NMR (298 K, $CDCl_3$): δ 176.70 (d, J_{Rh-C} = 45.0, NCN), 157.37 (C Ar), 129.75, 129.52 (CH Im), 129.56 (N*C*CH$_3$), 123.50 (C Ar), 123.00, 120.78, 111.03, 110.42 (CH Ar), 99.17, 67.51 (CH cod), 55.51 (OMe), 49.85 (NCH$_2$), 37.67 (MeIm), 32.23, 28.18 (CH$_2$cod), 3.58 (NC*C*H$_3$). MS (MALDI-TOF, DCTB matrix, CH_2Cl_2) *m/z* = 413.4 [M − CH_3CN] $^+$. Λ_M (acetone) = 72 $\Omega^{-1}cm^2mol^{-1}$.

Preparation of [Ir(cod)(MeIm(pyridin-2-ylmethyl))][BF_4] (17). The synthesis was carried out in two steps. Step 1: A mixture of [MeImH(pyridin-2-ylmethyl)]Br (**3**) (254 mg, 1.00 mmol), and Ag_2O (116 mg, 0.5 mmol) was refluxed in dichloromethane (20 mL) for 90 minutes. The excess of Ag_2O was removed by filtration to give a colorless solution of the NHC-silver complex. Step 2: The solvato complex $[Ir(cod)(OCMe_2)_2]^+$ (1 mmol), prepared *in situ* from $AgBF_4$ (195 mg, 1.00 mmol) and $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ (336 mg, 0.500 mmol) in acetone (15 mL), was added to concentrated solutions of the NHC-silver complexes in CH_2Cl_2 (1 mL) obtained from step 1. The mixture was stirred for 3 h at room temperature to give a brownish suspension. The AgX formed was filtered off to give an orange solution. The solvent was removed under vacuum and the residue treated with cold pentane several times to afford the compound as an orange solid which was separated by decantation and dried in vacuum. Yield: 77%. Anal. Calcd for $C_{18}H_{23}BF_4N_3Ir$: C, 38.58; H, 4.14; N, 7.50. Found: C, 38.57; H, 4.11; N, 7.51. ^{1}H NMR (298 K, acetone-d_6): δ 8.78 (d, J = 5.3, 1H, CH py), 8.09 (td, *J* = 7.6, 1.5, 1H, CH py), 7.94 (m, 1H, CH py), 7.62 (ddd, J = 7.6, 5.3, 1.5, 1H, CH py), 7.49 (d, *J* = 1.7, 1H, CH Im), 7.24 (d, *J* = 1.7, 1H, CH Im), 5.75 (AB system, δ_A = 5.77, δ_B = 5.63, J_{AB} = 14.3, 2H, NCH_2), 4.60, 4.46, 4.15, 4.07 (m, 1H, 1H, 1H, 1H, CH cod), 3.87 (s, 3H, MeIm), 2.45, 2.15, 1.77 (m, 2H, 4H, 2H, CH_2 cod). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 173.47 (NCN), 152.90 (C py), 151.86, 140.19, 126.53, 125.79 (CH py), 123.34, 121.62 (CH Im), 84.53, 83.70, 65.44 (CH cod), 65.23 (NCH_2), 58.77 (CH cod), 36.97 (MeIm), 32.76, 32.44, 29.84 (CH_2 cod). MS (MALDI-TOF, DCTB matrix, CH_2Cl_2) *m/z* = 474.2 $[M]^+$. Λ_M (acetone) = 67 $\Omega^{-1}cm^2mol^{-1}$.

Preparation of [Ir(cod)(MeIm(CH_2)$_3$$NMe_2$)][$BF_4$] (18). The compound was prepared from [MeImH(CH_2)$_3$$NHMe_2$)]$Cl_2$ (**5**) (120 mg, 0.500 mmol), Ag_2O (57.9 mg, 0.250 mmol) and $[Ir(cod)(OCMe_2)_2]BF_4$ (0.500 mmol) following the two-step procedure described above for **17**. Yield: 60%. Anal. Calcd for $C_{17}H_{29}BF_4N_3Ir$: C, 36.83; H, 5.27; N, 7.59. Found: C, 36.98; H, 6.79; N, 7.51. ^{1}H NMR (298 K, $CDCl_3$): δ 7.32 (s, 1H, CH Im), 7.01 (s, 1H, CH Im), 4.76 (m, 2H, CH_2N), 4.40 (m, 1H, NCH_2), 4.25 (br, 2H, CH cod), 4.16 (m, 1H, NCH_2), 3.93 (s, 3H, MeIm), 3.36 (m, 2H,

CH cod), 2.56 (s, 6H, NMe_2), 2.35 (m, 1H, CH_2), 2.30 (m, 4H, CH_2 cod), 1.93 (m, 1H, CH_2), 1.75 (m, 4H, CH_2 cod). $^{13}C\{^1H\}$ NMR (298 K, $CDCl_3$): δ 173.62 (NCN), 123.37, 12183 (CH Im), 85.17, 83.24, 70.70 (CH cod), 66.08 (NCH_2), 65.32 (CH cod), 47.10 (CH_2N), 44.20 (NMe_2), 37.34 (MeIm), 33.45, 32.10 (CH_2 cod), 31.23 (CH_2), 29.07, 26.60 (CH_2 cod). MS (MALDI-TOF, DCTB matrix, CH_2Cl_2) *m/z* = 468.2 $[M]^+$. Λ_M (acetone) = 78 $\Omega^{-1}cm^2mol^{-1}$.

