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Quinoline-functionalized N-heterocyclic carbene complexes of iridium: Synthesis, structures and catalytic activities in transfer hydrogenation

Jia-Feng Sun [a], Fei Chen [a], Brenda A. Dougan [b], Hui-Jun Xu [a], Yong Cheng [a], Yi-Zhi Li [a], Xue-Tai Chen [a,*], Zi-Ling Xue [b,*]

[a] Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China
[b] Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600, USA

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ABSTRACT

Iridium complexes containing quinoline-functionalized N-heterocyclic carbene (NHC) ligands have been synthesized by the transmetalation route from silver carbene precursors. The silver complexes undergo a facile reaction with $[Ir(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) to yield a series of carbene complexes [(NHC)Ir(COD)Cl] (NHC = 3-methyl-1-(8-quinolylmethyl)imidazole-2-ylidene (**2a**); 3-*n*-butyl-1-(8-quinolylmethyl)imidazole-2-ylidene (**2b**); 3-benzyl-1-(8-quinolylmethyl)imidazole-2-ylidene (**2c**); 1,3-di(8-quinolylmethyl)imidazole-2-ylidene (**2d**). The coordinated COD was replaced by carbon monoxide to yield the corresponding carbonyl species $[(NHC)Ir(CO)_2Cl]$ (**3**). Complexes **2** and **3** have been characterized by IR, ESI-MS, ^1H and ^{13}C NMR and elemental analyses. The molecular structures of complexes **2b** and **2c** have been confirmed by single-crystal X-ray diffraction. Two analogous Ir(I) complexes **5** and **6** with naphthalene-containing NHC have also been synthesized and characterized. These Ir(I) complexes in the current work have been proved to be active catalysts in the transfer hydrogenation of ketones to alcohols using 2-propanol as the hydrogen source.

1. Introduction

In the past decade, N-heterocyclic carbenes (NHCs), in particular imidazolin-2-ylidenes, have attracted much attention because their transition metal complexes display rich coordination chemistry [1–4], and the complexes demonstrate high homogeneous catalytic activities [5–8]. Among the various metal complexes, applications of the iridium NHC complexes in catalysis have been actively studied. It is known that Ir–NHC complexes can catalyze a variety of reactions including the Oppenauer-type oxidation [9], transfer hydrogenation of carbonyl [10–16] and nitro [17] compounds, cyclization of alkynylcarboxylic acids [15,18], hydrogenation of olefins [19–23], hydrosilylation [15,24–26], hydroamination [27], and bornylation [28], among which transfer hydrogenation of ketone is an important synthesis with applications in many fields [29,30]. In comparison to the commonly used reduction processes [30], catalytic transfer hydrogenation employs hydrogen donors, e.g., 2-propanol. The process is safer, highly selective, economic, and eco-friendly [31–34]. A broad range of alcohols are accessible by transfer hydrogenation under mild reactions in the presence of various metal catalysts [10–16].

In comparison to the electronically similar phosphine ligand systems [35], NHC-based catalysts are considered to be stable against heat, moisture, and oxygen [36]. Recently, research has also been devoted to the synthesis of nitrogen-functionalized ligands containing NHC moieties, in order to modify the ligand properties and catalytic activities [37–40]. The nitrogen donor atom would act as a hemilabile arm, capable of reversible dissociation from the metal center. For example, the combination of pyridine and NHC leads to a large diverse group of ligands, some of which have shown interesting coordination chemistry and efficient catalytic applications [15,16,41]. Some Ir(I) and Ir(III) complexes with pyridine-functionalized HNCs have been prepared and showed active transfer hydrogenation of ketones [15,16]. Here we report the synthesis and characterization of a series of new quinoline-functionalized NHC iridium(I) cyclooctene and carbonyl complexes [(NHC)Ir(COD)Cl] (NHC = 3-methyl-1-(8-quinolylmethyl)imidazole-2-ylidene (**2a**); 3-*n*-butyl-1-(8-quinolylmethyl)imidazole-2-ylidene (**2b**); 3-benzyl-1-(8-quinolylmethyl)imidazole-2-ylidene (**2c**); 1,3-di(8-quinolylmethyl)imidazole-2-ylidene (**2d**) and $[(NHC)Ir(CO)_2Cl]$ (**3**) and their catalytic activities toward the transfer hydrogenation of ketones. In addition, two analogous iridium(I) complexes with naphthalene-containing NHC have also been prepared and examined in order to probe the influence of the quinoline nitrogen donor in the transfer hydrogenation reaction. It is noted that when this paper is under review, Li et al. reported the

* Corresponding authors. Tel.: +86 25 83597147; fax: +86 25 83314502. (X.-T. Chen).
E-mail address: xtchen@netra.nju.edu.cn (X.-T. Chen).

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preparation of complex **2b** and a few other iridium(I), iridiium(III) [42] and palladium complexes [43] with quinoline-functionalized NHC.

2. Results and discussion

2.1. Synthesis and characterization

Quinoline-functionalized imidazolium salts were used as precursors to N-heterocyclic carbene ligands. The salts were synthesized by reacting 8-bromomethylquinoline with the corresponding substituted imidazoles according to Scheme 1. The salts **1a–1d** were found to be hygroscopic and soluble in chlorinated solvents. The NMR spectroscopic data of **1a–1d** agree with the proposed structures. In the ^{1}H NMR spectra of **1a–1d**, the imidazolium protons appear at δ 10.28–10.60 ppm.

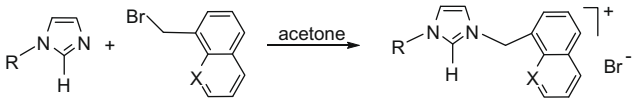
Transmetalation from Ag–NHC complex has been shown to be an efficient method for the preparation of NHC complexes of transition metals [44]. Here, a two-step process was used to prepare the iridium(I) cyclooctene complexes. The first involves deprotonation of the imidazolium salts with Ag_2O to form the Ag–NHC species [45–49]. Although these complexes can be isolated, we used our Ag–NHC complexes *in situ*. The addition of $[Ir(COD)Cl]_2$ to the mixture gave the yellow complexes **2a–2d** in good yields (see Scheme 2).

The ^{1}H NMR spectra of **2a–2d** do not exhibit a signal at 10–11 ppm, where the imidazolium C_2-H signals of the precursors are found, indicating the formation of iridium–carbene bond. The chemical shifts of the quinolyl rings are essentially similar to those of the corresponding precursors, indicating that the quinolyl nitrogen donor remains uncoordinated. Furthermore, ^{1}H NMR spectra show diastereotopic protons for the CH_2 linker (e.g., δ = 6.45 and 6.29, $^2J_{HH}$ = 14.5 Hz in **2a**). ^{13}C NMR data for the coordinating carbene carbons appear at δ *180.1–181.5* ppm, suggesting the formation of the Ir–C bond. These signals are in the typical range for Ir–$C_{carbene}$ analogues [15,17,18,25,50].

Complexes **2a–2d** were converted to the corresponding dicarbonyl complexes **3a–3d** through reactions with excess CO in CH_2Cl_2 at room temperature (Scheme 2). Cyclooctadiene is easily displaced in minutes, as shown by a color change from bright to pale yellow. The cis geometry proposed in Scheme 2 is supported by IR spectroscopy, which shows two CO stretching vibrations of similar intensity. Inequivalent CO carbon atoms were also observed in ^{13}C NMR spectroscopy. The geometry is consistent with the ^{1}H NMR spectrum, in which the N-CH_2 protons are diastereotopic.

Variable-temperature ^{1}H NMR studies of **2b**, **3a**, **3c**, and **3d** were conducted from −10 to 40 °C. The VT ^{1}H NMR spectra of **3a** from −10 to 40 °C are given in Fig. 1. Additional spectra are given in the Supplementary material. These VT NMR spectra show that the signals of the quinoline groups are independent with the temperature with no indication of quinoline nitrogen coordination to Ir(I) atoms.

In the case of both **3a** and **3c**, the –CH_2 linker, the NCH_2Qu, shows an AB system around 6.1 ppm at −10 °C (Fig. 1 for **3a** and Supplementary material for **3c**), indicating the two protons are diastereotopic, perhaps as a result of restricted ligand rotation. As the temperature was raised to 40 °C, they gradually coalesced into a broad peak at 6.15 ppm. Fast ligand rotation makes the two protons in the –CH_2 linker equivalent. For **2b** and **3d**, its VT ^{1}H NMR spectra (Supplementary material) remains an AB system till at least 40 °C.



X = N, R = Me, **1a**; *n*-Bu, **1b**;Bn, **1c**;Qu, **1d**
Qu=8-quinolylmethyl
X = C, R = *n*-Bu, **4**

Scheme 1.

The positive ion ESI-MS analyses for **2a–2d** and **3a–3d** in each case showed a major *m*/*z* peak corresponding to the $[MCl]^+$ fragment.

