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N-Benzyl Substituted N-Heterocyclic Carbene Complexes of Iridium(I): Assessment in Transfer Hydrogenation Catalyst

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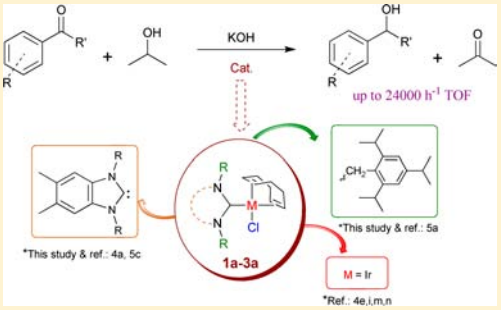
Supporting Information

ABSTRACT: Iridium(I) complexes of N-heterocyclic carbenes (NHCs) (**1a**−**3a**) were obtained by transmetalation reactions from the corresponding Ag(I)-NHC complexes. These complexes have been fully characterized by ^{1}H, ^{13}C, heteronuclear multiple-bond correlation NMR spectroscopies, and elemental analysis. X-ray diffraction studies on single crystals of **1a** and **2a** confirm the square planar geometry at the metal center. $[IrCl(CO)_2(NHC)]$ complexes **1b**−**3b** were also synthesized to compare σ-donor/π-acceptor strength of NHC ligands. Transfer hydrogenation (TH) reactions of various ketones and imines have been studied using complexes **1a**−**3a** as precatalysts. N-Benzyl substituted NHC complexes of Ir(I) proved to be highly efficient precatalysts in the reduction of aromatic and aliphatic ketones to afford the corresponding alcohol products with turnover frequencies values up to 24 000 h^{-1}.



INTRODUCTION

During the past decade, N-heterocyclic carbenes (NHCs), often compared to phosphine ligands, have emerged as a versalite class of ligands. For the purpose of catalytic applications, they often give more stable complexes due to the strength of the metal−NHC bond and thus avoid the use of an excess of phosphine ligands.[1] Examples of iridium, rhodium, and ruthenium complexes bearing NHC ligands have been shown to be very good precatalysts for numerous reduction reactions, among those hydrogenation, transfer hydrogenation (TH), and hydrosilylation reactions.[2]

TH is a metal-catalyzed process that requires a hydrogen donor atom, typically 2-propanol, in combination with a strong base.[2b] This process is preferred for large-scale industrial use in the hope of developing a greener process by reducing waste production, energy use, and lowering toxicity.[3] TH is a safer and more valuable atom-efficient method when compared with the conventional hydrogenation reaction using the highly flammable dihydrogen molecule. In a number of recent examples, NHC complexes of iridium,[4] rhodium,[4c,d,i,m,n,s,5] and ruthenium[6] have been successfully used as precatalysts for TH reactions.

The nature of the transition metal is very important in TH; for example, it was found that Ir(I)-NHC complexes show superior activities when compared with their Rh(I) analogues.[4e,i,m,n] This is preferred for industrial use because of relatively low cost of iridium when compared to rhodium. The steric and electronic nature of the NHC ligand also plays an important role for the catalytic activity.[4i,k] In a very recent study, the efficiencies of Rh(I) complexes with symmetrical and unsymmetrical imidazol(in)-2-ylidenes bearing 2,4,6-trimethylphenyl (Mes) or 2,4,6-trimethylbenzyl (CH_2Mes) substituents on nitrogen atoms have been comparatively investigated in the TH reaction of acetophenone. It has been found that the introduction of flexible benzyl substituent (CH_2Mes) to the nitrogen atoms enhanced the TH performance.[5a] We also noticed that attachment of methyl groups on the 5,6-position of the benzene ring of benzimidazole also played an important role in Rh(I)[5c,7] and Ir(I)[4a] catalyzed reduction reactions. In view of these facts, Ir(I) complexes derived from 1,3-bis(2,4,6-triisopropylbenzyl)imidazol-2-ylidene (**1a**), 1,3-bis(2,4,6-triisopropylbenzyl)-5,6-dimethylbenzimidazol-2-ylidene (**2a**), and 1,3-dibenzyl-5,6-dimethylbenzimidazol-2-ylidene (**3a**) ligands were synthesized and applied as precatalysts for TH reactions. All complexes showed superior activities for the Ir(I)-catalyzed TH reaction of ketones and imines with a variety of substrate scales.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Compounds. The ligand precursors 1,3-bis(2,4,6-triisopropylbenzyl)-imidazolium bromide **1**, 1,3-bis(2,4,6-triisopropylbenzyl)-5,6-dimethylbenzimidazolium bromide **2**, and 1,3-dibenzyl-5,6-dimethylbenzimidazolium bromide **3** were synthesized from imidazole or 5,6-dimethylbenzimidazole (Scheme 1). The salts are colorless powders and were obtained in 72−93% yields. The spectral properties are similar to those of other reported imidazolium or benzimidazolium salts. In the ^{1}H NMR spectrum of **1**−**3**, the NC*H*N^{+} protons appear at 10.27, 7.74, and 11.72 ppm, respectively, and these downfield signals indicate the formation of azolium salts.

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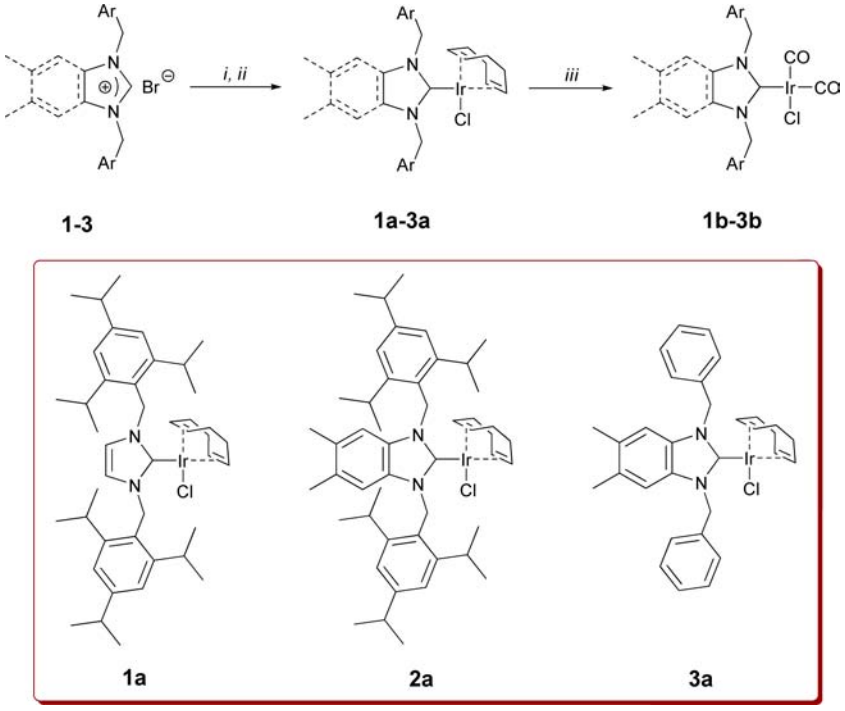
Scheme 1. Synthesis of [IrCl(COD)(NHC)] and [IrCl(CO)$_2$(NHC)] Complexes: (i) Ag_2O (0.5 equiv), CH_2Cl_2, RT, 1 h; (ii) [IrCl(COD)]$_2$ (0.5 equiv), CH_2Cl_2, RT, 12 h; (iii) CO, CH_2Cl_2, RT, 30 min