Reaction of 7 with potassium isopropoxide. [IrBr(cod)(MeIm(2-methoxybenzyl))] (**7**) (20.0 mg, 0.034 mmol) and K[O*i*Pr] (2.79 mg, 0.034 mmol) were reacted in THF-d_8 (0.5 mL, NMR tube) to give a solution of [Ir(O*i*Pr)(cod)(MeIm(2-methoxybenzyl))] (**19**). ^1H NMR (298 K, THF-d_8): δ 7.43 (d, *J* = 7.7, 1H, CH Ar), 7.33 (dd, *J* = 8.2, 7.7, 1H, CH Ar), 7.06 (d, *J* = 8.2, 1H, CH Ar), 7.04 (d, *J* = 2.0, 1H, CH Im), 6.95 (d, *J* = 7.7, 1H, CH Ar), 6.93 (d, *J* = 2.0, 1H, CH Im), 5.77 (AB system, δ_A = 5.91, δ_B = 5.64, J_{AB} = 14.7, 2H, NCH_2), 4.38 (m, 2H, CH cod), 4.06 (s, 3H, OMe), 3.95 (s, 3H, MeIm), 3.90 (m, 2H, CH cod), 3.67 (m, 1H, C*H*$(CH_3)_2$), 2.40, 2.22, 1.65 (m, 2H, 4H, 2H, CH_2 cod), 0.95 (dd, *J* = 5.6, 4.0, m, 6H, CH(C*H*$_3)_2$). ESI-MS (*i*-PrOH) *m/z* = 503.1 ($[M - PrO]^+$, 100%). MS (MALDI-TOF, DCTB matrix, *i*-PrOH, linear analysis) *m/z* = 585 $[M + Na]^+$, 503.1 $[M - OPr]^+$.

Reaction of 7 with sodium cyclohexanoxide. A suspension of [IrBr(cod)(MeIm(2-methoxybenzyl))] (**7**) (20 mg, 0.03 mmol) and NaOCy (4.2 mg, 0.03 mmol) in THF-d_8 (0.5 mL, NMR tube) was stirred at 298 K to give a orange solution containing [Ir(OCy)(cod)(MeIm(2-methoxybenzyl))] (**20**). ^{1}NMR (298 K, TDF-d_8) data for **20**: δ 7.39 (d, *J* = 7.5, 1H, CH Ar), 7.29 (t, *J* = 7.5, 1H, CH Ar), 7.13 (m, 1H, CH Ar), 7.00 (d, *J* = 1.8, 1H, CH Im), 6.92 (m, 1H, CH Ar), 6.89 (d, *J* = 1.8, 1H, CH Im), 5.73 (AB system, δ_A = 5.63, δ_B = 5.84, J_{AB} = 15.0, 2H, NCH_2), 4.37 (m, 2H, CH-cod), 4.02 (s, 3H, OMe), 3.92 (s, 3H, MeIm), 3.47 (m, 1H, CH OC_6H_{11}), 3.16 (m, 2H, CH cod), 2.19 (m, 4H, CH_2 cod), 2.40 (m, 4H, CH_2 OC_6H_{11}), 1.59 (m, 2H, CH_2 cod), 1.54, 1.24 (m, 4H, CH_2 OC_6H_{11}),1.09 (m, 2H, CH_2 cod), 0.91(m, 2H, CH_2 OC_6H_{11}).

