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ORIGINAL PAPER

The catalytic activity of new iridium(I) *N*-heterocyclic carbene complexes for hydrogen transfer reaction of ketones

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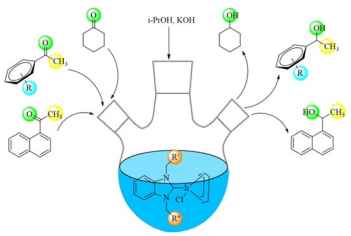
Abstract

In this paper, the reaction of $[Ir(COD)Cl]_2$ with in situ prepared Ag–*N*-heterocyclic carbene (NHC) complexes yields a series of [IrCl(COD)(NHC)] complexes. All compounds were fully characterized by ^{1}H NMR, ^{13}C NMR, and FT–IR spectroscopy. The manuscript focused on the preparation of new Ir–NHC complexes, characterization and catalytic behavior. A series of hydrogenation transfer reactions were performed to reveal the effects of the Ir–NHC complexes. The new Ir–NHC complexes of benzimidazole-2-ylidene are effective catalysts for the transfer of hydrogenation of different ketones, using *i*-PrOH as the source of hydrogen in the presence of KOH. The reactions were conducted at a substrate/catalyst/base (S/C/base) molar ratio of 1:0.001:2. Although all of the complexes are active catalysts for the transfer hydrogenation of ketones, moderate yields were obtained with acetylnaphthalene and conversion was not observed with very substituted ketones such as 2′,3′,4′,5′,6′-pentamethylacetophenone. It was observed that for transfer hydrogenation reactions Ir–NHC catalysts were more active, compared to Ru–NHC catalyzed studies performed by our team.

Graphic abstract



Keywords Iridium–NHC complexes · Carbenes · Hydrogen transfer · Benzimidazole · Alcohols

Introduction

Catalysts that increase the speed of a reaction by reducing the activation energy are amongst the most important elements in modern organic synthesis. Because an effective and selective catalyst minimizes operating costs by keeping raw material sources, toxic reagents (solvents), by-products, and toxic products to a minimum. Increasing environmental awareness and limited raw material resources have increased the importance of catalysts, leading to green technology. Catalysts have played a very important role in the economic success of the chemical industry in recent years. For this purpose, efficient, alternative, environmentally friendly catalysts and catalytic systems are needed [1].

N-Heterocyclic carbenes are ligands commonly used in transition metal compounds. The first NHC complexes were described by Öfele and Wanzlick in 1960 [2]. However, with the isolation of free imidazole-2-ylidene carbene by Arduengo et al. in 1991 [3], the studies on this subject increased rapidly. Metal-NHC complexes are more stable, odorless and show much more activity in many chemical reactions than metal phosphine complexes.

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Transfer hydrogenation is the incorporation of hydrogen into a molecule from a source other than hydrogen gas. Although there are difficulties in the storage and use of hydrogen gas, transfer hydrogenation can be easily applied in industry and organic synthesis [4, 5].

Most of the elements of the second pass series of the periodic table are suitable metals for catalytic homogeneous reduction. Salts and complexes of Pd, Pt, Ru, Ir, Rh, Ni, and Co elements have been used as catalysts for hydrogen transfer reactions [1]. Generally, Rh [6, 7], Ir [6–8], and Ru [8–10] salts and complexes are the most active catalysts. Homogeneous and heterogeneous catalysts can be used in hydrogen transfer reactions. Homogeneous catalysts are preferred due to their selectivity, low catalysts loadings normally being sufficient and the reaction medium being moderate.

The most active catalysts used in transfer hydrogenation reactions are iridium catalysts [11]. This has caused many research groups to deal with this issue in recent years. From the pioneering work on iridium catalyzed transfer hydrogenation of ketones by Mestroni and co-worker [12, 13], interest in this area has increased [14–16].