The new [IrCl(COD)(NHC)] complexes **1a**−**3a** were prepared by transmetalation[8] from the corresponding silver-NHC derivatives by employing a two-step process (Scheme 1). The silver-NHC species were used in situ without isolation. In the second step, the addition of [IrCl(COD)]$_2$ to the mixture gave the yellow complexes in good yields (83% **1a**, 81% **2a**, and 88% **3a**) as air and moisture stable solids.

The structure of complexes **1a**−**3a** was unambiguously confirmed by ^{1}H, ^{13}C, heteronuclear multiple-bond correlation (HMBC) NMR analyses and elemental analysis. X-ray diffraction studies on single crystals of **1a** and **2a** were also been achieved. The characteristic downfield signals for the NCHN$^+$ protons of the azolium salts **1**−**3** disappeared in the ^{1}H NMR spectra of complexes **1a**−**3a**. These complexes exhibit ^{13}C chemical shifts at 180.2, 191.8, and 191.7 ppm for the complexes **1a**−**3a**, respectively, and are comparable to those of other reported Ir(I)-NHC complexes.[4,9] The ^{13}C chemical shifts showed that $C_{carbene}$ is substantially deshielded.

NHC ligands exhibit, in principal, good σ-donor and weak π-acceptor electronic properties.[10] Measuring of carbonyl stretching frequencies in [M(X)(CO)$_2$(NHC)] (M = Rh or Ir, X = halogen) complexes with infrared (IR) spectroscopy allowed us to compare donor properties of NHC ligands, which are an important factor for homogeneous catalysis.[11] Thus, the corresponding [IrCl(CO)$_2$(NHC)] complexes **1b**−**3b** were prepared in order to compare the electronic properties of each NHC ligand. The corresponding carbonyl substituted Ir(I) complexes **1b**−**3b** were obtained by passing carbon monoxide gas through a dichloromethane solution of the Ir(I)-COD complexes at room temperature (Scheme 1).[12] These reactions resulted in almost quantitative substitution of COD by CO ligands.

The cis conformation of the CO ligands in complexes **1b**−**3b** was confirmed by IR and NMR spectroscopies. The average carbonyl stretching frequencies in the IR spectra were found to be ν_{CO}^{av} = 2027 cm^{-1}, 2025 cm^{-1}, and 2030 cm^{-1} for complexes **1b** to **3b**, respectively. The Tolman electronic parameters (TEP)[13] could be calculated for [IrCl(CO)$_2$(L)] type complexes via the linear regression equation described by Crabtree[12f] and more recently by Nolan.[12d] The calculated TEP values were found to be 2056, 2055, 2058 cm^{-1} (Crabtree's equation: 0.722 × ν_{CO}^{av}+593) and 2053, 2051, 2055 cm^{-1} (Nolan's equation: 0.847 × ν_{CO}^{av} + 336) for the corresponding complexes **1b** to **3b**, respectively. These differences could be explained by the donor strength of the 5,6-dimethylbenzimidazol-2-ylidene skeleton also in addition to the electron donating 2,4,6-triisopropylbenzyl substituents attached to the N atoms. ^{13}C NMR spectra exhibit three signals at 181.9, 173.3, and 168.2 ppm for the complex **1b**, 183.2, 181.8, and 168.3 ppm for the complex **2b**, and 182.8, 181.4, and 168.0 ppm for the complex **3b** for the two CO and $C_{carbene}$ ligands, which are consistent with known [IrCl(CO)$_2$(NHC)] type complexes.[12c]

Structural Studies. The crystal structures of the iridium complexes **1a** and **2a** (Figures 1 and 2) were determined by single crystal X-ray diffraction to obtain detailed information on their respective structural parameters. Details of data collection and refinement are summarized in Supporting Information, Table S1.

Structural analyses of **1a** and **2a** revealed that the iridium atoms lie in a slightly distorted square-planar coordination environments defined by the coordination of the metal to the two olefinic bonds of the cyclooctadiene ligand, the carbon atom of the NHC ligand and the chlorine atom. The significant bond distances and angles are listed in Table 1.

In the case of **2a**, there is one molecule in the asymmetric unit, while the molecules of **1a** are located on a crystallographic mirror plane with one symmetry independent half molecule in the asymmetric unit. This mirror plane is parallel to [001] and bisects the double bonds of the COD ligand, the C atom of the NHC ligand, Ir and Cl atoms lying on special positions of *m*

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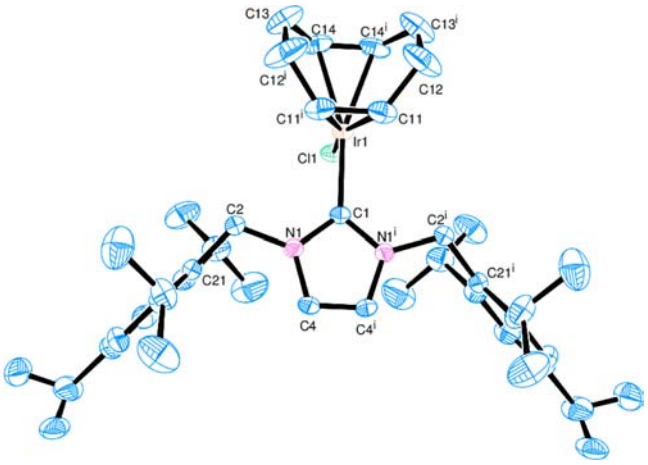

Figure 1. The molecular structure of **1a** with displacement ellipsoids drawn at the 30% probability level. Only the major components of the disordered atoms associated with the isopropyl groups are shown for clarity. [Symmetry code: (i) $x, y, 3/2 - z$].