The analogous naphthalene-functionalized imidazolium salt **4** and the corresponding iridium(I) complexes **5** and **6** were prepared by the same procedures (Schemes 1 and 2). Complexes **4–6** were characterized by IR, ESI-MS, ^{1}H and ^{13}C NMR and elemental analyses. Their spectroscopic data are consistent with their suggested compositions and structures.

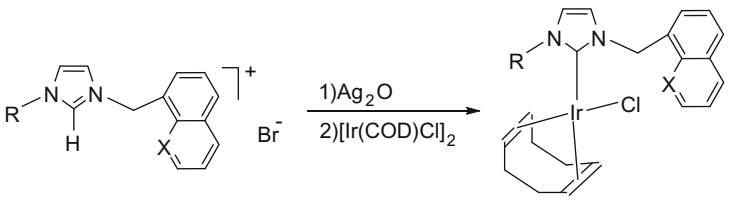
2.2. Structural studies

Detailed coordination spheres around the metal center of **2b** and **2c** are confirmed by the X-ray crystal analyses. The molecular structures of **2b** and **2c** in the solid state are depicted in Figs. 2 and 3, respectively. For **2b**, the asymmetric unit contains two crystallographically nonequivalent molecules A and B, whose structures are almost identical, with only small differences in bond distances and bond angles.

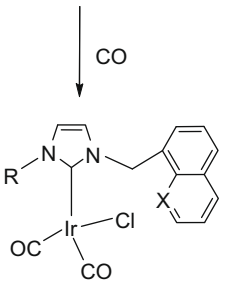
Crystallographic analysis confirms the C_2 binding mode in both **2b** and **2c**. The coordination sphere is square planar for both complexes, and the selected bond distances, bond angles and torsion angles are given in Table 1. The Ir–$C_{carbene}$ distances of 2.024(10), 2.033(10) Å for **2b** and 2.024(7) Å for **2c** are typical for this type of carbene coordination [17,50]. The C–C distances of 1.335(14), 1.307(16) Å for **2b** and 1.346(11) Å for **2c** in the imidazole ring are consistent with a double bond and supports the perturbed aromatization [4] proposed to occur upon carbene formation. The average distance of Ir–C_{COD} trans to the carbene donor (2.16 Å for **2b** and **2c**) appears to be longer than those in the cis arrangement (2.10 Å for **2b** and **2c**), suggesting that the σ-donor nature of the diaminocarbene is stronger than that of the chloride. The torsion angles for N–C–Ir–Cl (Table 1) indicated that the imidazole ring is almost orthogonal to the square plane, which accounts for the diastereotopic N-CH_2 protons if Ir–C rotation is slow.

2.3. IR and electrochemistry

The infrared carbonyl stretching frequencies of the iridium complexes *cis*-[(L)Ir$(CO)_2$Cl] are well documented as a good evaluation of the electron-donating properties of L ligand [50–53]. In Table 2, the carbonyl frequencies of [(NHC)Ir$(CO)_2$Cl] (**3a–3d** and **6**) are listed and compared with those of analogous complexes. The carbonyl stretching frequencies show that the υ_{av}(CO) values are nearly the same for **3a–3d**, leading to the close values of Tolman electronic parameter (TEP) of NHCs ligands. However, TEP values of these quinoline-functionalized carbenes are significantly higher than those commonly used NHCs reported in the literature, indicating that these quinoline-containing NHCs are less electron-donating. It is also very interesting to note that TEP value of the naphthalene-containing NHC derived from the imidazolium salt **4** is lower than the quinoline-functionalized NHCs, indicating that the electronic effect induced by the substitution of nitrogen atom in place of carbon is very significant and naphthalene-containing NHC is more electron-donating than the quinoline-functionalized NHC. The TEP values of these quinoline-functionalized NHC of [(NHC)Ir$(CO)_2$Cl] (**3**) display nearly the same values as [(PCy_3)Ir $(CO)_2$Cl]. Therefore, the quinoline-functionalized NHCs ligands



X = N, R = Me, **2a**; *n*-Bu, **2b** ;Bn, **2c**; Qu, **2d**
X = C, R = n-Bu, **5**



X = N, R = Me, **3a**; *n*-Bu, **3b**;Bn, **3c**; Qu, **3d**
X = C, R = n-Bu, **6**

Scheme 2.

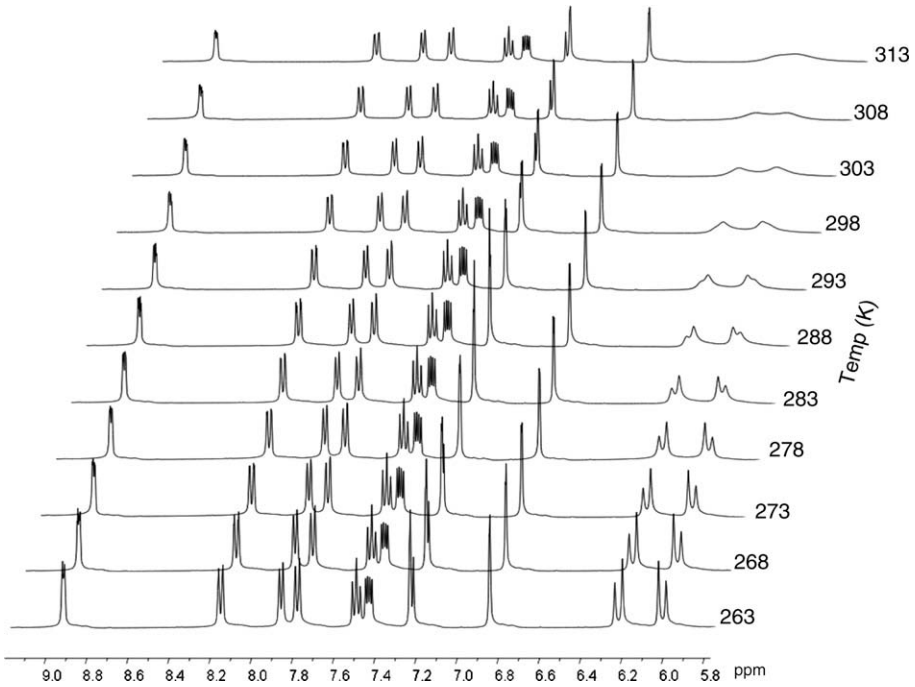


Fig. 1. ^{1}H NMR spectra of **3a** between −10 and 40 °C in $CDCl_3$.

have almost the same electron-donating capacity as PCy_3, one of the most donating phosphine ligands known.

The electrochemical properties of transition metal complexes of NHCs have been probed previously [54–56]. CV of complexes **2a–2d** was performed at a scan rate of 100 mV s^{-1} at a GC electrode in CH_2Cl_2 and the results are shown in Table 3. These complexes undergo a one-electron oxidation process with the anodic peak potential (E_{pa}) in the range 0.642–0.701 V and one reduction process with the cathodic peak potential (E_{pc}) ranging 0.501–0.531 V when the scan direction was reversed. Moreover, the peak current for the anodic process is larger than that of the cathodic process, indicating that the oxidized species are not stable. The oxidized species undergoes some chemical reactions after the anodic process [42]. We also examined the naphthalene-containing iridium(I) complex **5** under the same condition. The cyclic voltammogram of **5** (Fig. 4) shows one anodic peak, but no obvious cathodic peak is observed. The more positive E_{pa} value of 0.926 V indicated that complex **5** is more difficult to be oxidized than **2a–2d**. In other

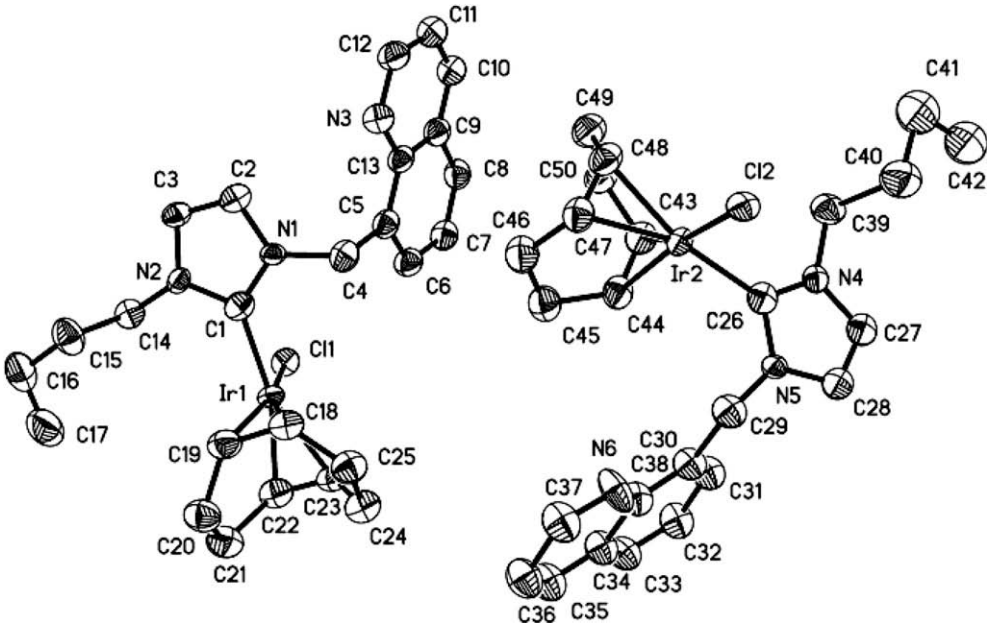


Fig. 2. Molecular structure and atom numbering scheme for complex **2b** (drawn with 30% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