The first use of a metal-NHC complex in transfer hydrogenation was reported by Nolan et al. in 2001 [17]. His team prepared Ir complexes which proved to be active catalysts for the reduction of ketones to the corresponding alcohol using *i*-PrOH with KOH. In 2002 Crabtree et al. [18] prepared a series of Ir-bis(NHC) complexes bearing a range of different alkyl sidearms such as methyl, butyl, isopropyl, and neopentyl groups and applied these in a series of transfer hydrogenation processes. Several other iridium-NHC complexes have been successfully applied as catalysts for the transfer hydrogenation of ketones, including the interesting complex reported by Royo's group [19], whereby a cyclopentadienyl ring is tethered to the NHC. In 2013 a series of new Ir–NHC complexes were synthesized and good results have been obtained by Gülcemal et al. [20, 21]. Other iridium catalysts with various mono-NHC units were also successfully synthesized and used such as complexes containing, IPr-based iridium complex [22], 3,4,5-trimethoxybenzyl *N*-substituted iridium-NHC complexes [23], an abnormal NHC [24], a hemilabile NHC [25], and containing a NHC with an extended ring and a donor substituent [1, 26].

We have previously reported imidazolidine, benzimidazole-2-ylidene-ruthenium(II) complexes and the in situ formed tetrahydropyrimidine ruthenium(II) system which exhibits high activity [27–32]. To find more efficient catalysts, a series of new Ir–NHC complex **2a**–**2c** (Scheme 2) was prepared. For transfer hydrogenation of ketones in *i*-PrOH for 30 min, **2a**–**2c** was used as a carbene catalyst and KOH as a base. All synthesized compounds were characterized by ^{1}H NMR, ^{13}C NMR, and FT-IR spectroscopy techniques the results of which support the proposed structures.

Results and discussion

Preparation of benzimidazolium salts

Dialkylbenzimidazolium salts **1a**–**1c** were prepared accordingly known methods [33] as conventional NHC precursors. The ligand precursors **1a**–**1c** were synthesized in approximately quantitative yield by quaternization of 1-alkylbenzimidazole in DMF with the corresponding aryl chlorides [33]. **1a** and **1b** benzimidazolium salts have already been reported in the literature [34]. The salts were obtained in 79–90% yields (Scheme 1).

The salts are air and moisture stable in the solid-state and solution. All salts are soluble in chlorinated solvents, alcohols, and water. In the ^{1}H NMR spectrum of **1a**–**1c**, the NC*H*N protons appear at 12.15, 11.59, and 10.95 ppm, respectively, and these downfield signals indicate the formation of benzimidazolium salts. The ^{1}H NMR shifts of **1a**–**1c** are similar to other characterized benzimidazolium salts [34].

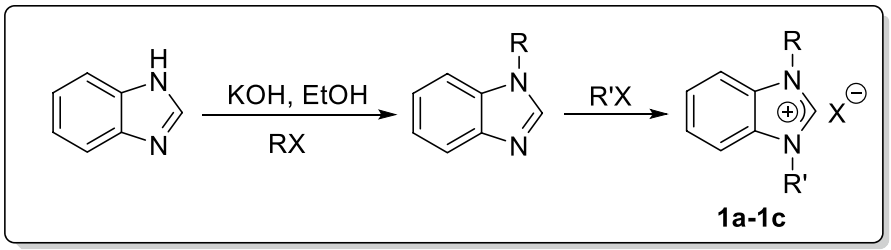
Preparation of iridium-carbene complexes 2a–2c

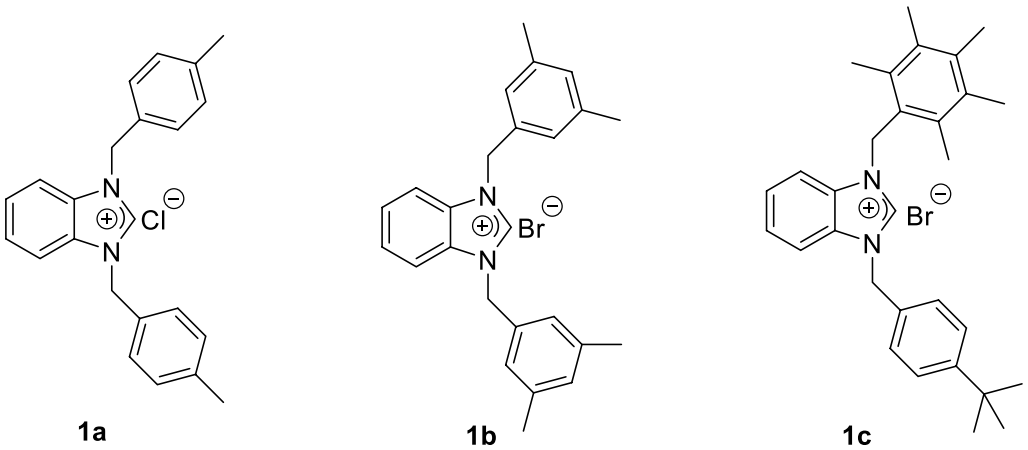
There are several methods for the formation of NHC complexes. In this respect, one of the most useful methods is transmetalation with Ag–NHC complexes. The use of Ag–NHC reagents as a carbene transfer agent makes it easy to overcome the inert atmosphere and complicated working difficulties. In most cases, transmetalation reactions can be carried out under aerobic conditions and this process can be successfully applied with metal types such as Cu, Au, Pd, Ni, Pt, Rh, Ru, and Ir [5].