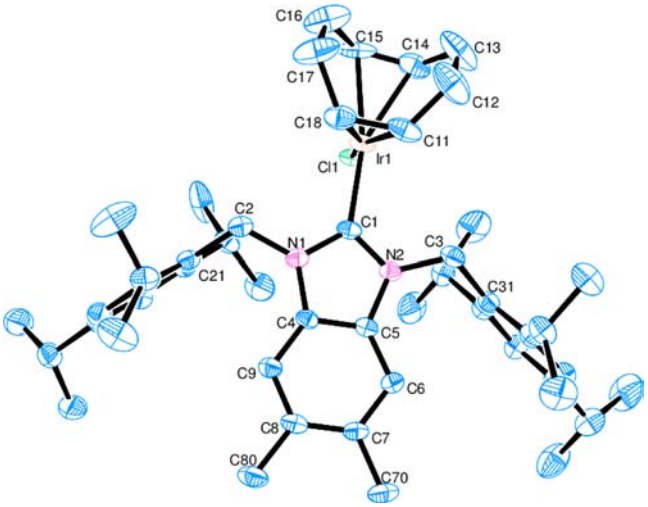

Figure 2. The molecular structure of **2a** with displacement ellipsoids drawn at the 30% probability level. Only the major components of the disordered atoms associated with the isopropyl groups are shown for clarity.

site symmetry. The orientation of NHC ligands in **1a** and **2a** is parallel with the COD double bonds which may lead to the COD and NHC ligands having optimal π-interactions with the metal *d*-orbitals. The iridium−NHC bond lengths (2.019(6) Å for **1a**, 2.035(6) Å for **2a**) agreed well with the values found in other NHC-supported [Ir(COD)Cl] complexes[4a,d,k,l,s,9c,12d] (2.001−2.090 Å). In **2a**, an intramolecular C−H···N hydrogen bond occurs between NHC and one of the isopropyl groups generating an S(6) ring motif (see the Supporting Information (SI), Table S2). In both complexes, the Ir−COD bond lengths trans to the NHC are 2.174(7), 2.184(9) Å [**2a**], and 2.183(6) Å [**1a**], whereas the distances for the Ir−COD bonds trans to chloride are 2.094(8), 2.114(8) Å [**2a**], and 2.093(6) Å [**1a**]. The difference in these bond lengths is a consequence of larger trans influence of the NHC ligand when compared to chloride. In **1a**, molecules are linked into a zigzag chain along the *c* axis by intermolecular C−H···π interactions. The molecular packing of **2a** is stabilized by a combination of two C−H···π interactions, forming sheets parallel to $(1\bar{1}0)$ (see Figures S1 and S2, Table S3 in the SI).

Table 1. Selected Bond Lengths (Å) and Angles (°) for 1a and 2a

Complex **1a**[a]			
Ir1−C1	2.019(6)	Ir1−Cl1	2.4312(17)
Ir1−C11	2.093(6)	Ir1−C14	2.183(6)
C1−N1	1.363(5)		
C1−Ir1−Cl1	91.10(17)	M1−Ir1−C1	90.20
M2−Ir1−Cl1	91.88	M1−Ir1−M2	86.82
M1−Ir1−Cl1	178.71	M2−Ir1−C1	177.02
Complex **2a**[b]			
Ir1−C1	2.035(6)	Ir1−Cl1	2.4263(13)
Ir1−C11	2.114(8)	Ir1−C18	2.094(8)
Ir1−C14	2.184(9)	Ir1−C15	2.174(7)
C1−N1	1.373(9)	C1−N2	1.333(9)
C1−Ir1−Cl1	92.33(17)	M3−Ir1−M4	86.45
M3−Ir1−C1	92.18	M4−Ir1−Cl1	89.19
M3−Ir1−Cl1	175.38	M4−Ir1−C1	173.73

[a]M1 and M2 represent the midpoints of the olefinic bonds C11−C11[i] and C14−C14[i], respectively. [b]M3 and M4 represent the midpoints of the olefinic bonds C11−C18 and C14−C15, respectively.

Catalytic Studies. [IrCl(COD)(NHC)] complexes (**1a**−**3a**) were screened as precatalysts for TH of acetophenone to 1-phenylethanol using 2-propanol as a hydrogen donor in the presence of KOH. The catalytic experiments were carried out using 1.0 mmol of acetophenone, 5×10^{-4} to 2.5×10^{-3} mmol (0.05−0.25 mol %) of **1a**−**3a**, 5×10^{-2} mmol of KOH, and 5 mL of 2-propanol, with a catalyst/base/substrate ratio of 0.05:5:100 or 0.25:5:100 (Figure 3). 1,3,5-Trimethoxybenzene

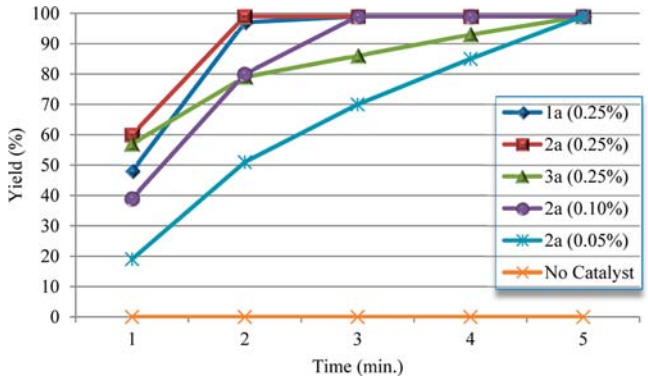

Figure 3. Time course of the catalytic transfer hydrogenation of acetophenone to 1-phenylethanol.

(1 mmol) was used as internal standard. The precatalyst and internal standard were added to a solution of 2-propanol containing KOH, which was kept at 82 °C for 5 min, and acetophenone was added into this solution. At the end of the desired reaction time, the reaction was quenched with 1 M HCl, and time-dependent yields were calculated by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard (Figure 1).