Preparation of [IrHBr(NCCH$_3$)(cod)(MeIm(2-methoxybenzyl))][BF$_4$] (22). $HBF_4 \cdot Et_2O$ (27.8 mg, 0.172 mmol) was added to a solution of [IrBr(cod)(MeIm(2-methoxybenzyl))] (**7**) (100 mg, 0.172 mmol) in acetone (10 mL) and CH_3CN (52 μL, 1 mmol). After 1 hour of stirring at room temperature the colorless solution was concentrated to *ca.* 1 mL. Treatment of the pale yellow residue with cold pentane rendered a yellowish solid which was separated by decantation, washed with hexane and dried in vacuo. Yield: 85.9%. Anal. calcd for $C_{20}H_{27}N_2OIrBrBF_4$: C, 35.83; H, 4.05; N, 4.17. Found: C, 35.55; H, 4.55; N, 4.29. MS (MALDI-TOF, DCTB matrix, CH_2Cl_2) *m/z* = 623.1 $[M - H]^+$, 503.1 $[M - H - Br - NCCH_3]^+$. Λ_M (acetone) = 77 $\Omega^{-1}cm^2mol^{-1}$. **Isomer 22a**: ^{1}H NMR (253 K, CD_2Cl_2): δ 7.39 (t, *J* = 7.7, 1H, CH Ar), 7.19 (d, *J* = 7.0, 1H, CH Ar), 7.05 (m, 2H, CH Ar), 7.03, 7.00 (s, 1H, 1H, CH Im), 5.76 (AB system, δ_A = 6.45, δ_B = 5.07, J_{AB} = 16.2, 2H, NCH_2), 4.90, 4.54 (m, 2H, CH-cod), 3.99 (s, 3H, OMe), 3.94 (s, 3H, MeIm), 3.57 (m, 2H, CH_2 cod), 1.24 (s, 3H, $NCCH_3$), 2.77, 2.15, 2.08 (m, 2H, 2H, 2H, CH_2 cod), -14.51 (s, 1H, Ir-H). $^{13}C\{^1H\}$ NMR (253 K, CD_2Cl_2): δ 173.46 (NCN), 156.84, 142.45 (C Ar), 129.75 127.74 (CH Ar), 124.55 (N*C*CH$_3$), 120.78, 110.55 (CH Ar), 101.34, 98.75 (CH Im), 77.07, 75.47, 65.41, 62.95 (CH cod), 55.67 (OMe), 51.96 (CH_2), 39.19 (MeIm), 33.28, 29.95, 29.10, 27.87 (CH_2 cod), 4.24 (NC*C*H$_3$). **Isomer 22b**: ^{1}H NMR (298 K, CD_2Cl_2): δ 7.38 (t, *J* = 7.8, 1H, CH Ar), 7.29 (d, *J* = 7.2, 1H, CH Ar), 7.19 (d, *J* = 2.0, 1H, CH Im), 6.90 (m, 1H, CH Ar), 6.81 (d, *J* = 2.0, 1H, CH Im), 6.69 (d, *J* = 7.2, 1H, CH Ar), 5.68 (m, 1H, CH cod), 5.40 (AB system, δ_A = 5.45, δ_B = 5.36, J_{AB} = 14.0, 2H, NCH_2), 5.45 (m, 1H, CH cod), 4.45, 4.21 (m, 1H, 1H, CH cod), 4.15 (s, 3H, OMe), 3.92 (s, 3H, MeIm), 2.75 (s, 3H, $NCCH_3$), 2.67, 2.21, 1.92, 1.40 (m, 2H, 2H, 2H, 2H, CH_2 cod), -14.30 (s, 1H, Ir-H). $^{13}C\{^1H\}$ NMR (253 K, CD_2Cl_2): δ 172.54 (NCN), 156.17, 143.37 (C Ar), 130.14, 127.14, (CH Ar), 124.39 (N*C*CH$_3$), 120.19, 110.10 (CH Ar), 102.96, 100.34 (CH Im), 83.07, 82.64, 75.65, 74.69 (CH cod), 55.58 (OMe), 49.77 (CH_2), 41.57 (MeIm), 35.44, 32.19, 30.71, 25.57 (CH_2 cod), 2.60 (NC*C*H$_3$).

Preparation of 1-(2-methoxyphenyl)-3-methyl-1*H*-imidazol-3-ium iodide (23). Methyliodide (326 μL, 5.24 mmol) was added to a solution of 2-methoxyphenyl imidazole (900 mg, 5.24 mmol), prepared following the general procedure described by Zhang[51] for the preparation of 1-arylimidazoles, and the mixture was refluxed for 12 h. The yellow solid formed was separated by decantation, washed with hot diethyl ether and dried in vacuum. Yield: 85%. Anal. Calcd for $C_{11}H_{13}IN_2O$: C, 41.79; H, 4.14; N, 8.86. Found: C, 41.33; H 4.09; N, 8.89. ^{1}H NMR (298 K, CD_3OD): δ 9.35 (s, 1H, NCHN), 7.88 (m, 1H, CH Im), 7.79 (m, 1H, CH Im), 7.62 (d, *J* = 7.6, 1H, CH Ar), 7.62 (d, *J* = 7.8, 1H, CH Ar), 7.36 (dd, *J* = 8.9, 1.2, 1H, CH Ar), 7.20 (td, *J* = 7.7, 1.2, 1H, CH Ar), 4.08 (s, 3H, OMe), 3.96 (s, 3H, MeIm). ^{13}C{^{1}H} NMR (298 K, $CDCl_3$): δ 153.82 (C Ar), 142.43 (NCHN), 133.14, 127.06 (CH Ar), 126.18 (C Ar), 125.02, 124.73 (CH Im), 122.50, 114.19 (CH Ar), 57.04 (OMe), 37.13 (MeIm). ESI-MS (CH_3OH) *m/z* = 189.3 $[M]^+$.