The new [IrCl(COD)(NHC)] complexes **2a**–**2c** were prepared by transmetallation from the corresponding silver-NHC derivatives using a two-step method (Scheme 2). Silver-NHC complexes were used in situ without isolation. In the second stage, adding $[IrCl(COD)]_2$ to the mixture gave yellow complexes that were resistant to air and moisture and which were obtained with good yields (78–82%). The moisture and air resistant iridium carbene complexes **2a**–**2c** were soluble in solvents such as chloroform, dichloromethane, tetrahydrofuran, and toluene but not in nonpolar solvents. The structure of **2a**–**2c** complexes was confirmed by ^{1}H, ^{13}C, and FT–IR spectroscopies. The characteristic downfield signals for the NC*H*N protons of the benzimidazolium salts **1a**–**1c** disappeared in the ^{1}H NMR spectra of complexes **2a**–**2c**.

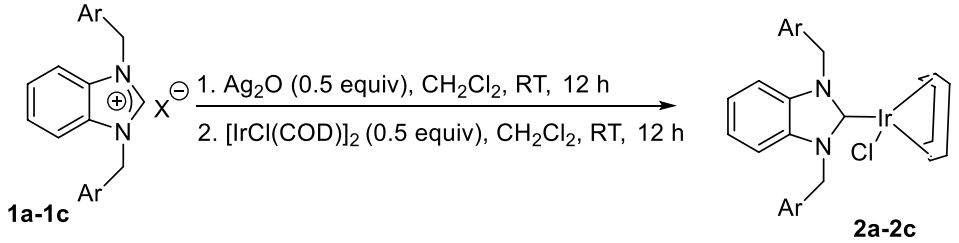
These complexes exhibit ^{13}C chemical shifts at 193.5, 192.7, and 192.8 ppm and are comparable to those of other reported Ir(I)–NHC complexes [20]. The ^{13}C chemical shifts showed that C_{carb} is substantially deshielded.

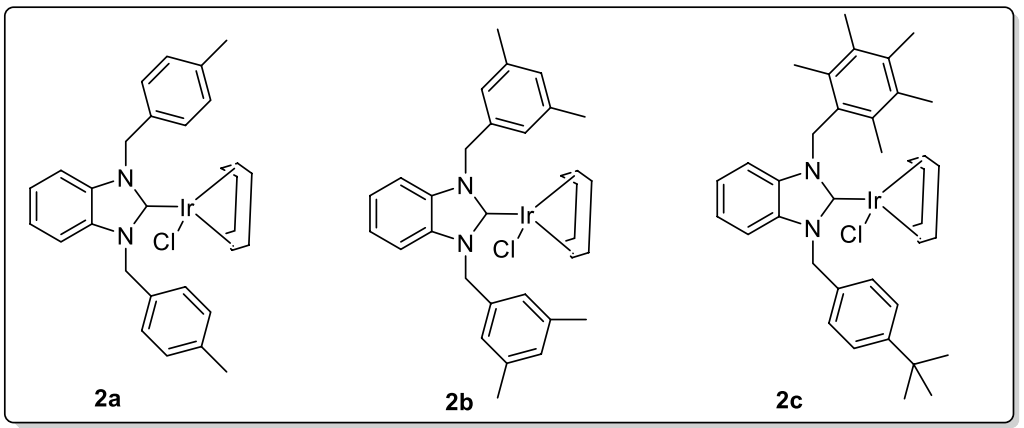
Scheme 1





Scheme 2





General procedure for transfer hydrogenation reactions

The reduction of organic compounds is one of the important synthetic processes both in the laboratory and industrially. Transfer hydrogenation performed by metal catalysis is an important reaction in this regard. It is economical, moderate and environmentally friendly as hydrogen donor molecules are used instead of gas hydrogen in the reduction of multiple bonds. The use of a solvent that can donate hydrogen