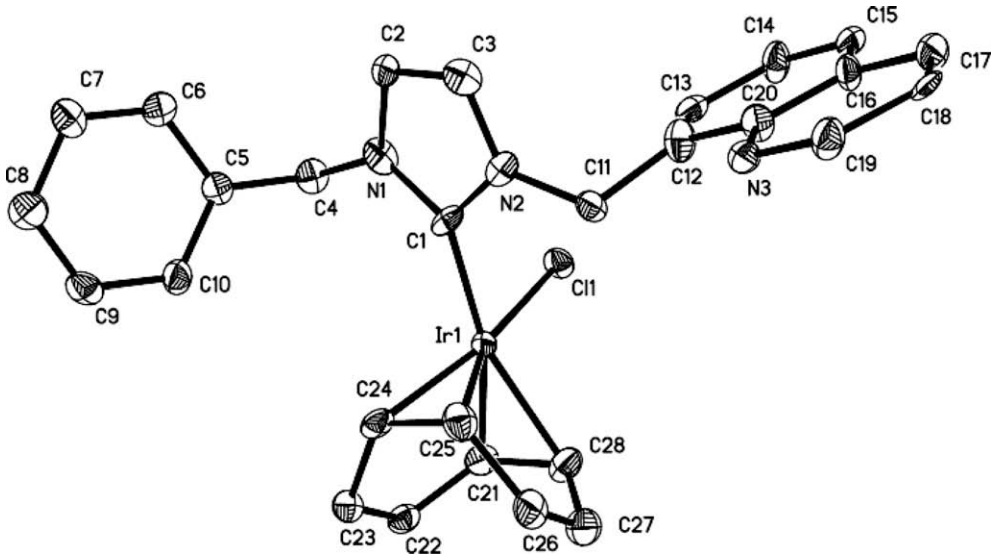


Fig. 3. Molecular structure and atom numbering scheme for complex **2c** (drawn with 30% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

words, naphthalene-containing NHC is more electron-donating than quinoline-functionalized carbenes, which is consistent with the conclusions from IR results.

2.4. Catalytic studies

Complexes of type (COD)Ir(NHC)X (X = Br, NHC = 1,3-di(propyl)benzimidazol-2-ylidene [12]; X = Cl, 1,3-mesitylimidazol-2-ylidene [13]; X = Cl, NHC = 3-methyl-1-(6-methylpicolyl)imidazol-2-ylidene [16]; X = Cl, 3-methyl-1-(6-mesitylpicolyl) imidazol-2-ylidene [16], and X = Br, annulated NHC derived from 2-methylaminopiperidine [17]) have been tested for the transfer hydrogenation of some ketones such as cyclohexanone and acetophenone. It should be noted that these catalytic studies were reported to be carried out under different reaction conditions and even with different substrates and bases. These results promoted us to investigate the transfer hydrogenation of ketone by **2a–2d** and **3a–3d**. Complexes **5** and **6** were also tested under the same catalytic conditions to probe the possible influence of the quinoline nitrogen atom. The reduction of acetophenone to 1-phenylethanol by 2-propanol was chosen as a model reaction in the current work to explore the catalytic behavior in transfer hydrogenation (Scheme 3). Thus, in a typical experiment, the catalyst precursor (0.05 mol%) was added to a solution of KOH (1.5 mol%) and ^{i}PrOH (10 mL). Acetophenone (8 mmol) was then add at 82 °C. The reaction was monitored by gas chromatograph (GC) and time-dependent conversion for transfer hydrogenation of acetophenone were followed (Fig. 5). Among all the quinoline-functionalized NHC Ir complexes, **2a** and **2b** are very active, giving more than 90% conversion after 40 min. The complexes of the type [(NHC)Ir(CO)$_2$Cl] (**3**, **6**) are generally less active than [(NHC)Ir(COD)Cl] (**2, 5**), probably due to the fact that COD is more easily removed from the metal center than CO. Among the tested complexes, **2b** is the most efficient in the transfer hydrogenation of acetophenone to

Table 1
Selected bond distances (Å) and angles (°) for **2b** and **2c**.

2b				**2c**	
Molecule A		Molecule B			
Bond distances					
Ir1–C1	2.024(10)	Ir2–C26	2.033(10)	Ir1–C1	2.024(7)
Ir1–Cl1	2.366(2)	Ir2–Cl2	2.366(2)	Ir1–Cl1	2.3569(18)
Ir1–C18	2.107(11)	Ir2–C43	2.109(10)	Ir1–C21	2.150(8)
Ir1–C19	2.119(16)	Ir2–C44	2.077(10)	Ir1–C24	2.119(8)
Ir1–C22	2.152(11)	Ir2–C47	2.165(11)	Ir1–C25	2.100(9)
Ir1–C23	2.166(10)	Ir2–C48	2.159(11)	Ir1–C28	2.178(9)
C2–C3	1.335(14)	C27–C28	1.307(16)	C2–C3	1.346(11)
Bond angles					
C1–Ir1–C18	91.7(4)	C26–Ir2–C43	93.4(4)	C1–Ir1–C21	161.9(3)
C1–Ir1–C19	93.2(4)	C26–Ir2–C44	91.6(4	C1–Ir1–C24	81.8(3)
C1–Ir1–C22	164.2(5)	C26–Ir2–C47	160.2(5)	C1–Ir1–C25	95.8(3)
C1–Ir1–C23	161.2(5)	C26–Ir2–C48	164.7(5)	C1–Ir1–C28	158.7(3)
C1–Ir1–Cl1	90.9(3)	C26–Ir2–Cl2	89.3(3)	C1–Ir1–Cl1	89.5(2)
Cl1–Ir1–C18	164.1(4)	Cl2–Ir2–C43	160.0(3)	Cl1–Ir1–C21	90.3(3)
Cl1–Ir1–C19	159.0(4)	Cl2–Ir2–C44	162.6(3)	Cl1–Ir1–C24	161.8(2)
Cl1–Ir1–C22	88.5(3)	Cl2–Ir2–C47	92.4(3)	Cl1–Ir1–C25	159.5(2)
Cl1–Ir1–C23	91.2(3)	Cl2–Ir2–C48	90.0(3)	Cl1–Ir1–C28	89.9(2)
N1–C1–N2	104.1(8)	N4–C26–N5	104.8(8)	N1–C1–N2	103.0(6)
N1–C1–Ir1	130.0(8)	N4–C26–Ir2	129.1(8)	N1–C1–Ir1	130.9(6)
N2–C1–Ir1	125.3(8)	N5–C26–Ir2	126.1(8)	N2–C1–Ir1	125.0(5)
Torsion angles					
N1–C1–Ir1–Cl1	−94.3(10)	N4–C26–Ir2–Cl2	−88.2(8)	N1–C1–Ir1–Cl1	76.4(7)
N2–C1–Ir1–Cl1	75.0(9)	N5–C26–Ir2–Cl2	90.0(7)	N2–C1–Ir1–Cl1	−89.5(6)

Table 2
Carbonyl stretching frequencies for [(L)Ir(CO)$_2$Cl].

L[a]	υ(CO) (cm^{-1})	υ_{av}(CO) (cm^{-1})	TEP (cm^{-1})	Ref.
1a*	2069.6, 1986.0	2027.8	2057.1[b]	This work
1b*	2068.8, 1984.9	2026.9	2056.4[b]	This work
1c*	2070.2, 1986.6	2028.4	2057.5[b]	This work
1d*	2068.5, 1985.8	2027.2	2056.6[b]	This work
4*	2062.5, 1978.8	2020.7	2051.9[b]	This work
tmiy	2063, 1976	2020	2050	50
biy	2062, 1978	2020	2051	50
ItBu	2064.6, 1980.0	2022.3	2050.1	53
IAd	2063.4, 1979.8	2021.6	2049.5	53
ICy	2064.8, 1981.2	2023.0	2049.6	53
IPr	2066.8, 1981.0	2023.9	2051.5	53
IMes	2066.4, 1979.8	2023.1	2050.7	53
PCy$_3$	2072, 1984	2028.0	2056.4	50

[a] **1a***–**1d***, **4*** represent the carbenes derived from precursors **1a**–**1d** and **4**. tmiy = 1,3-di(4-tolylmethyl)imidazole-2-ylidene, biy = 1,3-di-*n*-butylimidazole-2-ylidene, ItBu = 1,3-di-*t*-butylimidazole-2-ylidene, IAd = 1,3-diadamantylimidazole-2-ylidene, ICy = 1,3-di cyclohexylimidazole-2-ylidene, IPr = 1,3-di(2,6-diisopropylphenyl)imidazole-2-ylidene, IMes = 1,3-di(2,4,6-trimethylphenyl)imidazole-2-ylidene.
[b] Values calculated by equation TEP = 0.722 υ_{av}(CO) + 593 cm^{-1} [50].