Preparation of [IrBr(cod)(MeIm(2-methoxyphenyl))] (24). [{Ir(μ-OMe)(cod)}$_2$] (106 mg, 0.160 mmol) and [MeImH(2-methoxybenzyl)]I (100 mg, 0.319 mmol) were reacted in THF (10 mL). Work up as described above for compounds **6**-**9** gave the compound as a yellow brownish solid. Yield: 69%. Anal. Calcd for $C_{19}H_{24}IN_2OIr$: C, 37.07; H, 3.93; N, 4.55. Found: C, 37.15; H, 4.41; N, 4.87. ^{1}H NMR (298 K, C_6D_6): δ 8.86 (dd, *J* = 7.7, 1.5, 1H, CH), 7.13 (ddd, *J* = 8.5, 7.7, 1.8, 1H, CH), 6.94 (td, *J* = 7.7, 1.3, 1H, CH), 6.63 (d, *J* = 2.0, 1H, CH Im), 6.53 (dd, *J* = 8.5, 1.3, 1H, CH), 6.15 (d, *J* = 2.0, 1H, CH Im), 5.29, 5.23 (m, 1H, 1H, CH cod), 3.59 (s, 3H, MeIm), 3.13 (s, 3H, OMe), 3.10, 2.72 (m, 1H, 1H, CH cod), 2.13, 1.88, 1.63, 1.51, 1.34, 1.15 (m, 2H, 1H, 1H, 2H, 1H, 1H, CH_2 cod). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 181.47 (NCN), 153.55 (C Ar), 131.28, 129.57 (CH Ar), 123.30, 121.14 (CH Im), 124.82 (C Ar), 120.53, 110.94 (CH Ar), 83.45, 81.57 (CH cod), 55.07 (CH cod), 53.61 (OMe), 53.45 (CH cod), 37.51 (MeIm), 34.03, 32.29, 30.91, 30.45 (CH_2 cod). MS (MALDI-TOF, DCTB matrix, CH_2Cl_2) *m/z* = 615.1 $[M]^+$, 488.2 $[M - Br]^+$. Λ_M (acetone) = 18 $\Omega^{-1}cm^2mol^{-1}$.

General Procedure for Transfer Hydrogenation Catalysis. The catalytic transfer hydrogenation reactions were carried out under an argon atmosphere in thick glass reaction tubes fitted with a greaseless high-vacuum stopcock. In a typical experiment, the reactor was charged with a solution of the substrate (5 mmol) in 2-propanol (4.5 mL), internal standard (mesitylene, 70 μL, 0.5 mmol), base (104 μL, 0.025 mmol of a KOH solution 0.24 M in 2-propanol) and the catalyst (0.005 mmol, 0.1 mol%). The resulting mixture was stirred at room temperature until complete solution of the catalyst and then placed in a thermostatized oil bath at the required temperature, typically 80 ºC. Conversions were determined by Gas Chromatography analysis under the following conditions: column temperature 35 ºC (2 min) to 220 ºC at 10 ºC/min at flow rate of 1 mL/min using ultra pure He as carrier gas.

Calculation details. DFT calculations have been carried out with Gaussian 09[62] using the B3LYP functional with a 6-31G** basis set for all atoms but Ir where the LANL2DZ basis set and pseudopotential has been used. The molecular structure was treated in full without any simplification of the ligands. Optimizations have been carried out using the "verytight" keyword and an "ultrafine" grid for integration. All the minima have been characterized by frequency calculations, all the intermediates, but **19'**, show positive frequencies. For the intermediate **19'** a small negative frequency remains (-12.89 cm^{-1}) which, by visual inspection, seems to be associated to a rotational movement on the ligands.

X-ray Structural Determination of Complexes [IrBr(cod)(MeIm(*o*-methoxybenzyl))] (7) and [IrHBr(NCCH$_3$)(cod)(MeIm(2-methoxybenzyl))][BF$_4$] (22). Suitable crystals for the X-ray diffraction experiments were obtained at 273K for complex **7** by slow diffusion of pentane into a concentrated THF solution and for complex **22** by slow diffusion of diethyl ether into a concentrated acetone/acetonitrile solution. Intensity data were collected at low temperature (100(2)K) on a Bruker SMART CCD area detector diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) using narrow frames (0.3˚ in ω). Cell parameters were refined from the

observed setting angles and detector positions of strong reflections (5259 refl., $2\theta < 54.0^{o}$ for **7**, and 6751 refl., $2\theta < 53.96^{o}$ for **22**). Data were corrected for Lorentz and polarization effects, and a semi empirical absorption correction was applied using SADABS program.[63] The structure was solved by Patterson method and completed by successive difference Fourier syntheses (SHELXS-86).[64] Refinement was carried out by full-matrix least-squares on F^2 with SHELXL97,[64] including isotropic and subsequent anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were included from calculated positions and refined riding on their carbon atoms. For **22**, high values of the Flack parameter suggested the existence of a partial component of a racemic twin, so this parameter was included as a free variable in the refinement; a final value of 0.234(5) was obtained. The hydride atoms in this second complex (**22**) were included in the last cycles of refinement from an electrostatic potential calculation and were refined with a light geometrical restriction affecting the Ir-H bond distance. All the highest electronic residuals in both structures (smaller than 1.41 e/Å^3) were observed in close proximity of the Ir metal and have no chemical sense. Atomic scattering factors, corrected for anomalous dispersion, were used as implemented in the refinement programs.[64]