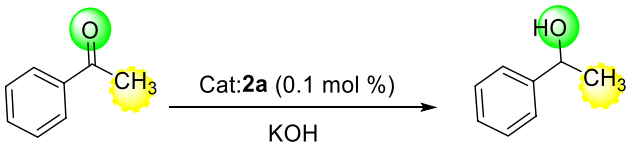
overcomes these difficulties. *i*-PrOH is a popular reactive solvent for the hydrogen transfer reactions as it is readily applied (b.p. 82 °C) and inexpensive, environmentally benign, and relatively non-toxic. The product of acetone, a volatile compound, can also be easily removed to shift an unfavorable equilibrium.

The pre-synthesized, isolated crystalline catalyst (0.001 mmol) was dissolved in 3 cm^3 *i*-PrOH in a standard experiment. Substrate (1 mmol) and KOH (2 mmol) were added to the mixture of iridium catalysts **2a**–**2c**. Then the mixture was heated for 30 min to 80 °C. The solution was then cooled to room temperature and applied to a short column of silica gel. The volatiles was then removed under reduced pressure, and GC calculated the conversion distribution. The yields are dependent upon the corresponding alcohol. The reactions were performed at 1:0.001:2 molar ratio of substrate/catalyst/base (S/C/base).

The base promotes the formation of iridium alkoxide by abstracting a proton from the alcohol, in the transfer hydrogenation reaction. In this reaction, the alkoxide undergoes β-elimination to give an iridium hydride which is an active species. Since the base promotes the formation of an iridium alkoxide by abstracting the proton from *i*-PrOH various bases have been used as promoters in the hydrogenation transfer of ketones. Acetophenone was held as a test substrate and permitted to react in *i*-PrOH in the presence of different bases with the catalytic amounts of complex **2a**. KO*t*-Bu, NaOAc, Cs_2CO_3, K_2CO_3, NaOH, and KOH were used for base selection. Although the application of bases such as KOH or NaOH results in similar conversions (Table 1, entries 3, 4) when using KOH the highest rate was achieved (Table 1, entry 3). No transfer hydrogenation of the ketones was observed in the absence of a base (Table 1, entry 7). It is common knowledge that the foundation acts as a co-catalyst. The function of the Ir–NHC complex was screened, and a control experiment in the absence of Ir–NHC yielded only a trace of alcohol [30, 31].

A series of hydrogenation transfer reactions were performed to uncover the benefits of the Ir–NHC complexes. The nature of the catalysts and substrate that can affect the yield in the transfer hydrogenation reaction was investigated according to the specified optimum reaction conditions. **2c** has proven to be the most effective catalyst compared to **2a** and **2b** under the reaction conditions. Acetophenone reduction with **2c** was achieved within 30 min, reaching 99%. In comparison, Table 2 reveals that in 99% and 96% respectively, **2a** and **2b** decreased acetophenone (Table 2, entries 1–3). In addition, when this reaction was tried for 5 min, 30% conversion was obtained (Table 2, entry 4). The conversion was 10% when the base value was reduced to 0.5 mmol (Table 2, entry 6). It was found that when the amount of catalyst was increased by 0.2 mol%, the conversion changed very little (Table 2, entry 5).

Table 1 Screening of transfer hydrogenation reaction conditions



Entry	Base	Time/min	Yield/%
1	K_2CO_3	30	52
2	Cs_2CO_3	30	59
3	KOH	30	99
4	NaOH	30	90
5	NaOAc	30	51
6	$KOBu^t$	30	79
7	–	30	0[b]

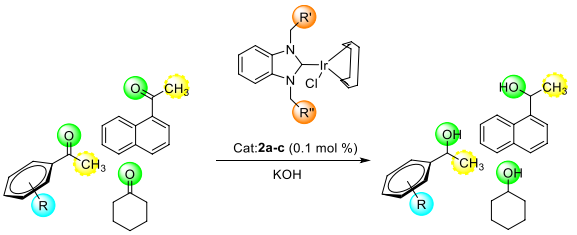
[a]Reaction conditions: Ir–NHC **2a** (0.1 mol%), KOH (2 mmol), 3 cm^3 *i*-PrOH, substrate (1.0 mmol), 80 °C, 30 min