Table 3
Redox potentials of the [(NHC)Ir(COD)Cl] complexes in CH_2Cl_2 (scan rate 100 mV s^{-1}).[a]

[(NHC)Ir(COD)Cl]	E_{pa} (V)	E_{pc} (V)	i_{pa}/i_{pc}
2a	0.656	0.503	2.660
2b	0.674	0.513	2.820
2c	0.701	0.531	2.704
2d	0.642	0.501	2.086
5	0.926	–	–

[a] E_{pa} and E_{pc} is the anodic and cathodic peak potentials (vs. Ag/AgCl in 0.1 M Bu_4NClO_4), respectively. i_{pa} and i_{pc} is the anodic and cathodic peak currents, respectively.

1-phenylethanol. These data indicated that the influence of the substituents at the ring nitrogen atom on the catalytic activity.

The comparison between **2b** and **5**, **3b** and **6** would provide the possible influence of the quinolyl group in the catalytic transfer

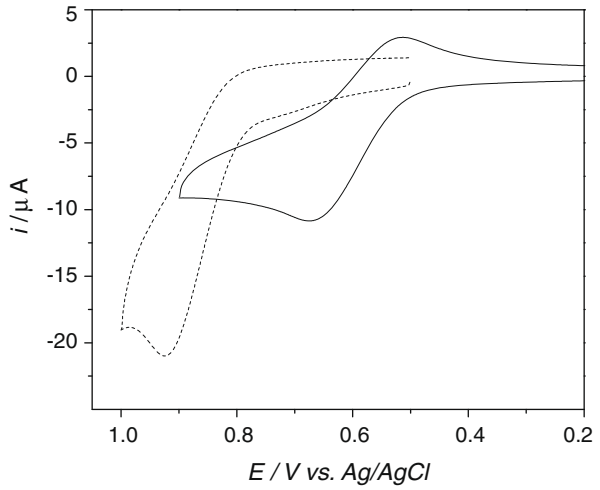
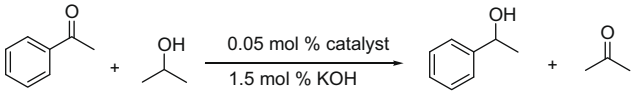


Fig. 4. Cyclic voltammograms of 1 mM solutions of complexes **2b** (solid line) and **5** (dashed line) performed at a 2 mm diameter GC electrode in CH_2Cl_2 (containing 0.1 M Bu_4NClO_4) at a scan rate of 100 mV s^{-1}.



Scheme 3.

hydrogenation. The iridium(I) complexes **5** and **6** with naphthalene-containing NHC have lower activities than those quinoline-containing complexes, indicating that the employment of quinoline tether is beneficial for the catalytic reaction. The possible reasons for this improvement could be due to the probable coordination of the quinolyl group in the catalytic cycle. Li et al. have demonstrated that the quinolyl group would coordinate to the iridium atom when [(NHC)IrCl] was treated with KPF_6 [42]. It is possible that similar coordination of quinolyl group could occur in the unsaturated active catalytic species, which is favorable for the

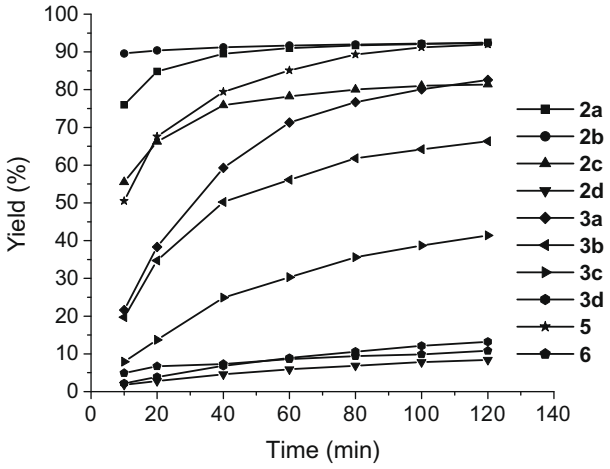


Fig. 5. Time dependence of the catalytic transfer hydrogenation of acetophenone. Conditions: reactions were carried out at 82 °C using 8 mmol of acetophenone. Ketone/complex/KOH ratio: 2000:1:30. Yield of 1-phenylethanol determined by GC analysis.

catalytic reaction. Another possible reason is the different electronic effect between the NHCs derived from **1b** and **4**.

On the basis of the high activity shown by **2b** in the transfer hydrogenation of acetophenone, we decided to further explore its catalytic potential in the reduction of other ketones. The results are listed in Table 4. Generally, a good efficiency of **2b** as a precatalyst has been observed for all the ketones employed. The higher TOF (11 400 h^{-1}) were obtained for the acetophenone derivatives with electro-withdrawing group (Cl) in the para position (Table 4, entry 2). In comparison, slower reduction was observed for its electro-donating groups (OMe, Me) substituted derivatives (entries 3 and 4; TOF = 670, 620 h^{-1}). The presence of an electron-withdrawing group has generally been found to facilitate the hydrogen transfer reaction [57–59], and this has been attributed to the hydridic nature of the reducing species involved. Furthermore, it has been shown to be less efficient in the reduction of benzophenone (entry 5) and dialkyl ketones (entries 6 and 7) compared to acetophenone (entry 1). These differences in the catalytic activities could be attributed to the electronic and steric effects of the substituents in ketones.

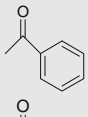
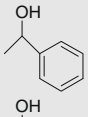
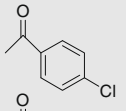
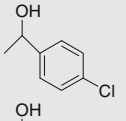
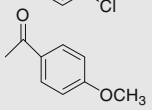
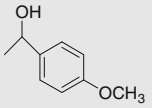
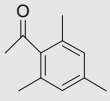
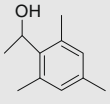
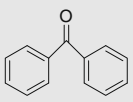
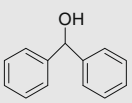
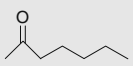
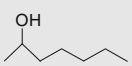
3. Experimental

3.1. Reagents and general procedures

All reactions and manipulations were carried out in either a nitrogen-filled glove-box or under nitrogen using standard Schlenk-line techniques. Dichloromethane was dried over P_2O_5 and distilled under nitrogen. Other solvents were used as received. 8-Bromomethylquinoline and 1-bromomethylnaphthalene [60,61] and metal precursor $[Ir(COD)Cl]_2$ [62] were synthesized according to the literature methods. All other chemicals were purchased from commercial sources and used without further purification.

^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer operating at 500 MHz (^1H NMR) and 125 MHz (^{13}C NMR), respectively, and referenced to $SiMe_4$ (δ in parts per million, J in hertz). Variable-temperature ^1H NMR spectra were recorded on a Bruker AMX-400 spectrometer and referenced to residual proton in $CDCl_3$. Electrospray mass spectra (ESI-MS) were recorded using an LCQ electron spray mass spectrometer (Finnigan). Infrared spectra were measured on a Nicolet NEXUS870 FT-IR spectrometer. Elemental analyses were performed on a Perkin–Elmer 240C analytic instrument. GC measurements were made on Shimadzu GC-2010 equipment. Cyclic voltammetric measurements were performed on a 273A Potentiostat/Gawanostat (EG&G) using a glassy carbon working electrode, a platinum wire counter electrode, and Bu_4N-

Table 4
Catalytic transfer hydrogenation of ketones by complex **2b**.[a]

Entry	Ketone	Product	Yield% (min)[b]	Final TOF (h^{-1})[c]
1			90(20)	5400
2			95(10)	11400
3			67(120)	670
4			62(120)	620
5			91(60)	1800
6			75(60)	1500
7			91(30)	3600

[a] Conditions: reactions were carried out at 82 °C using 8 mmol of ketone. Ketone/complex/KOH ratio: 2000:1:30.
[b] Yield determined by GC analysis.
[c] Turnover frequency (mol of product per mol of complex per hour).

ClO_4 (TBAP) as supporting electrolyte. All the potentials were referenced to Ag^+/Ag electrode and the solutions were purged with N_2 before each set of experiments.