The blank experiment was carried out without catalyst, and no product formation is observed in these conditions (Figure 1). Less than 5% yield is determined even after 24 h. It was observed that, the activation period was very short for all precatalysts. With a 0.25 mol % catalyst loading, 48% (TOF = 11520 h^{-1}), 60% (TOF = 14400 h^{-1}), and 57% (TOF = 13680 h^{-1}) yields were achieved only in 1 min for **1a**, **2a**, and **3a**,

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respectively. For the total conversion only 2 min was required for precatalysts **1a** and **2a** (TOF = 12000 h^{-1}), while the dibenzyl substituted complex (**3a**) necessitated a longer reaction time (5 min). Therefore, the effect of precatalyst loading was studied by using the complex **2a** under the same reaction conditions. The total conversion required 3 min with 0.1 mol % precatalyst loading (TOF = 20000 h^{-1}) and 5 min with 0.05 mol % precatalyst loading (TOF = 24000 h^{-1}). It is clear that the "transport phenomena", which has been suggested by Herrmann,[4k] does not dominate the initial period in the low precatalyst concentrations. These high TOF values could be addressed as one of the highest results for NHC-based TH reaction of acetophenone to produce 1-phenylethanol. Precatalysts **1a** and **2a** display superior activities when compared with their non-benzylic counterparts. For example, by changing the NHC ligand from 1,3-diisopropyl-5,6-dimethylbenzimidazol-2-ylidene[4a] (TOF = 1200 h^{-1}) or 1,3-diisopropylimidazol-2-ylidene[4k] (TOF = 546 h^{-1}) to 1,3-bis(2,4,6-triisopropylbenzyl)-5,6-dimethylbenzimidazol-2-ylidene or 1,3-bis(2,4,6-triisopropylbenzyl)imidazol-2-ylidene the corresponding TOF values were increased considerably (t20 times higher) for the total conversion of acetophenone to 1-phenylethanol under the same reaction conditions. The obtained activities for the precatalysts **1a**−**3a** are also significantly higher than those of related iridium(I) complexes of electron-rich benzimidazol-2-ylidene ligand bearing bulky benzyl substituents on N-atom(s).[4m]

The lifetime/stability of the precatalyst **2a** was also tested by Cavell's previous method.[4i] A catalytic run was initiated using 5 mmol of acetophenone, 0.25 mmol of precatalyst **2a** (0.05 mol %), 25 × 10^{-2} mmol of KOH, and 25 mL of 2-propanol. After 5 min of operating time, an additional 5 mmol of substrate was added to the solution, and the reaction was monitored for an additional 5 min. Finally, a third (5 mmol) and fourth (5 mmol) aliquot of substrate was added, and the reaction was again monitored. These results are shown in Figure 4. It is clear that the catalyst maintained high activity during the entire experiment despite the decrease of the catalyst concentration.

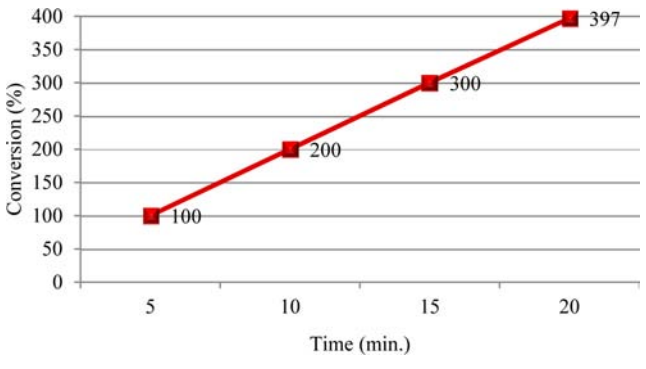

Figure 4. Catalytic conditions: 20.0 mmol of acetophenone, added in four separate stages; 0.25 mmol of precatalyst **2a**; 25 × 10^{-2} mmol of KOH; 25 mL of IPA; 82 °C.

Encouraged by the results obtained with complexes **1a**−**3a**, we decided to determine the catalytic activities of these complexes with different substituted aromatic and aliphatic ketones. The average turnover frequencies (TOF) for all the catalysts examined were determined after over 95% yields reached (measured by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard), and the results are shown in Table 2. The precatalysts were found to be highly active for a variety of substrates. Generally, high yields were obtained in 2−20 min (TOF between 800 and 12 000 h^{-1}). The same activity trend (**2a** > **1a** > **3a**) was observed in the TH of substituted aromatic ketones. TH of aliphatic ketones by catalyst **2a** took place at relatively lower rates when compared with the aromatic ketones. The reduction of cyclohexanone and 2-heptanone by **2a** resulted in quantitative formation of cyclohexanol and heptan-2-ol ca. 15 min (Table 2 entries 19 and 20). These differences in the catalytic activity of substituted ketones could be addressed to the effects of the different steric and electronic environments.[4l]

It was observed that the steric effect of the wing type was more important than the type of NHC skeleton for the TH of ketones. The catalytic activity of complexes with 2,4,6-triisopropybenzyl substituents (**1a** and **2a**) is higher than the complex with simple benzyl substituent (**3a**). Although highly active NHC complexes bearing sterically bulky N-aryl substituents facilitate the reductive elimination steps, the role of the benzyl substituents is not clear at this stage. However, it is noteworthy that in complexes **1a** and **2a**, one of the benzylic hydrogens is more acidic than in complex **3a**. Presumably, the flexible character of N-benzyl systems might be electronically more sensitive and tunable to the need of the substrates to enhance the TH performance,[5a] and also the Ar group of the benzyl substituent may protect the active center via π-interactions.[14]

It is known that imines are more difficult to reduce than ketones.[4d,o,5] Considering the high catalytic activities of complexes **1a**−**3a** toward TH of ketones, we were interested in testing these precatalysts for the TH of imines. When compared to the TH of ketones, higher precatalyst loading and longer reaction times were required for the reduction of imines to amines. TH reactions of imine were achieved in good yields (Table 3). Overall, our precatalysts were highly effective in TH reactions with the complexes bearing 5,6-dimethylbenzimidazol-2-ylidene ligand being more active than the corresponding complexes supported by imidazol-2-ylidene ligand. It is interesting to note that dimethylbenzene annulations at the 4,5-position of imidazole increased the catalytic activity especially in TH of imines.