Crystal data for compound 7: $C_{20}H_{26}BrIrN_2O$, M = 582.54; yellow block, 0.16 x 0.15 x 0.15 mm^3; monoclinic, $P2_1/n$; a = 14.346(2), b = 10.8182(17), c = 14.463(2) Å; β = 119.226(2)°; Z = 4; V = 1958.9(5) Å^3; D_c = 1.975 g/cm^3; μ = 8.866 mm^{-1}, min. and max. transmission factors 0.245 and 0.265; $2\theta_{max}$ = 54.20°; 12159 reflections collected, 4289 unique [R_{int} = 0.0301]; number of data/restrains/parameters 4289/0/228; final *GoF* 1.039, R_1 = 0.0269 [3856 reflections, $I > 2\sigma(I)$], wR_2 = 0.0651 for all data.

Crystal data for compound 22: $C_{22}H_{30}BBrF_4IrN_3O$, M = 711.41; pale yellow block, 0.12 x 0.11 x 0.09 mm^3; monoclinic, $P2_1$; a = 14.611(3), b = 7.7625(16), c = 21.751(5) Å; β = 96.143(3)°; Z = 4; V = 2452.9(9) Å^3; D_c = 1.926 g/cm^3; μ = 7.122 mm^{-1}, min. and max. transmission factors 0.482 and

0.567; $2\theta_{max}$ = 54.12º; 29262 reflections collected, 10682 unique [R_{int} = 0.0337]; number of data/restrains/parameters 10682/27/610; final *GoF* 1.051, R_1 = 0.0265 [10389 reflections, $I > 2\sigma(I)$], wR_2 = 0.0563 for all data.

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Supporting Information Available: Kinetic data for hydrogen transfer catalysis. Full ESI and MALDI-TOF MS. Computational information: calculated data (B3LYP) for catalytic intermediates. X-ray crystallographic information files containing full details of the structural analysis of complexes **7** and **22** (CIF format) is available free of charge via Internet at http://pubs.acs.org.

References

(1) (a) Hahn, F. E.; Jahnke. M. C. *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172. (b) Crudden, C. M.; Allen. D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247–2273. (c) Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309.

(2) (a) Benhamou, L.; Chardon, E.; Lavigne G.; Bellemin-Laponnaz, S.; César, V. *Chem. Rev.* **2011,** *111*, 2705–2733. (b) Peris E. *Top. Organomet. Chem* **2007**, *21*, 83–116.

(3) (a) Peris, E.; Crabtree, R. H. Iridium *N*-Heterocyclic Carbene Complexes and their Application as Homogeneous Catalysts. In *Iridium Complexes Organic Synthesis*; Oro, L. A., Claver, C., Eds.; Wiley-VCH-Verlag: Weinheim, Germany, 2009; pp 39–54. (b) Markò, I. E.; Stèrin, S.; Buisine, O.;

Mignani, G.; Branlard, P.; Tinant, B.; Declercq, J. P. *Science* **2002**, *298*, 204–206. (c) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics* **2001**, *20*, 5314–5318. (d) Weskamp, T.; Böhm, V. P. W.; Herrmann, W. A. *J. Organomet. Chem.* **2000**, *600*, 12–22. (e) Torres, O.; Martín, M.; Sola, E. *Organometallics* **2009**, *28*, 863-870.

(4) (a) Kwong, F. Y.; Chan, A. S. C. *Synlett* **2008**, 1440–1448. (b) Braunstein P.; Naud, F. *Angew. Chem. Int. Ed.* **2001**, *40*, 680–699. (c) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27–110.

(5) (a) Kühl, O. *Functionalised N-heterocyclic carbene complexes*; Wiley: Chichester, U.K., 2010. (b) Normand, A. T.; Cavell, K. J. *Eur. J. Inorg. Chem.* **2008**, 2781–2800 (c) Kühl, O. *Chem. Soc. Rev.* **2007**, *36*, 592–607.

(6) (a) Jiménez, M. V.; Pérez-Torrente, J. J.; Bartolomé, M. I.; Gierz, V.; Lahoz, F. J.; Oro, L. A. *Organometallics*, **2008**, *27*, 224–234. (b) Díez-González, S.; Nolan S. P. *Coord. Chem. Rev.* **2007**, *251*, 874–883. (c) Lee, H. M.; Lee, C. -C.; Cheng, P. -Y. *Curr. Org. Chem.* **2007**, *11*, 1491–1524. (d) Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309.