3.2. Preparation of ligands and iridium complexes

3.2.1. 3-Methyl-1-(8-quinolylmethyl)imidazolium bromide (**1a**)

To a solution of 8-bromomethylquinoline (2.615 g, 11.78 mmol) in acetone (20 mL) was added 1-methylimidazole (0.967 g, 11.78 mmol). The mixture was stirred for 24 h at room temperature, and the desired product precipitated as a white solid from the solution. The solid was collected and washed with THF (2×10 mL) and then dried under vacuum. Yield: 3.410 g (95%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 10.39 (s, 1H, NCHN), 8.96 (d, 1H, $^3J_{HH}$ = 2.1 Hz, QuH^2), 8.30 (d, 1H, $^3J_{HH}$ = 6.7 Hz, QuH^4), 8.20 (d, 1H, $^3J_{HH}$ = 8.0 Hz, QuH^5), 7.86 (d, 1H, $^3J_{HH}$ = 8.0 Hz, QuH^7), 7.73 (s, 1H, HCCH), 7.55 (t, 1H, $^3J_{HH}$ = 7.5 Hz, QuH^6), 7.47 (dd, 1H, $^3J_{HH}$ = 7.8 and 4.0 Hz, QuH^3), 7.36 (s, 1H, HCCH), 6.14 (s, 2H, NCH_2Qu), 4.01 (s, 3H, NCH_3). ^{13}C NMR ($CDCl_3$, 25 °C): 150.3, 145.5, 136.8, 136.4, 131.4, 131.2, 129.7, 128.1, 126.3, 123.1, 122.7, 121.6 (Qu and Im), 48.7 (NCH_2Qu), 36.5 (NCH_3). Anal. Calc. for $C_{14}H_{14}BrN_3$: C, 55.28; H, 4.64; N, 13.81. Found: C, 55.21; H, 4.57; N, 13.80%.

3.2.2. 3-n-Butyl-1-(8-quinolylmethyl)imidazolium bromide (**1b**)

To a solution of 8-bromomethylquinoline (2.683 g, 12.08 mmol) in acetone (20 mL) was added 1-*n*-butylimidazole (1.500 g, 12.08 mmol). After it was stirred for 48 h at room temperature, the solvent was removed under vacuum to afford thick brown syrup. The syrup was redissolved in CH_2Cl_2 (10 mL). Addition of ether (20 mL) caused an oil to separate out. The solvent was decanted off, and the oily solid that formed was triturated with THF (20 mL) to give a powder. This was further washed with THF (2×10 mL) and then dried under vacuum. Yield: 3.636 g (87%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 10.39 (s, 1H, NCHN), 8.90 (br, 1H, QuH^2), 8.27 (d, 1H, $^3J_{HH}$ = 4.0 Hz, QuH^4), 8.14 (d, 1H, $^3J_{HH}$ = 6.7 Hz, QuH^5), 7.79 (d, 1H, $^3J_{HH}$ = 6.8 Hz, QuH^7), 7.70 (s, 1H, HCCH), 7.47 (t, 1H, QuH^6), 7.40 (m, 2H, QuH^3 and HCCH), 6.11 (s, 2H, NCH_2Qu), 4.21 (br, 2H, NCH_2), 1.77 (br, 2H, NCH_2CH_2), 1.24 (br, 2H, $NCH_2CH_2CH_2$), 0.81 (br, 3H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 25 °C): 150.7, 146.1, 137.3, 136.8, 132.1, 131.8, 130.2, 128.7, 126.9, 123.3, 122.3, 122.1 (Qu and Im), 49.2 (NCH_2Qu), 49.9, 32.3, 19.6, 13.6 ($NCH_2CH_2CH_2CH_3$). Anal. Calc. for $C_{17}H_{20}BrN_3$: C, 58.97; H, 5.82; N, 12.14. Found: C, 56.88; H, 5.65; N, 10.66%. This compound is highly hydroscopic, and this may have led to the current EA results. The identity of this compound was confirmed in its subsequent reaction with Ag_2O and then $[Ir(COD)Cl]_2$ to give **2b**.

3.2.3. 3-Benzyl-1-(8-quinolylmethyl)imidazolium bromide (**1c**)

A procedure analogous to the synthesis of **1b**, except using 8-bromomethylquinoline (3.063 g, 13.79 mmol) and 1-benzylimidazole (2.181 g, 13.79 mmol) in acetone (20 mL), gave **1c** as a solid. Yield: 4.192 g (80%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 10.28 (s, 1H, NCHN), 8.79 (br, 1H, QuH^2), 8.10 (br, 1H, QuH^4), 8.03 (br, 1H, QuH^5), 7.69 (br, 1H, QuH^7), 7.58 (s, 1H, HCCH), 7.33 (m, 5H, QuH^6, QuH^3 and Ph), 7.12 (m, 3H, Ph and HCCH), 5.94 (s, 2H, NCH_2Qu), 5.44 (s, 2H, NCH_2Ph). ^{13}C NMR ($CDCl_3$, 25 °C): 150.3, 145.6, 136.6, 134.1, 131.7, 131.1, 129.9, 129.1, 128.7, 128.3, 126.5, 123.0, 121.5, 119.4 (Qu, Im and Ph), 52.9 (NCH_2Ph), 49.2 (NCH_2Qu). Anal. Calc. for $C_{20}H_{18}BrN_3$: C, 63.17; H, 4.77; N, 11.05. Found: C, 63.02; H, 4.79; N, 10.90%.

3.2.4. 2-(1H-Imidazol-1-ylmethyl)quinoline

A mixture of 8-bromomethylquinoline (3.122 g, 14.06 mmol), imidazole (0.958 g, 14.07 mmol), and potassium hydroxide (2.363 g, 42.11 mmol) in THF (20 mL) was refluxed for 48 h. The solvent was completely removed under reduced pressure. CH_2Cl_2 (20 mL) was added, and thoroughly washed by several portions of H_2O (20 mL). After separation, the organic layer was dried with anhydrous $MgSO_4$. The solution was filtered, and the solvent was removed under reduced pressure to give a brown liquid as pure product. Yield: 2.173 g (74%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 8.93 (d, 1H, $^3J_{HH}$ = 3.2 Hz, QuH^2), 8.14 (d, 1H, $^3J_{HH}$ = 7.9 Hz, QuH^4), 7.76 (d, 1H, $^3J_{HH}$ = 8.2 Hz, QuH^5), 7.72 (s, 1H, NCHN), 7.46-7.42 (m, 2H, QuH^7 and QuH^6), 7.31 (d, 1H, $^3J_{HH}$ = 6.9 Hz, QuH^3), 7.05 (s, 2H, HCCH), 5.80 (s, 2H, NCH_2Qu). ^{13}C NMR ($CDCl_3$, 25 °C): 150.3, 146.0, 138.3, 136.7, 135.3, 129.4, 128.7, 128.6, 128.5, 126.7, 122.0, 120.2 (Qu and Im), 47.3 (NCH_2Qu).

3.2.5. 1,3-Di(8-quinolylmethyl)imidazolium bromide (**1d**)

A procedure analogous to the synthesis of **1a**, except using 8-bromomethylquinoline (2.306 g, 10.38 mmol) and 2-(1*H*-imidazol-1-ylmethyl)quinoline (2.173 g, 10.39 mmol) in acetone (20 mL), gave **1d** as a solid. Yield: 3.757 g (84%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 10.60 (s, 1H, NCHN), 8.84 (d, 2H, $^3J_{HH}$ = 2.6 Hz, QuH^2), 8.28 (d, 2H, $^3J_{HH}$ = 6.8 Hz, QuH^4), 8.13 (d, 2H, $^3J_{HH}$ = 8.1 Hz, QuH^5), 7.80 (d, 2H, $^3J_{HH}$ = 8.1 Hz, QuH^7), 7.62 (s, 2H, HCCH), 7.50 (t, 2H, $^3J_{HH}$ = 7.6 Hz, QuH^6), 7.40 (dd, 2H, $^3J_{HH}$ = 8.1 and 4.1 Hz, QuH^3), 6.07 (s, 4H, NCH_2Qu). ^{13}C NMR ($CDCl_3$, 25 °C): 150.7, 146.3, 137.7, 137.0, 132.4, 131.9, 130.3, 128.8, 127.1, 122.8, 122.1 (Qu and Im), 49.4 (NCH_2Qu). Anal. Calc. for $C_{23}H_{19}BrN_4$: C, 64.05; H, 4.44; N, 12.99. Found: C, 63.89; H, 4.37; N, 12.92%.