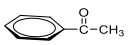
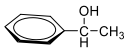
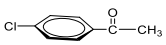
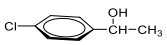
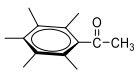
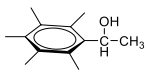
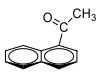
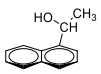
[b]No base. The purity of compounds was checked by GC and yields are based on alcohol

Acetophenone, *p*-chloroacetophenone, and cyclohexanone reacted very cleanly and turned into corresponding alcohol in good yields. Subsequently, various substrates were screened for the transfer hydrogenation reaction. No product was seen when pentamethylacetophenone (Table 2, entries 14–16) was used. On the transfer hydrogenation reaction catalyzed by **2a**–**2c** (Table 2, entries 17–19) the low yield was observed when 1-acetylnaphthalene was used as a substrate. It was assumed that the existence of a substrate can also provide low yields. The **2a**–**2c** efficiency was tested on cyclohexanone, depending on the time. Results showed that the linear association between reaction time and conversion does not occur (Table 2, entries 24–26). The catalytic activity of **2a**–**2c** is highly dependent on the steric bulky and electronic factors of the NHC ligands, given the above explanations. Results showed that even at low catalyst loading, these Ir–NHC complexes are an efficient catalyst for the transfer hydrogenation reactions with *p*-chloro substituted acetophenone and cyclohexanone substrates.

Here, synthesis and catalytic applications of Ir–NHC complexes with different steric and electronic properties were reported. The role of steric and electronic effects plays on the catalytic activity for NHC ligands has been investigated using a variety of techniques in the literature [35]. Even though benzimidazole-2-ylidenes have received limited attention as NHC ligands, they provide a suitable platform for tuning the electron density on the carbene carbon. Also, altering the *N*-substituent would allow the topography around the metal to be tuned to ensure the required steric bulk for reductive elimination is in place. Therefore, benzimidazol-2-ylidene ligands with sterically bulky benzyl substituents were preferred. Since the σ-donor abilities of

Table 2 The transfer hydrogenation reaction of ketones catalyzed by Ir–NHC complexes **2a**–**2c**



Entry	Substrate	Product	Cat	Yield[a](%)
1			**2a**	99
2			**2b**	96
3			**2c**	99
4			**2a**	30[b]
5			**2a**	98[c]
6			**2a**	10[d]
7			**2a**	59
8			**2b**	59
9			**2c**	72
10			**2a**	96
11			**2b**	94
12			**2c**	95
13			**2c**	46[e]
14			**2a**	-
15			**2b**	-
16			**2c**	-
17			**2a**	32
18			**2b**	31
19			**2c**	28
20			**2a**	99
21			**2b**	99
22			**2c**	99
23			**2a**	25[f]
24			**2a**	99[g]
25			**2a**	99[h]
26			**2a**	98[b]

[a]*Reaction conditions*: Ir–NHC **2a**–**c** (0.1 mol%), KOH (2 mmol), ^{i}PrOH (3 cm^3), substrate (1.0 mmol), 80 °C, 30 min. Purity of compounds is checked by GC and yields are based on alcohols

[b]5 min

[c]Ir–NHC **2a** (0.2 mol%)

[d]KOH (0.5 mmol)

[e]Ir–NHC **2c** (0.05 mol%)

[f]Ir–NHC **2a** (0.05 mol%), KOH (1 mmol)

[g]20 min

[h]10 min

carbene ligands of **2a**–**2c** complexes are similar, steric factors are likely at work in the improved performance of the complex **2c**.

Conclusion

In this study, the $[Ir(COD)Cl]_2$ reaction with Ag–NHC complexes prepared in situ yields a sequence of Ir–NHC complexes **2a**–**2c**. During the catalytic studies, various alcohol derivatives were obtained with high conversions under the catalysis of iridium carbene complexes. While all of the complexes are active catalysts for the transfer of ketone hydrogenation, modest yields were obtained with acetylnaphthalene and no conversion was observed with very substituted ketones such as 2′,3′,4′,5′,6′-pentamethylacetophenone. It was observed that Ir–NHC catalysts were more effective for transfer hydrogenation reactions, compared to our team's catalyzed Ru–NHC studies [27–32]. Experiments on the more active iridium carbene catalysts will be tested on various reaction forms.