CONCLUSIONS

Iridium(I) complexes of various N-substituted NHC ligands have been examined in the catalytic transfer hydrogenation of a number of ketones and imines. In particular, complexes containing 1,3-bis(2,4,6-triisopropylbenzyl)imidazol-2-ylidene (**1a**) and 1,3-bis(2,4,6-triisopropylbenzyl)(5,6-dimethyl)-benzimidazol-2-ylidene (**2a**) were found to be extremely effective. These catalyst systems displayed excellent activity for a range of substrates tested and also showed excellent stability. This study also shows that an optimization of the catalytic system is required for each substrate in order to obtain the highest efficiency. The essential features for efficient transfer hydrogenation with Ir-NHC catalysts appear to include a flexible and sterically demanding benzyl substituent(s) on N atom(s) of NHC and a strong σ donor 5,6-dimethylbenzimidazol-2-ylidene skeleton. The successful introduction of alkylated benzyl substituents to the nitrogens of 5,6-dimethylbenzimidazole ligand instead of the more common IMes or SIMes derivatives offers additional options to the fine-tuning [IrCl(COD)(NHC)] catalyst precursors.

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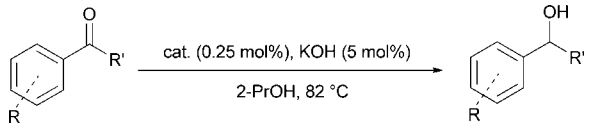
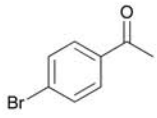
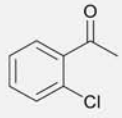
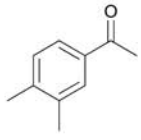
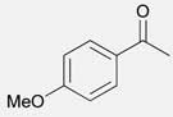
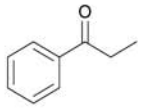
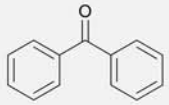
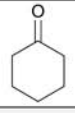
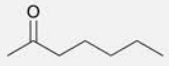
Table 2. Transfer Hydrogenation of Ketones to Alcohols with Precatalysts 1a−3a[a]



Entry	Substrate	Cat	Time/min.	Yield.[b] (%)	TOF [c,d] (h^{-1})
1		**1a**	2	95	11400
2		**2a**	2	>99	12000
3		**3a**	5	>99	4800
4		**1a**	5	>99	4800
5		**2a**	5	>99	4800
6		**3a**	10	>99	2400
7		**1a**	15	>99	1600
8		**2a**	10	98	2352
9		**3a**	20	>99	800
10		**1a**	10	>99	2400
11		**2a**	10	>99	2400
12		**3a**	15	>99	1600
13		**1a**	10	>99	2400
14		**2a**	5	>99	4800
15		**3a**	10	95	2280
16		**1a**	15	96	1536
17		**2a**	15	>99	1600
18		**3a**	20	>99	1200
19		**2a**	15	>99	1600
20		**2a**	15	>99	1600

[a]Substrate (1 mmol), KOH (5 mol %), cat. (0.25 mol %), IPA (5 mL), 82 °C. One mmol of 1,3,5-trimethoxybenzene was used as an internal standard. [b]Determined by and ^{1}H NMR analysis (average of two runs) after desired reaction time. [c]TOF: turnover frequency ([(mol of product)/(mol of catalyst)]/h). [d]TOF values were calculated after more than 95% yields observed.

EXPERIMENTAL SECTION

General Comments. Unless otherwise noted all manipulations were performed in air. The solvents were used as received. The reagents were purchased from Sigma-Aldrich, Merck, and Alfa Aesar. 2,4,6-Ttriisopropylbenzyl bromide was synthesized according to a slightly modified procedure from ref 15. $[IrCl(COD)]_2$ was prepared according to the published procedure.[16] ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on Varian AS 400 Mercury spectrometers with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) were reported in units (ppm) by assigning TMS resonance in the ^{1}H spectrum as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.0 ppm. All coupling constants (J values) were reported in Hertz (Hz). Melting points were recorded with Gallenkamp electrothermal melting point apparatus. Elemental analyses were performed on a Perkin-Elmer PE 2400 elemental

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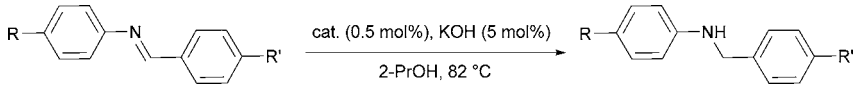
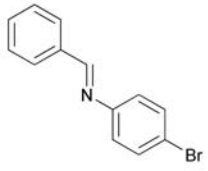
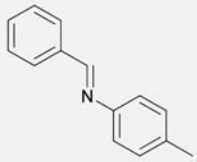
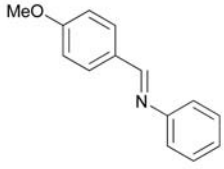
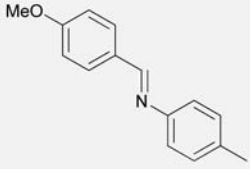
Table 3. Transfer Hydrogenation of Imines to Amines with Precatalysts 1a−3a[a]



Entry	Substrate	Cat	Time/min.	Yield.[b] (%)	TOF [c,d] (h^{-1})
1		**1a**	30	96	384
2		**2a**	15	>99	800
3		**3a**	30	>99	400
4		**1a**	120	98	98
5		**2a**	60	>99	200
6		**3a**	60	93	186
7		**1a**	120	>99	100
8		**2a**	45	>99	267
9		**3a**	60	>99	200
10		**1a**	180	98	65
11		**2a**	30	>99	400
12		**3a**	60	>99	200

[a]Substrate (1 mmol), KOH (5 mol %), cat. (0.5 mol %), IPA (5 mL), 82 °C. One mmol of 1,3,5-trimethoxybenzene was used as internal standard. [b]Determined by and ^{1}H NMR analysis (average of two runs) after desired reaction time. [c]TOF: turnover frequency ([(mol of product)/(mol of catalyst)]/h). [d]TOF values were calculated after more than 90% yields observed.

analyzer. FTIR spectra were recorded on a Perkin-Elmer Spectrum 100 series.