3.2.6. [3-Methyl-1-(8-quinolylmethyl)imidazole-2-ylidene][(1,2,5,6-η)-1,5-cyclooactadiene]chloroiridium (**2a**)

A mixture of Ag_2O (0.118 g, 0.51 mmol) and **1a** (0.149 g, 0.49 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 12 h. $[Ir(COD)Cl]_2$ (0.161 g, 0.24 mmol) was then added. The mixture was stirred for 12 h and filtered through Celite, and the volatile components were removed under reduced pressure. The residue was chromatographied through a column of silica gel using ethyl acetate to give analytically pure products after the removal of ethyl acetate. Yield: 0.197 g (72%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 8.98 (br, 1H, QuH^2), 8.20 (d, 1H, $^3J_{HH}$ = 7.4 Hz, QuH^4), 7.97 (d, 1H, $^3J_{HH}$ = 6.8 Hz, QuH^5), 7.79 (d, 1H, $^3J_{HH}$ = 8.0 Hz, QuH^7), 7.54 (t, 1H, $^3J_{HH}$ = 7.5 Hz, QuH^6), 7.47 (dd, 1H, $^3J_{HH}$ = 7.3 and 3.6 Hz, QuH^3), 6.91 (s, 1H, HCCH), 6.74 (s, 1H, HCCH), 6.45 (d, 1H, $^2J_{HH}$ = 14.5 Hz, NCH_2Qu), 6.29 (d, 1H, $^2J_{HH}$ = 14.5 Hz, NCH_2Qu), 4.62 (m, 2H, CH_{COD}), 3.99 (s, 3H, NCH_3), 3.07 (m, 2H, CH_{COD}), 2.22 (m, 4H, $(CH_2)_{COD}$), 1.57 (m, 4H, $(CH_2)_{COD}$). ^{13}C NMR ($CDCl_3$, 25 °C): 180.6 (C–Ir), 150.0, 146.4, 136.6, 134.9, 131.0, 128.4, 128.3, 126.9, 121.8, 121.4, 121.2 (Qu and Im), 84.7, 84.2, 52.2, 51.6 (CH_{COD}), 49.3 (NCH_2Qu), 37.6 (NCH_3), 34.2, 33.2, 30.1, 29.4 ($(CH_2)_{COD}$). Anal. Calc. for $C_{22}H_{25}ClIrN_3$: C, 47.26; H, 4.51; N, 7.52. Found: C, 47.16; H, 4.57; N, 7.54%. ESI-MS (*m*/*z*): calc., 523.68, $[M-Cl]^+$; found, 524.25.

3.2.7. [3-n-Butyl-1-(8-quinolylmethyl)imidazole-2-ylidene][(1,2,5,6-η)-1,5-cyclooactadiene]chloroiridium (**2b**)

The procedure for the preparation of **2b** was similar to that for **2a**, from Ag_2O (0.178 g, 0.77 mmol), **1b** (0.258 g, 0.75 mmol) and $[Ir(COD)Cl]_2$ (0.242 g, 0.36 mmol). Yield: 0.278 g (62%). Crystals suitable for X-ray crystallography were obtained by layering a CH_2Cl_2 solution with hexane. ^{1}H NMR ($CDCl_3$, 25 °C): δ 8.97 (d, 1H, $^3J_{HH}$ = 2.7 Hz, QuH^2), 8.19 (d, 1H, $^3J_{HH}$ = 8.2 Hz, QuH^4), 7.94 (d, 1H, $^3J_{HH}$ = 7.0 Hz, QuH^5), 7.78 (d, 1H, $^3J_{HH}$ = 8.0 Hz, QuH^7), 7.53 (t, 1H, $^3J_{HH}$ = 7.7 Hz, QuH^6), 7.46 (dd, 1H, $^3J_{HH}$ = 8.2 and 4.2 Hz, QuH^3), 6.88 (s, 1H, HCCH), 6.77 (s, 1H, HCCH), 6.44 (d, 1H, $^2J_{HH}$ = 14.6 Hz, NCH_2Qu), 6.27 (d, 1H, $^2J_{HH}$ = 14.6 Hz, NCH_2Qu), 4.62 (m, 2H, CH_{COD}), 4.40 (m, 2H, NCH_2), 3.06 (m, 2H, CH_{COD}), 2.20 (m, 4H, $(CH_2)_{COD}$), 1.72-1.56 (m, 6H, $(CH_2)_{COD}$ and NCH_2CH_2), 1.45 (m, 2H, $NCH_2CH_2CH_2$), 1.01 (t, 3H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 25 °C): 180.1 (C–Ir), 150.0, 146.4, 136.6, 134.9, 131.0, 128.3, 128.2, 126.9, 121.4, 121.2, 120.0 (Qu and Im), 84.2, 84.0, 52.0, 51.9 (CH_{COD}), 49.4 (NCH_2Qu), 33.9, 33.6, 29.8, 29.7

($(CH_2)_{COD}$), 50.4, 33.1, 20.2, 14.0 ($NCH_2CH_2CH_2CH_3$). Anal. Calc. for $C_{25}H_{31}ClIrN_3$: C, 49.94; H, 5.20; N, 6.99. Found: C, 50.07; H, 5.19; N, 6.94%. ES-MS (*m*/*z*): calc., 565.76, $[M-Cl]^+$; found, 566.33.

3.2.8. [3-Benzyl-1-(8-quinolylmethyl)imidazole-2-ylidene][(1,2,5,6-η)-1,5-cyclooactadiene]chloroiridium (**2c**)

The procedure for the preparation of **2c** is similar to that for **2a**, from Ag_2O (0.139 g, 0.60 mmol), **1c** (0.221 g, 0.58 mmol) and $[Ir(COD)Cl]_2$ (0.188 g, 0.28 mmol). Yield: 0.256 g (69%). Crystals suitable for X-ray crystallography were obtained by layering a CH_2Cl_2 solution with hexane. ^1H NMR ($CDCl_3$, 25 °C): δ 8.98 (br, 1H, QuH^2), 8.21 (d, 1H, $^3J_{HH}$ = 7.7 Hz, QuH^4), 8.00 (d, 1H, $^3J_{HH}$ = 6.4 Hz, QuH^5), 7.81 (d, 1H, $^3J_{HH}$ = 7.9 Hz, QuH^7), 7.57 (t, 1H, $^3J_{HH}$ = 7.6 Hz, QuH^6), 7.47 (dd, 1H, $^3J_{HH}$ = 7.3 and 3.7 Hz, QuH^3), 7.37-7.31 (m, 5H, Ph), 6.91 (s, 1H, HCCH), 6.61 (s, 1H, HCCH), 6.50 (d, 1H, $^2J_{HH}$ = 14.5 Hz, NCH_2Qu), 6.32 (d, 1H, $^2J_{HH}$ = 14.5 Hz, NCH_2Qu), 5.75 (d, 1H, $^2J_{HH}$ = 14.8 Hz, NCH_2Ph), 5.67 (d, 1H, $^2J_{HH}$ = 14.8 Hz, NCH_2Ph), 4.66 (m, 2H, CH_{COD}), 3.10 (m, 2H, CH_{COD}), 2.22 (m, 4H, $(CH_2)_{COD}$), 1.57 (m, 4H, $(CH_2)_{COD}$). ^{13}C NMR ($CDCl_3$, 25 °C): 181.1 (C–Ir), 150.3, 146.7, 136.9, 136.8, 135.1, 131.3, 129.2, 128.6, 128.4, 127.2, 121.9, 121.7, 120.5 (Qu, Im and Ph), 85.1, 85.0, 52.7, 52.4 (CH_{COD}), 54.7 (NCH_2Ph), 49.7 (NCH_2Qu), 34.1, 33.8, 30.1, 29.8 ($(CH_2)_{COD}$). Anal. Calc. for $C_{28}H_{29}ClIrN_3$: C, 52.94; H, 4.60; N, 6.62. Found: C, 52.93; H, 4.79; N, 6.97%. ESI-MS (*m*/*z*): calc., 599.78, $[M-Cl]^+$; found, 600.42.