(7) (a) Gulcemal, S.; Daran, J.-C.; Cetinkaya, B. *Inorg. Chim. Acta* **2011**, *365*, 264–268. (b) Yang, X.; Fei, Z.; Geldbach, T. J.; Phillips, A. D.; Hartinger, C. G.; Li, Y.; Dyson, P. J. *Organometallics* **2008**, *27*, 3971–3977. (c) Ohta, H.; Fujihara, T.; Tsuji, Y. *Dalton Trans.* **2008**, 379–385. (d) Kuhlman, E.; Himmler, S.; Giebelhaus, H.; Wasserscheid, P. *Green Chem.* **2007**, *9*, 233–242.

(8) (a) Jiménez, M. V.; Pérez-Torrente, J. J.; Bartolomé, M. I.; Vispe, E.; Lahoz, F. J.; Oro, L. A. *Macromolecules* **2009**, *42*, 8146–8156. (b) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Chem. Soc. Rev.* **2004**, *33*, 619–636. (c) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750–3781. (d) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009–3066.

(9) (a) Guijarro, D.; Oscar, P.; Yus, M. *Tetrahedron Lett.* **2011**, *52*, 789–791. (b) Haraguchi, N.; Tsuru, K.; Arakawa, Y.; Itsuno, S. *Org. Biomol. Chem.* **2009**, *7*, 69–75. (c) Canivet, J.; Süss-Fink, G. *Green Chem.* **2007**, *9*, 391–397. (d) Ikariya, T.; Blacker, A. J. *Acc. Chem. Res.* **2007**, *40*, 1300–1308.

(10) (a) Gladiali, S.; Alberico, E. *Chem. Soc. Rev.* **2006**, *35*, 226–236. (b) Gladiali, S.; Mestroni, G. Transferhydrogenations. In *Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, Germany, 1998, vol. 2; pp 97–119.

(11) (a) Noyori, R.; Hashiguchi. S. *Acc. Chem. Res.* **1997**, *30*, 97–102. (b) Hashiguchi, S.; Fujii, A.; Takehara, J.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.*, **1995**, *117*, 7562–7563.

(12) (a) Pontes da Costa, A.; Viciano, M.; Sanaú, M.; Merino, S.; Tejeda, J.; Peris, E.; Royo, B. *Organometallics* **2008,** *27*, 1305–1309. (b) Hahn, F. E.; Holtgrewe, C.; Pape, T.; Martin, M.; Sola, E.; Oro, L. A. *Organometallics* **2005**, *24*, 2203–2209. (c) Mas-Marzá, E.; Poyatos, M.; Sanaú, M.; Peris, E. *Organometallics* **2004**, *23*, 323–325. (d) Albrecht, M.; Crabtree, R. H.; Mata, J. A.; Peris, E. *Chem. Commun.* **2002**, 32–33. (e) Hillier, A. C.; Lee, H. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001,** *20*, 4246–4252. (f) Kownacki, I.; Kubicki, M.; Szubert, K.; Marciniec, B. *J. Organomet. Chem.* **2008**, *693*, 321–328.

(13) (a) Miecznikowski, J. R.; Crabtree, R. H. *Organometallics* **2004**, *23*, 629–631. (b) Miecznikowski, J. R.; Crabtree, R. H. *Polyhedron* **2004**, *23*, 2857–2872. (c) Albrecht, M.; Miecznikowski, J. R.; Samuel, A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 3596–3604.

(14) Jiménez, M. V.; Pérez-Torrente, J. J.; Bartolomé, M. I.; Oro, L. A. *Synthesis*, **2009**, 1916–1922.

(15) Jiménez, M. V.; Pérez-Torrente, J. J.; Bartolomé, M. I.; Lahoz, F. J.; Oro, L. A. *Chem. Commun.* **2010**, *46*, 5322–5324.

(16) Angoy, M.; Bartolomé, M. I.; Vispe, E.; Lebeda, P.; Jiménez, M. V.; Pérez-Torrente, J. J.; Collins, S.; Oro, L. A. *Macromolecules* **2010**, *43*, 6278–6283.

(17) Türkmen, H.; Pape, T.; Hahn, F. E.; Çetinkaya, B. *Eur. J. Inorg. Chem.* **2008**, 5418–5423.

(18) Binobaid, A.; Iglesias, M.; Beetstra, D.; Dervisi, A.; Fallis, I.; Cavell, K. J. *Eur. J. Inorg. Chem.* **2010**, 5426–5431.

(19) (a) Wasserscheid, P.; Welton, T. in *Ionic Liquids in Synthesis*; Wiley-VCH: Weinheim, Germany, 2003. (b) Fei, Z.; Ang, W. H.; Zhao, D.; Scopelliti, R.; Zvereva, E. E.; Katsyuba, S. A.; Dyson P. J. *J. Phys. Chem. B* **2007**, *111*, 10095–10108. (c) Jahnke, M. C.; Pape, T.; Hahn, E. F. *Eur. J. Inorg. Chem.* **2009**, 1960–1969.

(20) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741–748.