Syntheses. *1,3-Bis(2,4,6-triisopropylbenzyl)imidazolium Bromide (**1**).* A mixture of 1-*H*-imidazole (340 mg, 5 mmol) and K_2CO_3 (760 g, 11 mmol) was suspended in CH_3CN (10 mL) and stirred at ambient temperature for 1 h. 2,4,6-Triisopropylbenzyl bromide (1.49 g, 5 mmol) was then added to the suspension. The reaction mixture was stirred under reflux conditions for 24 h. The solution was filtered-off, and the solvent was removed under reduced pressure. To the resulting crude product, a second portion of 2,4,6-triisopropylbenzyl bromide (1.49 g, 5 mmol) was added and stirred at 160 °C for 2 h. The brown mixture first melted and then precipitated. The resulting solid dissolved in CH_2Cl_2 (10 mL) and Et_2O (30 mL) was added. The colorless solid that separated out was filtered and washed with Et_2O (2 × 20 mL) and dried under reduced pressure (2.10 g, 72%). Mp: 252−253 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): δ = 10.27 (s, 1 H, NC*H*N$^+$), 7.05 (s, 4 H, Ar-*H*), 7.02 (d, J = 1.6 Hz, 2 H, NC*H*=C*H*N), 5.66 (s, 4 H, NCH_2Ar), 2.96 (m, 4 H, ArC*H*$(CH_3)_2$), 2.89 (m, 2 H, ArC*H*$(CH_3)_2$), 1.23 (d, J = 6.8 Hz, 12 H, ArCH(CH_3)$_2$), 1.11 (d, J = 6.8 Hz, 24 H, ArCH(CH_3)$_2$). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): δ = 151.5 (NCHN$^+$), 148.7 (Ar-*C*), 135.4 (Ar-*C*), 122.5 (Ar-*C*), 122.3 (NHC=CHN), 121.9 (Ar-*C*), 46.4 (NCH_2Ar), 34.5 (ArCH$(CH_3)_2$), 29.9 (ArCH-$(CH_3)_2$), 24.4 (ArCH$(CH_3)_2$), 24.0 (ArCH$(CH_3)_2$). Anal. Calc. for $C_{35}H_{53}BrN_2$: C, 72.26; H, 9.18; N, 4.82. Found: C, 72.49; H, 9.41; N, 4.76.

*1,3-Bis(2,4,6-triisopropylbenzyl)(5,6-dimethyl)benzimidazolium bromide (**2**).* The salt **2** was prepared in analogy to **1** from 5,6-dimethyl-1-*H*-benzimidazole (730 mg, 5 mmol), as colorless solid (2.96 g, 90%). Mp: 243−244 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): δ = 7.82 (s, 2 H, Ar-*H*-BI), 7.74 (s, 1 H, NC*H*N$^+$), 7.00 (s, 4 H, Ar-*H*), 5.68 (s, 4 H, NCH_2Ar), 2.92−2.85 (m, 6 H, ArC*H*$(CH_3)_2$), 2.48 (s, 6 H, Ar−CH_3-BI), 1.23 (d, J = 6.8 Hz, 12 H, ArCH(CH_3)$_2$), 1.00 (d, J = 6.8 Hz, 24 H, ArCH(CH_3)$_2$). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): δ = 151.8 (NCHN$^+$), 148.7 (Ar-*C*), 138.2 (Ar-*C*), 132.1 (Ar-*C*), 128.5 (Ar-*C*), 122.4 (Ar-*C*), 122.3 (Ar-*C*), 114.6 (Ar-*C*), 44.9 (NCH_2Ar), 34.6 (ArCH$(CH_3)_2$), 30.1 (Ar-CH_3−BI), 24.4 (ArCH$(CH_3)_2$), 24.1 (ArCH$(CH_3)_2$). Anal. Calc. for

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$C_{41}H_{59}BrN_2$: C, 74.63; H, 9.01; N, 4.25. Found: C, 74.25; H, 9.11; N, 4.31.

*1,3-Dibenzyl(5,6-dimethyl)benzimidazolium bromide (**3**).* A mixture of 5,6-dimethyl-1-*H*-benzimidazole (340 mg, 5 mmol) and K_2CO_3 (760 g, 11 mmol) was suspended in CH_3CN (10 mL) and stirred at ambient temperature for 1 h. Benzyl bromide (855 mg, 5 mmol) was then added to the suspension. The reaction mixture was stirred under reflux conditions for 24 h. The solution was filtered-off, and the solvent was removed under reduced pressure. The resulting crude product was dissolved in toluene (15 mL), and a second portion of benzyl bromide (855 mg, 5 mmol) was added and stirred at reflux conditions for 24 h. The white solid that separated out after cooling to room temperature was filtered off and washed with diethyl ether (2 × 20 mL) and dried under reduced pressure (1.90 g, 93%). Mp: 205−206 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): δ = 11.72 (s, 1 H, NC*H*N$^+$), 7.50−7.48 (m, 4 H, Ar-*H*), 7.39−7.33 (m, 6 H, Ar-*H*), 7.30 (s, 2 H, Ar-*H*-BI), 5.81 (s, 4 H, NCH_2Ar), 2.33 (s, 6 H, Ar−CH_3-BI), ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): δ = 142.2 (NCHN$^+$), 137.7 (Ar-*C*), 133.0 (Ar-*C*), 130.1 (Ar-*C*), 129.6 (Ar-*C*), 129.4 (Ar-*C*), 128.4 (Ar-*C*), 113.5 (Ar-*C*), 51.5 (NCH_2Ar), 20.9. Anal. Calc. for $C_{23}H_{23}BrN_2$: C, 67.82; H, 5.69; N, 6.88. Found: C, 67.68; H, 5.73; N, 6.81.

*Chloro(μ^4-1,5-cyclooctadiene)[1,3-bis(2,4,6-triisopropylbenzyl)-imidazol-2-ylidene] Iridium(I) (**1a**).* Under an argon atmosphere, a mixture of **1** (291 mg, 0.5 mmol) and Ag_2O (52 mg, 0.5 mmol) was suspended in degassed CH_2Cl_2 (5 mL) and stirred at ambient temperature for 1 h shielded from light. $[IrCl(COD)]_2$ (168 mg, 0.25 mmol) was then added to the suspension, and the reaction mixture was stirred at ambient temperature for more 12 h. The resulting suspension was filtered over Celite. The remaining solid was washed with CH_2Cl_2 (2 × 5 mL), and the solvent of the filtrate was evaporated. The residue was purified by column chromatography on silica gel (eluent: CH_2Cl_2) to give pure complex as a yellow solid (348 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): δ = 7.05 (s, 4 H, Ar-*H*), 6.15 (s, 2 H, NC*H*=C*H*N), 5.91 (d, J = 14.4 Hz, 2 H, NCH_2Ar), 5.38 (d, J = 14.4 Hz, 2 H, NCH_2Ar), 4.71 (t, J = 2.4 Hz, 2 H, COD-C*H*), 3.25 (t, J = 2.4 Hz, 2 H, COD-C*H*), 3.22−3.14 (m, 4 H, ArC*H*(CH_3)$_2$), 2.94−2.87 (m, 2 H, ArC*H*(CH_3)$_2$), 2.32−2.28 (m, 4 H, COD-CH_2), 1.81−1.71 (m, 4 H, COD-CH_2), 1.26 (d, J = 6.8 Hz, 12 H, ArCH(CH_3)$_2$), 1.22 (d, J = 6.8 Hz, 12 H, ArCH(CH_3)$_2$), 1.15 (d, J = 6.8 Hz, 12 H, ArCH(CH_3)$_2$). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): δ = 180.2 (Ir-$C_{carbene}$), 149.9 (Ar-*C*), 149.2 (Ar-*C*), 125.9 (Ar-*C*), 121.7 (NHC=CHN),), 118.4 (Ar-*C*), 84.6 (COD-CH), 51.8 (COD-CH), 47.0 (NCH_2Ar), 34.5 (ArCH(CH_3)$_2$), 34.0 (COD-CH_2), 29.9 (COD-CH_2), 29.8 (ArCH(CH_3)$_2$), 24.6 (ArCH(CH_3)$_2$), 24.3 (ArCH(CH_3)$_2$), 24.2 (ArCH(CH_3)$_2$). Anal. Calc. for $C_{43}H_{64}ClN_2Ir$: C, 61.73; H, 7.71; N, 3.35. Found: C, 61.99; H, 7.64; N, 3.31.