3.2.9. [1,3-Di(8-quinolylmethyl)imidazole-2-ylidene][(1,2,5,6-η)-1,5-cyclooactadiene]chloroiridium (**2d**)

The procedure for the preparation of **2d** is similar to that for **2a**, from Ag_2O (0.171 g, 0.74 mmol), **1d** (0.312 g, 0.72 mmol) and $[Ir(COD)Cl]_2$ (0.228 g, 0.34 mmol). Yield: 0.284 g (57%). ^1H NMR ($CDCl_3$, 25 °C): δ 8.97 (br, 2H, QuH^2), 8.20 (d, 2H, $^3J_{HH}$ = 7.6 Hz, QuH^4), 7.99 (d, 2H, $^3J_{HH}$ = 6.5 Hz, QuH^5), 7.80 (d, 2H, $^3J_{HH}$ = 7.9 Hz, QuH^7), 7.56 (t, 2H, $^3J_{HH}$ = 7.5 Hz, QuH^6), 7.46 (dd, 2H, $^3J_{HH}$ = 7.6 and 3.9 Hz, QuH^3), 6.85 (s, 2H, HCCH), 6.52 (d, 2H, $^2J_{HH}$ = 14.6 Hz, NCH_2Qu), 6.33 (d, 2H, $^2J_{HH}$ = 14.6 Hz, NCH_2Qu), 4.67 (m, 2H, CH_{COD}), 3.20 (m, 2H, CH_{COD}), 2.20 (m, 4H, $(CH_2)_{COD}$), 1.60 (m, 4H, $(CH_2)_{COD}$). ^{13}C NMR ($CDCl_3$, 25 °C): 180.8 (C–Ir), 150.2, 146.7, 136.8, 135.3, 131.2, 128.6, 128.5, 127.2, 121.6, 121.5 (Qu and Im), 84.6, 52.7 (CH_{COD}), 49.8 (NCH_2Qu), 34.0, 30.0, ($(CH_2)_{COD}$). Anal. Calc. for $C_{31}H_{30}ClIrN_4$: C, 54.25; H, 4.41; N, 8.16. Found: C, 54.21; H, 4.40; N, 8.11%. ESI-MS (*m*/*z*): calc., 650.82, $[M-Cl]^+$; found, 651.33.

3.2.10. [3-Methyl-1-(8-quinolylmethyl)imidazole-2-ylidene]dicarbonylchloroiridium (**3a**)

CO gas was passed though a solution of **2a** (0.089 g, 0.16 mmol) in CH_2Cl_2 (20 mL) with stirring for 30 min. The solvent was evaporated under pressure at room temperature. The pale yellow powder obtained was washed with hexane (3 × 5 mL) and dried in vacuo. Yield: 0.076 g (94%). ^1H NMR (d^6-acetone, 25 °C): δ 9.00 (d, 1H, $^3J_{HH}$ = 3.1 Hz, QuH^2), 8.40 (d, 1H, $^3J_{HH}$ = 8.2 Hz, QuH^4), 7.97 (d, 1H, $^3J_{HH}$ = 8.2 Hz, QuH^5), 7.67 (d, 1H, $^3J_{HH}$ = 7.0 Hz, QuH^7), 7.60 (m, 2H, QuH^6 and QuH^3), 7.50 (s, 1H, HCCH), 7.40 (s, 1H, HCCH), 6.35 (br, 1H, NCH_2Qu), 6.03 (br, 1H, NCH_2Qu), 3.95 (s, 3H, NCH_3). ^{13}C NMR ($CDCl_3$, 25 °C): 181.5 (C–Ir), 174.0, 168.1 (CO), 150.0, 146.2, 136.4, 133.9, 130.7, 128.8, 128.4, 126.5, 122.6, 122.4, 121.5 (Qu and Im), 50.3 (NCH_2Qu), 38.5 (NCH_3). FT-IR ($CHCl_3$): ν(CO) 2069.6, 1986.0 cm^{-1}. Anal. Calc. for $C_{16}H_{13}ClIrN_3O_2$: C, 37.91; H, 2.58; N, 8.29. Found: C, 38.01; H, 2.53; N, 8.24%. ESI-MS (*m*/*z*): calc., 471.51, $[M-Cl]^+$; found, 472.08.

3.2.11. [3-n-Butyl-1-(8-quinolylmethyl)imidazole-2-ylidene]dicarbonylchloroiridium (**3b**)

The procedure for the preparation of **3b** is similar to that for **3a**, from **2b** (0.138 g, 0.23 mmol). Yield: 0.114 g (90%). ^1H NMR (d^6-acetone, 25 °C): δ 9.00 (br, 1H, QuH^2), 8.40 (d, 1H, $^3J_{HH}$ = 6.4 Hz, QuH^4), 7.97 (d, 1H, $^3J_{HH}$ = 7.7 Hz, QuH^5), 7.67 (d, 1H, $^3J_{HH}$ = 6.4 Hz, QuH^7), 7.60 (m, 2H, QuH^6 and QuH^3), 7.51 (s, 1H, HCCH), 7.45 (s, 1H, HCCH), 6.37 (d, 1H, $^2J_{HH}$ = 13.8 Hz, NCH_2Qu), 6.01 (d, 1H, $^2J_{HH}$ = 13.8 Hz, NCH_2Qu), 4.37 (m, 2H, NCH_2), 1.91 (m, 2H, NCH_2CH_2), 1.40 (m, 2H, $NCH_2CH_2CH_2$), 0.97 (t, 3H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 25 °C): 181.7 (C–Ir), 173.5, 168.3 (CO), 150.2, 146.3, 136.5, 134.1, 130.8, 128.8, 128.5, 126.6, 122.7, 121.6, 121.0 (Qu and Im), 50.6 (NCH_2Qu), 51.3, 32.9, 19.9, 13.8 (N $CH_2CH_2CH_2CH_3$). FT-IR ($CHCl_3$): ν(CO) 2068.8, 1984.9 cm^{-1}. Anal. Calc. for $C_{19}H_{19}ClIrN_3O_2$: C, 41.56; H, 3.49; N, 7.65. Found: C, 41.66; H, 3.17; N, 7.83%. ESI-MS (*m*/*z*): calc., 513.60, $[M-Cl]^+$; found, 514.17.

3.2.12. [3-Benzyl-1-(8-quinolylmethyl)imidazole-2-ylidene]dicarbonylchloroiridium (**3c**)

The procedure for the preparation of **3c** is similar to that for **3a**, from **2c** (0.121 g, 0.19 mmol). Yield: 0.096 g (87%). ^1H NMR (d^6-acetone, 25 °C): δ 9.01 (d, 1H, $^3J_{HH}$ = 2.4 Hz, QuH^2), 8.41 (d, 1H, $^3J_{HH}$ = 7.5 Hz, QuH^4), 7.99 (d, 1H, $^3J_{HH}$ = 7.6 Hz, QuH^5), 7.74 (d, 1H, $^3J_{HH}$ = 6.9 Hz, QuH^7), 7.61–7.34 (m, 9H, QuH^6, QuH^3, Ph and HCCH), 6.41 (d, 1H, $^2J_{HH}$ = 15.5 Hz, NCH_2Qu), 6.04 (d, 1H, $^2J_{HH}$ = 15.5 Hz, NCH_2Qu), 5.63 (s, 2H, NCH_2Ph). ^{13}C NMR ($CDCl_3$): 181.4 (C–Ir), 174.0, 168.0 (CO), 150.1, 146.3, 136.4, 135.5, 133.8, 130.9, 129.0, 128.8, 128.5, 128.4, 128.3, 126.5, 123.0, 121.5, 120.9 (Qu, Im and Ph), 55.0 (NCH_2Ph), 50.6 (NCH_2Qu). FT-IR ($CHCl_3$): ν(CO) 2070.2, 1986.6 cm^{-1}. Anal. Calc. for $C_{22}H_{17}ClIrN_3O_2$: C, 45.32; H, 2.94; N, 7.21. Found: C, 45.21; H, 3.37; N, 6.91%. ESI-MS (*m*/*z*): calc., 547.61, $[M-Cl]^+$; found, 548.08.

3.2.13. [1,3-Di(8-quinolylmethyl)imidazole-2-ylidene]dicarbonylchloroiridium (**3d**)

The procedure for the preparation of **3d** is similar to that for **3a**, from **2d** (0.130 g, 0.19 mmol). Yield: 0.106 g (88%). ^1H NMR ($CDCl_3$, 25 °C): δ 8.98 (d, 2H, $^3J_{HH}$ = 2.6 Hz, QuH^2), 8.22 (d, 2H, $^3J_{HH}$ = 8.1 Hz, QuH^4), 7.99 (d, 2H, $^3J_{HH}$ = 6.9 Hz, QuH^5), 7.85 (d, 2H, $^3J_{HH}$ = 8.0 Hz, QuH^7), 7.58 (t, 2H, $^3J_{HH}$ = 7.6 Hz, QuH^6), 7.49 (dd, 2H, $^3J_{HH}$ = 8.1 and 4.0 Hz, QuH^3), 7.21 (s, 2H, HCCH), 6.36 (d, 2H, $^2J_{HH}$ = 14.5 Hz, NCH_2Qu), 6.13 (d, 2H, $^2J_{HH}$ = 14.5 Hz, NCH_2Qu). ^{13}C NMR ($CDCl_3$, 25 °C): 181.7 (C–Ir), 173.9, 168.1 (CO), 150.0, 146.2, 136.4, 134.0, 130.6, 128.7, 128.4, 126.5, 122.3, 121.5 (Qu and Im), 50.5 (NCH_2Qu). FT-IR ($CHCl_3$): ν(CO) 2068.5, 1985.8 cm^{-1}. Anal. Calc. for $C_{25}H_{18}ClIrN_4O_2$: C, 47.35; H, 2.86; N, 8.84. Found: C, 47.41; H, 2.87; N, 8.81%. ESI-MS (*m*/*z*): calc., 598.66, $[M-Cl]^+$; found, 599.08.