Experimental

All reactions for the prepared compounds were carried out under argon in flame-dried glassware using standard Schlenk techniques. Chemicals and solvents were purchased from Sigma-Aldrich, and Merck. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: Et_2O (Na/K alloy), CH_2Cl_2 (P_4O_{10}), hexane, toluene (Na).

The Schlenk line technique was used for performing all the synthesis and catalytic reactions. ^1H NMR and ^{13}C NMR spectra were recorded using a Varian As 300 Merkur spectrometer operating at 300 MHz (^1H), 75 MHz (^{13}C) in $CDCl_3$ and DMSO-d_6 with tetramethylsilane as an internal reference. The NMR studies were carried out in high-quality 5 mm NMR tubes. Signals are quoted in parts per million as δ a downfield from tetramethylsilane ($\delta = 0.00$ ppm) as an internal standard. Coupling constants (J values) are given in hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet signal. For the measurement of catalytic results (conversion and yield), Shimadzu GC 2025 with the specification of GC-FID sensor, column of RX-5 ms which have 30 m length, 0.25 mm diameter and 0.25 µM film thickness was used. FT-IR spectra were recorded on a Mattson 1000 spectrophotometer, wavenumbers in cm^{-1}. Column chromatography was performed using silica gel 60 (70–230 mesh). Solvent ratios are given as v/v.

General method for the preparation of benzimidazolium salts

A solution of *N*-alkylbenzimidazole (10.0 mmol) in 5 cm^3 DMF was added slowly to the alkyl or aryl halide (10.0 mmol), and the resulting mixture was stirred at room temperature for 5 h. Ethyl ether (10 cm^3) was added to obtain a white crystalline solid, which was filtered off. The solid was washed with diethyl ether (3–10 cm^3) and dried under vacuum, and the crude product was recrystallized from ethanol/diethyl ether.

1,3-Bis(4-methylbenzyl)benzimidazolium chloride (1a) This known compound was synthesized and characterized by m.p., ^1H and ^{13}C NMR analyses. The results found are consistent with the literature [34].

1,3-Bis(3,5-dimethylbenzyl)benzimidazolium bromide (1b) This known compound was synthesized and characterized by m.p., ^1H and ^{13}C NMR analyses. The results found are consistent with the literature [34].

1-(2,3,4,5,6-Pentamethylbenzyl)-3-(4-tert-butylbenzyl)-benzimidazolium bromide (1c, $C_{32}H_{37}BrN_2$) Yield: 3.99 g (79%); m.p.: 267–268 °C; IR: $\overline{\nu} = 1418$ (CN) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.28$ (s, 9H, $CH_2C_6H_4[C(CH_3)_3$–4]), 2.30 (s, 15H, $CH_2C_6(CH_3)_5$-2,3,4,5,6), 5.84 (s, 2H, $CH_2C_6(CH_3)_5$-2,3,4,5,6), 5.93 (s, 2H, $CH_2C_6H_4[C(CH_3)_3$-4]), 7.29–7.61 (m, 8H, $CH_2C_6H_4[C(CH_3)_3$-4] and C_6H_4), 10.95 (s, 1H, NC*H*N) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 17.1$, 17.2, and 17.3 ($CH_2C_6(CH_3)_5$-2,3,4,5,6), 31.1 and 34.6 ($CH_2C_6H_4[C(CH_3)_3$-4]), 48.2 ($CH_2C_6(CH_3)_5$-2,3,4,5,6), 51.1 ($CH_2C_6H_4[C(CH_3)_3$-4]), 113.6, 113.9, 124.7, 126.1, 127.1, 127.2, 127.9, 130.0, 131.5, 133.5, 134.0, 137.4, 142.2 ($CH_2C_6H_4[C(CH_3)_3$-4], ($CH_2C_6(CH_3)_5$-2,3,4,5,6), C_6H_4), 152.1 (NCHN) ppm.

General method for the preparation of [Ir(NHC)(COD)Cl] complexes

Under an argon atmosphere, a mixture of benzimidazolium salt (1 mmol) and Ag_2O (0.5 mmol) was suspended in 10 cm^3 degassed CH_2Cl_2 and stirred at ambient temperature for 12 h shielded from light. $[IrCl(COD)]_2$ (0.5 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 cm^3), 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.