*Chloro(μ^4-1,5-cyclooctadiene)[1,3-bis(2,4,6-triisopropylbenzyl)-(5,6-dimethyl)benzimidazol-2-ylidene] Iridium(I) (**2a**).* Complex **2a** was prepared in analogy to **1a** from the salt **2** (330 mg, 0.5 mmol). Yellow solid (371 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): δ = 7.08 (s, 4 H, Ar-*H*), 6.50 (d, J = 14.8 Hz, 2 H, NCH_2Ar), 5.78 (d, J = 14.8 Hz, 2 H, NCH_2Ar), 5.69 (s, 2 H, Ar-*H*-BI), 4.77 (t, J = 2.8 Hz, 2 H, COD-C*H*), 3.41−3.34 (m, 4 H, ArC*H*(CH_3)$_2$), 3.18 (t, J = 2.4 Hz, 2 H, COD-C*H*), 2.96−2.92 (m, 2 H, ArC*H*(CH_3)$_2$), 2.34−2.27 (m, 4 H, COD-CH_2), 1.84 (s, 6 H, Ar−CH_3-BI), 1.76−1.71 (m, 4 H, COD-CH_2), 1.29 (d, J = 6.4 Hz, 24 H, ArCH(CH_3)$_2$), 1.22 (d, J = 6.4 Hz, 12 H, ArCH(CH_3)$_2$). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): δ = 191.8 (Ir-$C_{carbene}$), 150.2 (Ar-*C*), 134.2 (Ar-*C*), 130.0 (Ar-*C*), 126.3 (Ar-*C*), 121.8 (Ar-*C*), 112.3 (Ar-*C*), 85.9 (COD-CH), 51.8 (COD-CH), 48.4 (NCH_2Ar), 34.7 (ArCH(CH_3)$_2$), 33.9 (COD-CH_2), 30.0 (COD-CH_2), 29.7 (ArCH-(CH_3)$_2$), 24.5 (ArCH(CH_3)$_2$), 24.4 (ArCH(CH_3)$_2$), 20.0 (Ar-CH_3−BI). Anal. Calc. for $C_{49}H_{70}ClN_2Ir$: C, 64.34; H, 7.71; N, 3.06. Found: C, 64.43; H, 7.78; N, 3.09.

*Chloro(μ^4-1,5-cyclooctadiene)[1,3-dibenzyl-(5,6-dimethyl)-benzimidazol-2-ylidene] Iridium(I) (**3a**).* Complex **3a** was prepared in analogy to **1a** from the salt **3** (204 mg, 0.5 mmol). Yellow solid (292 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): δ = 7.39−7.24 (m, 10 H, Ar-*H*), 6.77 (s, 2 H, Ar-*H*-BI), 6.04 (s, 4 H, NCH_2Ar), 4.72 (t, J = 2.8 Hz, 2 H, COD-C*H*), 2.90 (t, J = 2.8 Hz, 2 H, COD-C*H*), 2.21−2.11 (m, 2 H, COD-CH_2), 2.16 (s, 6 H, Ar−CH_3-BI), 2.01−1.95 (m, 2 H, COD-CH_2), 1.74−1.68 (m, 2 H, COD-CH_2), 1.58−1.48 (m, 2 H, COD-CH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): δ = 191.7 (Ir-$C_{carbene}$), 136.6 (Ar-*C*), 133.9 (Ar-*C*), 131.9 (Ar-*C*), 129.0 (Ar-*C*), 127.9 (Ar-*C*), 127.3 (Ar-*C*), 111.8 (Ar-*C*), 87.0 (COD-CH), 53.1 (NCH_2Ar), 52.6 (COD-CH), 33.6 (COD-CH_2), 29.5 (COD-CH_2), 20.4 (Ar-CH_3−BI). Anal. Calc. for $C_{31}H_{34}ClN_2Ir$: C, 56.22; H, 5.17; N, 4.23. Found: C, 56.31; H, 5.13; N, 4.19.

*Chloro(dicarbonyl)[1,3-bis(2,4,6-triisopropylbenzyl)imidazol-2-ylidene] Iridium(I) (**1b**).* Complex **1a** (83.7 mg, 0.1 mmol) was dissolved in CH_2Cl_2 (5 mL) and carbon monoxide was bubbled through the solution for 30 min. Color of the solution changed from yellow to pale yellow. The solution was concentrated ca. 1 mL and pentane (5 mL) was added. The pale yellow solid that separated out was filtered and washed with pentane and dried under reduced pressure (72 mg, 92%). IR (CH_2Cl_2): ν_{CO} = 2068, 1985 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): δ = 7.17 (s, 4 H, Ar-*H*), 6.23 (s, 2 H, NC*H*=C*H*N), 5.54 (d, J = 14.8 Hz, 2 H, NCH_2Ar), 5.31 (d, J = 14.8 Hz, 2 H, NCH_2Ar), 3.10−3.02 (m, 4 H, ArC*H*(CH_3)$_2$), 2.85−2.78 (m, 2 H, ArC*H*(CH_3)$_2$), 1.17 (d, J = 6.8 Hz, 24 H, ArCH(CH_3)$_2$), 1.02 (d, J = 6.8 Hz, 12 H, ArCH(CH_3)$_2$). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): δ = 181.9 (Ir-CO), 173.3 (Ir-$C_{carbene}$), 168.2 (Ir-CO), 150.4 (Ar-*C*), 148.9 (Ar-*C*), 125.3 (Ar-*C*), 121.9 (NHC=CHN),), 119.8 (Ar-*C*), 48.0 (NCH_2Ar), 34.5 (ArCH-(CH_3)$_2$), 29.9 (ArCH(CH_3)$_2$), 24.5 (ArCH(CH_3)$_2$), 24.2 (ArCH-(CH_3)$_2$), 24.1 (ArCH(CH_3)$_2$).