3.2.14. 3-n-Butyl-1-(8-naphthylmethyl)imidazolium bromide (**4**)

To a solution of 1-bromomethylnaphthalene (2.000 g, 9.05 mmol) in acetone (20 mL) were added 1-*n*-butylimidazole (1.123 g, 9.05 mmol). After it was stirred for 12 h at room temperature, and the desired product precipitated as a white solid from the solution. The solid was collected and washed with THF (2 × 10 mL) and then dried under vacuum. Yield: 2.874 g (92%). ^1H NMR ($CDCl_3$, 25 °C): δ 10.71 (s, 1H, NCHN), 8.12 (d, 1H, naphthyl-H), 7.88 (t, 2H, naphthyl-H), 7.68 (d, 1H, naphthyl-H), 7.57 (d, 1H, naphthyl-H), 7.52–7.45 (m, 2H, naphthyl-H), 7.35 (s, 1H, HCCH), 7.17 (s, 1H, HCCH), 6.08 (s, 2H, naphthyl-NCH_2), 4.26 (t, 2H, NCH_2), 1.85 (m, 2H, NCH_2CH_2), 1.31 (m, 2H, $NCH_2CH_2CH_2$), 0.90 (t, 3H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 25 °C): 136.8, 134.0, 131.0, 130.7, 129.3, 129.2, 128.5, 127.9, 126.7, 125.6, 123.0, 122.4, 122.1 (naphthyl and Im), 51.2 (naphthyl-NCH_2), 50.0, 32.1, 19.5, 13.5 ($NCH_2CH_2CH_2CH_3$). Anal. Calc. for $C_{18}H_{20}BrN_2$: C, 62.61; H, 6.13; N, 8.11. Found: C, 62.57; H, 6.01; N, 8.07%.

3.2.15. [3-n-Butyl-1-(8-naphthylmethyl)imidazole-2-ylidene][(1,2,5,6-η)-1,5-cyclooactadiene]chloroiridium (**5**)

The procedure for the preparation of **5** was similar to that for **2a**, from Ag_2O (0.301 g, 1.30 mmol), **4** (0.345 g, 1.00 mmol) and

Table 5
Crystal data and structure refinements for **2b** and **2c**.

	2b	**2c**
Crystal size (mm)	0.19 × 0.16 × 0.15	0.20 × 0.16 × 0.14
Empirical formula	$C_{25}H_{31}ClIrN_3$	$C_{28}H_{29}ClIrN_3$
Formula weight	601.20	635.19
T (K)	293(2)	291(2)
λ (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.3150(11)	10.6590(10)
b (Å)	11.6587(12)	11.188(3)
c (Å)	21.351(2)	11.649(2)
α (°)	76.8960(10)	74.949(2)
β (°)	79.4780(10)	75.733(3)
γ (°)	73.2850(10)	63.079(2)
V (Å^3)	2376.1(4)	1182.7(4)
Z	4	2
Absorption coefficient (mm^{-1})	5.748	5.780
Index ranges	$-12 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 13$, $-16 \leqslant l \leqslant 25$	$-13 \leqslant h \leqslant 11$, $-13 \leqslant k \leqslant 11$, $-11 \leqslant l \leqslant 14$
Reflections collected	12053	6421
Independent reflections (R_{int})	8280(0.1246)	4546(0.0276)
Completeness to θ = 25.02 (%)	98.8	97.8
Maximum and minimum transmission	0.42 and 0.35	0.45 and 0.34
Data/restraints/parameters	8280/2423/537	4546/0/298
Goodness-of-fit (GOF)	0.987	1.080
Final R indices [$I > 2\sigma(I)$][a]	R_1 = 0.0580, wR_2 = 0.1485	R_1 = 0.0476, wR_2 = 0.1038
R indices (all data)	R_1 = 0.0735, wR_2 = 0.1634	R_1 = 0.0568, wR_2 = 0.1055
Largest difference in peak and hole (e Å^{-3})	2.385 and −1.920	1.629 and −3.039

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; GOF = $[\sum w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$.

$[Ir(COD)Cl]_2$ (0.336 g, 0.50 mmol). Yield: 0.391 g (65%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 8.23 (d, 1H, naphthyl-H), 7.92–7.88 (m, 2H, naphthyl-H), 7.61 (t, 1H, naphthyl-H), 7.55 (t, 1H, naphthyl-H), 7.48 (t, 1H, naphthyl-H), 7.40 (d, 1H, naphthyl-H), 6.80 (d, 1H, HCCH), 6.56 (d, 1H, HCCH), 6.27 (d, 1H, $^2J_{HH}$ = 14.9 Hz, Naphthyl-NCH_2), 5.98 (d, 1H, $^2J_{HH}$ = 15.0 Hz, naphthyl-NCH_2), 4.67 (m, 2H, CH_{COD}), 4.45 (m, 2H, NCH_2), 3.09 (m, 2H, CH_{COD}), 2.55-1.65 (m, 10H, $(CH_2)_{COD}$ and NCH_2CH_2), 1.49 (m, 2H, $NCH_2CH_2CH_2$), 1.05 (t, 3H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 25 °C): 180.4 (C–Ir), 133.9, 131.9, 131.6, 129.3, 128.8, 127.4, 127.3, 126.4, 125.5, 124.0, 120.3, 120.1 (naphthyl and Im), 84.8, 84.6, 51.8 (CH_{COD}), 52.3 (naphthyl-NCH_2), 33.8, 29.6 ($(CH_2)_{COD}$), 50.7, 33.2, 20.2, 14.0 ($NCH_2CH_2CH_2CH_3$). Anal. Calc. for $C_{26}H_{32}ClIrN_2$: C, 52.03; H, 5.37; N, 4.67. Found: C, 51.92; H, 5.30; N, 4.57%. ESI-MS (m/z): calc., 565.78, $[M-Cl]^+$; found, 565.17.

3.2.16. [3-n-Butyl-1-(8-naphthylmethyl)imidazole-2-ylidene]dicarbonylchloroiridium (**6**)

The procedure for the preparation of **6** was similar to that for **3a**, from **5** (0.108 g, 0.18 mmol). Yield: 0.085 g (86%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 8.11 (d, 1H, naphthyl-H), 7.91 (d, 2H, naphthyl-H), 7.56 (m, 2H, naphthyl-H), 7.50 (t, 1H, naphthyl-H), 7.42 (d, 1H, naphthyl-H), 6.90 (s, 1H, HCCH), 6.67 (s, 1H, HCCH), 6.05 (d, 1H, $^2J_{HH}$ = 14.7 Hz, naphthyl-NCH_2), 5.86 (d, 1H, $^2J_{HH}$ = 14.8 Hz, naphthyl-NCH_2), 4.34 (m, 2H, NCH_2), 1.91 (m, 2H, NCH_2CH_2), 1.44 (m, 2H, $NCH_2CH_2CH_2$), 1.02 (t, 3H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 25 °C): 181.5 (C–Ir), 173.7, 168.4 (CO), 134.1, 131.4, 130.7, 139.9, 129.0, 128.1, 127.3, 126.5, 125.5, 123.7, 121.3, 121.1 (naphthyl and Im) 53.4 (naphthyl-NCH_2), 51.5, 33.0, 19.9, 13.8 ($NCH_2CH_2CH_2CH_3$). FT-IR ($CHCl_3$): ν(CO) 2062.5, 1978.8 cm^{-1}. Anal. Calc. for $C_{20}H_{20}ClIrN_2O_2$: C, 43.83; H, 3.68; N, 5.11. Found: C, 43.97; H, 3.68; N, 5.04%. ESI-MS (m/z): calc., 513.62, $[M-Cl]^+$; found, 513.00.

3.3. General conditions of catalytic studies

Under an inert atmosphere, the tested complex (4 μmol) was dissolved in a solution of KOH (0.12 mmol) and isopropanol (10 mL) in a Schlenk tube. The solution was heated to 82 °C for 30 min. Subsequently, ketone (8 mmol) was added and the reaction progress was monitored by GC analysis.

3.4. X-ray crystallographic structure determination

Data for **2b** and **2c** were collected on a SMART APEX CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) and corrected for absorption using SADABS program [63]. These two structures were solved by direct methods and refined on F^2 against all reflections by full-matrix least-squares methods with SHELXTL (version 6.10) program [64]. The hydrogen atoms in these compounds were positioned geometrically and refined in the riding-model approximation. All non-hydrogen atoms were refined with anisotropic thermal parameters. Table 5 summarized the crystal data, data collection and refinement parameters for both compounds.

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Appendix A. Supplementary material

CCDC 697147 and 697146 contain the supplementary crystallographic data for **2b** and **2c**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.02.007.

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