(21) Danthi, S. N.; Hill, R. A. *J. Heterocyclic Chem.* **1997**, *34*, 835–844.

(22) Ray, L.; Shaikh, M. M.; Ghosh, P. *Organometallics* **2007**, *26*, 958–964.

(23) Crabtree, R. H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *135*, 395–403.

(24) (a) Wolf, S.; Plenio, H. *J. Organomet. Chem.* **2009**, *694*, 1487–1492. (b) Bittermann, A.; Härtera, P.; Herdtwecka, E.; Hoffmann, S. D.; Herrmann, W. A. *J. Organomet. Chem.* **2008**, *693*, 2079–2090. (c) Frey, G. D.; Rentzsch, C. F.; von Preysing, D.; Scherg, T.; Mühlhofer, M.; Herdtweck, E.; Herrmann, W. A. *J. Organomet. Chem.* **2006**, *691*, 5725–5738.

(25) (a) Wylie W. N. O; Lough, A. J.; Morris, R. H. *Organometallics* **2009**, *28*, 6755–6761. (b) Wang, C. -Y.; Fu, C. -F.; Liu, Y. -H.; Peng, S. -M.; Liu, S. -T. *Inorg. Chem.* **2007**, *46*, 5779–5786. (c) Winston, S.; Stylianides, N.; Tulloch, A. A. D.; Wright, J. A.; Danopoulos, A. A. *Polyhedron*, **2004**, *23*, 2813–2820. (d) Mas-Marza, E.; Sanau, M.; Peris, E. *Inorg. Chem.* **2005**, *44*, 9961–9967.

(26) Türkmen, H.; Pape, T.; Hahn, F. E.; ¸Çetinkaya, B. *Organometallics* **2008**, *27*, 571–575.

(27) (a) Carrión, M. C.; Sepúlveda, F.; Jalón, F. A.; Manzano, B. R.; Rodríguez, A. M. *Organometallics*, **2009**, *28*, 3822–3833. (b) Cohen, R.; Graves, C. R.; Nguyen, S. T.; Martin, J. M. L.; Ratner, M. A. *J. Am. Chem. Soc.* **2004**, *126*, 14796–14803.

(28) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2008**, *27*, 3240–3247.

(29) Baratta, W.; Siega, K.; Rigo, P. *Adv. Synth. Catal.* **2007**, *349*, 1633–1636.

(30) Wu, X.; Liu, J.; Li, X.; Zanotti-Gerosa, A.; Hancock, F.; Vinci, D.; Ruan, J.; Xiao, J. *Angew. Chem. Int. Ed.* **2006**, *45*, 6718–6722.

(31) Chaplin, A. B.; Dyson, P. J. *Organometallics* **2007,** *26*, 4357–4360.

(32) Jana, P. P.; Sarma, R.; Baruah, J. B. *J. Mol. Catal. A: Chem.* **2008**, *289*, 57–60.

(33) Ram, S.; Spicer, L. D. *Synth. Commun.* **1992**, *22*, 2673–2681.

(34) Clarke, Z. E.; Maragh, P. T.; Dasgupta, T. P.; Gusev, D. G.; Lough, A. J.; Abdur-Rashid K. *Organometallics* **2006**, *25*, 4113–4117.

(35) Bianchini, C.; Farnetti, E.; Glendenning, L.; Graziani, M.; Nardin, J. G.; Peruzzini, M.; Rocchini, E.; Zanobini, F. *Organometallics* **1996**, *14*, 1489–1502.

(36) Milone, C.; Crisafulli, C.; Ingogli, R.; Schipilliti, L.; Galvagno, S. *Catal. Today* **2007**, *122*, 341–351.

(37) Naskar, S.; Bhattacharjee, M. *Tetrahedron Lett.* **2007**, *48*, 465–467.

(38) Chin, C. S.; Lee, B. *J. Chem. Soc., Dalton Trans.* **1991**, 1323–1327.

(39) (a) Saidi, O.; Williams, J. M. J. *Top Organomet. Chem.* **2011**, *34*, 77–106. (b) Han, J.; Kang, S.; Lee, H. -K. *Chem. Commun.* **2011**, *47*, 4004–4006. (c) Casey, C. P.; Singer, S. W.; Powell, D. R.; Hayashi, R. K.; Kavana, M. *J. Am. Chem. Soc.* **2001**, *123*, 1090–1100. d) Wang, G. -Z.; Bäckvall, J.-E. *J. Chem. Soc., Chem. Commun.* **1992**, 980–982. (e) Watanabe, Y.; Tsuji, Y.; Ige, H.; Ohsugi, Y.; Ohta, T. *J. Org. Chem.* **1984**, *49*, 3359–3363.

(40) (a) Martín, M.; Sola, E.; Tejero, S.; Andrés, J. L.; Oro, L. A. *Chem. Eur. J.* **2006**, *12*, 4046–4056. (b) Fleury-Brégeot, N.; De la Fuente, V.; Castillón, S.; Claver, C. *ChemCatChem* **2010**, *2*, 1346–1371.