*Chloro(dicarbonyl)[1,3-bis(2,4,6-triisopropylbenzyl)-(5,6-dimethyl)benzimidazol-2-ylidene] Iridium(I) (**2b**).* Complex **2b** was prepared in analogy to **1b** from the complex **2a** (91.5 mg, 0.1 mmol). Pale yellow solid (81 mg, 94%). IR (CH_2Cl_2): ν_{CO} = 2067, 1983 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): δ = 7.00 (s, 4 H, Ar-*H*), 6.02 (d, *J* = 15.2 Hz, 2 H, NCH_2Ar), 5.98 (s, 2 H, Ar-*H*-BI), 5.65 (d, *J* = 15.2 Hz, 2 H, NCH_2Ar), 3.35−3.20 (m, 4 H, ArC*H*(CH_3)$_2$), 2.88−2.84 (m, 2 H, ArC*H*(CH_3)$_2$), 1.84 (s, 6 H, Ar−CH_3-BI), 1.20 (d, J = 6.8 Hz, 24 H, ArCH(CH_3)$_2$), 1.11 (d, *J* = 6.8 Hz, 12 H, ArCH(CH_3)$_2$). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): δ = 183.2 (Ir-$C_{carbene}$), 181.8 (Ir-CO), 168.3 (Ir-CO), 150.5 (Ar-*C*), 149.2 (Ar-*C*), 133.8 (Ar-*C*), 132.2 (Ar-*C*), 125.8 (Ar-*C*), 121.7 (Ar-*C*), 113.0 (Ar-*C*), 49.1 (NCH_2Ar), 34.6 (ArCH(CH_3)$_2$), 30.1 (ArCH-(CH_3)$_2$), 24.4 (ArCH(CH_3)$_2$), 24.3 (ArCH(CH_3)$_2$), 20.2 (Ar-CH_3−BI).

*Chloro(dicarbonyl)[1,3-dibenzyl-(5,6-dimethyl)benzimidazol-2-ylidene] Iridium(I) (**3b**).* Complex **3b** was prepared in analogy to **1b** from the complex **3a** (66 mg, 0.1 mmol). Pale yellow solid (58 mg, 95%). IR (CH_2Cl_2): ν_{CO} = 2071, 1988 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): δ = 7.35−7.29 (m, 10 H, Ar-*H*), 6.96 (s, 2 H, Ar-*H*-BI), 5.99 (d, *J* = 15.6 Hz, 2 H, NCH_2Ar), 5.76 (d, *J* = 15.6 Hz, 2 H, NCH_2Ar), 2.22 (s, 6 H, Ar−CH_3-BI). ^{13}C NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): δ = 182.8 (Ir-$C_{carbene}$), 181.4 (Ir-CO), 168.0 (Ir-CO), 135.4 (Ar-*C*), 133.8 (Ar-*C*), 133.2 (Ar-*C*), 129.2 (Ar-*C*), 128.4 (Ar-*C*), 127.4 (Ar-*C*), 112.4 (Ar-*C*), 52.9 (NCH_2Ar), 20.6 (Ar-CH_3−BI).

X-ray Diffraction Studies. Single crystal X-ray diffraction experiments were carried out with an Agilent XCalibur X-ray diffractometer with EOS CCD detector using Mo Kα radiation (graphite crystal monochromator λ = 0.7107 Å) at room temperature. The data collection, cell refinement, and data reduction were executed using the CrysAlis^{Pro19} program. Absorption corrections were based on multiple scans.[17] The structures were solved by direct methods (SHELXS-97[18]) and refined by full-matrix least-squares against F^2 (SHELXL-97[18]). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions (C−H = 0.95−0.99 Å) and were included in the refinement in the riding model approximation with U_{iso}(H) set to 1.2−1.5U_{eq}(C). Disorder refinement models were applied to some of the isopropyl fragments: C42A/C42B, C43A/C43B atoms with an occupancy ratio of 0.85(1) to 0.15(1) in **1a** and C40A/C40B, C41A/C41B, C50A/C50B, C51A/

C51B atoms with an occupancy ratio of 0.80(3) to 0.20(3) in **2a**. Equal U_{ij} constraints (*EADP*) were used for all of the disordered atom pairs. Ellipsoid displacement (DELU) restraint was also applied to C12/C13 and C16/C17 atoms in **2a**. Thermal ellipsoid plots were generated using the program ORTEP-3.[19]

General Procedure for the Transfer Hydrogenation of Ketones. The tested complex (0.0025 mmol; 0.25 mol %) was dissolved in a solution of KOH (0.5 mmol) and 2-propanol (5 mL) in a two-necked flask. 1,3,5-Trimethoxybenzene (1 mmol) was added to the solution as internal standard. The solution was heated to 82 °C for 10 min. Subsequently, the corresponding ketone (1 mmol) was added. After the desired reaction time, the reaction was quenched with 1 M HCl and extracted with Et_2O, and the organic phase was separated. The reaction progress was monitored by ^1H NMR, and the results for each experiment are averages over two runs.

General Procedure for the Transfer Hydrogenation of Imines. The tested complex (0.005 mmol; 0.5 mol %) was dissolved in a solution of KOH (0.5 mmol) and 2-propanol (5 mL) in a two-necked flask. 1,3,5-Trimethoxybenzene (1 mmol) was added to the solution as internal standard. The solution was heated to 82 °C for 10 min. Subsequently, corresponding imine (1 mmol) was added. After the desired reaction time, the reaction was quenched with water and extracted with Et_2O, and the organic phase was separated. The reaction progress was monitored by ^1H NMR, and the results for each experiment are averages over two runs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The crystal packings of **1a** and **2a** are given (CIFs). CCDC 936209 (for **1a**) and 936210 (for **2a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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