Chloro(μ⁴-1,5-cyclooctadiene)[1,3-bis(4-methylbenzyl)-benzimidazol-2-ylidene]iridium(I) (2a, $C_{31}H_{34}ClIrN_2$) Yield: 0.27 g (78%); m.p.: 232–233 °C; IR: $\overline{\nu}$ = 1600 (CN) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.39–2.17 (m, 8H, $CHCH_2$), 2.60 (s, 6H, $CH_2C_6H_4(CH_3)$-4), 2.90 and 4.73 (p, 4H, $CHCH_2$), 5.74 and 6.44 (d, 4H, J = 6 Hz, $CH_2C_6H_4(CH_3)$-4), 6.82–7.31 (m, 12H, $C_6H_4(CH_3)$-4 and C_6H_4) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.6, 19.7, ($CH_2C_6H_4(CH_3)$-4), 29.1, 33.4, 49.8, 53.0 ($CHCH_2$), 87.1 ($CHCH_2$), 110.9, 112.2 ($CH_2C_6H_4(CH_3)$-4), 122.8, 124.5, 125.8, 126.7, 127.4, 128.5, 130.4, 131.1, 132.6, 134.3, 135.0, 135.2 ($C_6H_4(CH_3)$-4 and C_6H_4), 193.5 (Ir-C_{carb}) ppm.

Chloro(μ⁴-1,5-cyclooctadiene)[1,3-bis(3,5-dimethylbenzyl)-benzimidazol-2-ylidene]iridium(I) (2b, $C_{33}H_{40}ClIrN_2$) Yield: 0.29 g (82%); m.p.: 239–240 °C; IR: $\overline{\nu}$ = 1603 (CN) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.28–1.80 (m, 8H, $CHCH_2$), 2.21 (s, 12H, $CH_2C_6H_4(CH_3)_2$-3,5), 2.86 and 4.68 (q, 4H, $CHCH_2$), 5.85–6.0 (m, 4H, $CH_2C_6H_4(CH_3)_2$-3,5), 6.85–7.19 (m, 10H, $C_6H_4(CH_3)_2$-3,5 and C_6H_4) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, ($CH_2C_6H_4(CH_3)_2$-3,5), 29.2, 33.4, 52.5 ($CHCH_2$), 86.9 ($CHCH_2$) 111.1 ($CH_2C_6H_4(CH_3)_2$-3,5), 122.4, 125.0, 127.1, 129.4, 135.2, 135.9, 138.3 ($C_6H_4(CH_3)_2$-3,5 and C_6H_4), 192.7 (Ir-C_{carb}) ppm.

Chloro(μ⁴-1,5-cyclooctadiene)[1-(2,3,4,5,6-pentamethylbenzyl)-3-(4-tert-butylbenzyl)benzimidazol-2-ylidene]-iridium(I) (2c, $C_{38}H_{48}ClIrN_2$) Yield: 0.31 g (80%); m.p.: 246–247 °C; IR: $\overline{\nu}$ = 1443 (CN) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.22 (s, 9H, $CH_2C_6H_4[C(CH_3)_3$-4]), 1.55–1.85 (m, 8H, $CHCH_2$), 2.21 (d, 15H, J = 6 Hz, $CH_2C_6(CH_3)_5$-2,3,4,5,6), 2.85–4.74 (m, 4H, $CHCH_2$), 5.74–6.35 (m, 4H, s, 2H, $CH_2C_6H_4[C(CH_3)_3$–4]) and $CH_2C_6(CH_3)_5$-2,3,4,5,6), 6.70–7.27 (m, 8H, $CH_2C_6H_4[C(CH_3)_3$-4] and C_6H_4) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.3, 16.9, 17.2 ($CH_2C_6(CH_3)_5$-2,3,4,5,6), 31.2, 31.3, 33.5, 34.6 ($CHCH_2$), 47.7, 53.9 ($CH_2C_6H_4[C(CH_3)_3$-4]), 65.7, 72.1 ($CHCH_2$), 86.5 ($CH_2C_6(CH_3)_5$-2,3,4,5,6), 111.3 ($CH_2C_6H_4[C(CH_3)_3$-4]), 112.3, 124.1, 124.4, 125.9, 126.4, 126.8, 131.9, 133.9, 134.4, 137.5, 151.4 ($CH_2C_6H_4[C(CH_3)_3$-4], [$CH_2C_6(CH_3)_5$-2,3,4,5,6] and C_6H_4), 192.8 (Ir-C_{carb}) ppm.

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