(41) (a) Shvo, Y.; Czarkie, D.; Rahamim, Y.; Chodosh, D. F. *J. Am. Chem. Soc*. **1986**, *108*, 7400–7402. (b) Samec, J. S. M.; Bäckvall J. -E. *Chem. Eur. J.* **2002**, *8*, 2955.

(42) Gnanamgari, D.; Moores, A.; Rajaseelan, E.; Crabtree, R. H. *Organometallics* **2007**, *26*, 1226–1230.

(43) Danopoulos, A. A.; Winston, S.; Motherwell, W. B. *Chem. Commun* **2002**, 1376–1377.

(44) Yamakawa, M.; Ito, H.; Noyori, R. *J. Am. Chem. Soc.* **2000**, *122*, 1466–1478.

(45) Samec, J. S. M.; Bäckvall, J. -E.; Andersson, P. G.; Brandt, P. *Chem. Soc. Rev.* **2006**, *35*, 237–248.

(46) Pàmies, O.; Bäckvall, J.-E. *Chem. Eur. J.* **2001**, *7*, 5052–5058.

(47) (a) Vicent, C.; Viciano, M.; Mas-Marza, E.; Sanau, M.; Peris, E. *Organometallics* **2006**, *25*, 3713–3720. (b) Bakhtiar, R; Hop, C. *J. Phys. Org. Chem.* **1999**, *12*, 511–527.

(48) The MALDI-TOF analysis has been preformed in linear mode due to the existence of meta-stable species. The MS spectra in reflector mode showed exclusively the species with a ratio m/z of 705.1, and those derived from its fragmentation, but no the ion molecular corresponding to the catalyst precursor. In spite of the lower resolution associated to the linear mode, it has been possible to obtain the isotopic pattern of the studied species.

(49) Guiral, V.; Delbecq, F.; Sautet, P. *Organometallics* **2000**, *19*, 1589-1598.

(50) Sun, J. -F.; Chen, F.; Dougan, B. A.; Xu, H. -J.; Cheng, Y.; Li, Y. -Z.; Chen, X. -T.; Xue, Z. -L. *J. Organomet. Chem.* **2009**, *694*, 2096–2105.

(51) Liu, J.; Chen, J.; Zhao, J.; Zhao, Y.; Li, L.; Zhang, H. *Synthesis* **2003**, 2661–2666.

(52) Niu, S.; Hall, M. B. *Chem. Rev.* **2000**, *100*, 353–405.

(53) Ng, S. M.; Zhao, C.; Lin, Z. *J. Organomet. Chem.* **2002**, *662*, 120–129.

(54) (a) Itagaki, H.; Koga, N.; Morokuma, K.; Saito, Y. *Organometallics* **1993**, *12*, 1648–1654. (b) Yamakawa, M.; Ito, H.; Noyori, R. *J. Am. Chem. Soc.* **2000**, *122*, 1466–1478.

(55) Blum, O.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 4582–4594.

(56) Macgregor, S. A.; Vadivelu, P. *Organometallics* **2007**, *26*, 3651−3659.

(57) Bernard, K. A.; Rees, W. M.; Atwood, J. D. *Organometallics* **1986**, *5*, 390−391.

(58) Zhao, J.; Hesslink, H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 7220−7227.

(59) Ulmer, L.; Mattay, J.; Torres-García, H. G.; Luftmann, H. *Eur. J. Mass Spectrom.* **2000**, *6*, 49–52.

(60) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 18–20.

(61) Usón, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 126–127.

(62) Gaussian 09, Revision **A.1**, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

(63) *SAINT+ Software for CCD Diffractometers*; Bruker AXS: Madison, WI, 2000. Sheldrick, G. M. *SADABS Program for Correction of Area Detector Data*; University of Göttingen: Göttingen, Germany, 1999.

(64) *SHELXTL Package*, v. 6.10; Bruker AXS: Madison, WI, 2000. Sheldrick, G. M. *SHELXS-86 and SHELXL-97*; University of Göttingen; Göttingen, Germany, 1997.

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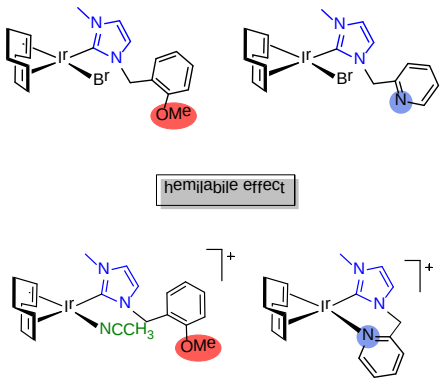

The design of hydrogen transfer catalyst based on O- and N-donor functionalized NHC ligands having methoxy, dimetylamino and pyridine as donor functions, has allowed establishing the basis for the positive hemilabile effect observed for the catalytic reduction of a range of unsaturated substrates including ketones, aldehydes and imines.