ChemPubSoc Europe

DOI: 10.1002/ejic.201600922

EurJIC European Journal of Inorganic Chemistry

Full Paper

Ir Complexes for Imine Reduction

# Iridium(III) Complexes Bearing Chelating Bis-NHC Ligands and Their Application in the Catalytic Reduction of Imines

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**Abstract:** The $Ir^{III}$ complexes **4** and **5** bearing bis-NHC ligands (NHC = N-heterocyclic carbene) composed of one classical NR,NR NHC and one N,NR NHC donor were prepared by the reaction of the azolium/azole compounds **2**I and **3**Br, respectively, with $[\{Cp^*IrCl(\mu\text{-}Cl)\}_2]$ ($Cp^*=\eta^5\text{-}C_5Me_5$) in the presence of NaOAc as base. Most likely, the salts **2**I and **3**Br were first selectively deprotonated at the C2 position of the disubstituted (NR,NR) diazaheterocycle to generate an NHC donor, which then coordinated to the $Ir^{III}$ center. Subsequently, NaOAc promoted C–H bond activation at the pendant imidazole moiety of the intermediate $Ir^{III}$ mono-NHC complexes led to the formation of the six-membered iridacycles **4** and **5**, which bear a chelating, doubly *C*-metalated C(NHC)^C(NHC') bis-NHC ligand. The $Ir^{III}$ complexes **4** and **5** were tested as precatalysts for the reduction of imines with molecular hydrogen. Moderate to good activity was observed at a catalyst loading of 5 mol-% and an $H_2$ pressure of 3 bar in MeOH.

## Introduction

Metal complexes bearing N-heterocyclic carbene (NHC) ligands are well known to catalyze a wide variety of chemical transformations,[1] including hydrogenation and transfer hydrogenation reactions of unsaturated compounds.[2] Recent years have seen increasing interest in the chemistry of transition metal complexes bearing the less common protic NHC (pNHC)[3] ligands due to the potential application of the their NH group in synthesis[4] and catalytic transformations.[5] The NH group of pNHC ligands (Figure 1, **A**) can act as a molecular-recognition unit by formation of hydrogen bonds to selected substrates.[5] Generally, the utility of ligands featuring NH groups for binding and activation of substrates has been recognized for some time, and various types of complexes featuring NH groups in close proximity to the metal center have been developed (Figure 1, **B** and **C**).[6]

Apart from acting as a molecular-recognition unit, the NH moiety of various pNHC ligands has been shown to directly participate in catalytic events. For example, on deprotonation at the NH group in the presence of molecular hydrogen or *i*PrOH, complex **D** featuring a chelating C(pNHC)^phosphine ligand

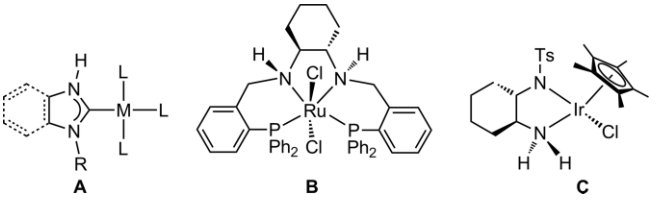


Figure 1. Selected complexes featuring ligands with NH groups for substrate recognition and binding.

acts as a catalyst for the transfer hydrogenation of ketones.[7] Such bifunctional catalysis involving both the metal center (M–H bond) and one ring nitrogen atom of the pNHC ligand (N–H bond) have so far only rarely been observed.[8] More recently, the cooperative activation of dihydrogen has been demonstrated with the $Ir^{III}$ complex **E**, which also bears a chelating C(pNHC)^$PCy_2$ ligand (Figure 2).[9]

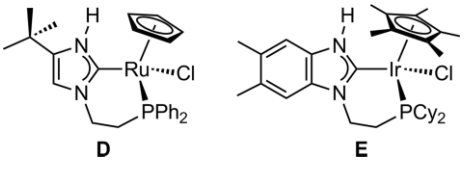


Figure 2. Selected complexes bearing protic pNHC ligands for applications in cooperative substrate activation and catalysis.

Complexes bearing pNHC ligands have been obtained by cyclization of β-functionalized isocyanides at suitable metal templates.[10] However, this synthetic method involves the cumbersome preparation of the isocyanides, and hence some novel synthetic methodologies to afford transition metal complexes with protic NHC ligands have subsequently been developed. We have described the reaction of 2-halo-*N*-alkylazoles and 2-

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*Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201600922.*

haloazoles with transition metal complexes to yield, in the presence of a proton source, complexes with protic NH,NR[11] and NH,NH NHC ligands,[12] respectively.

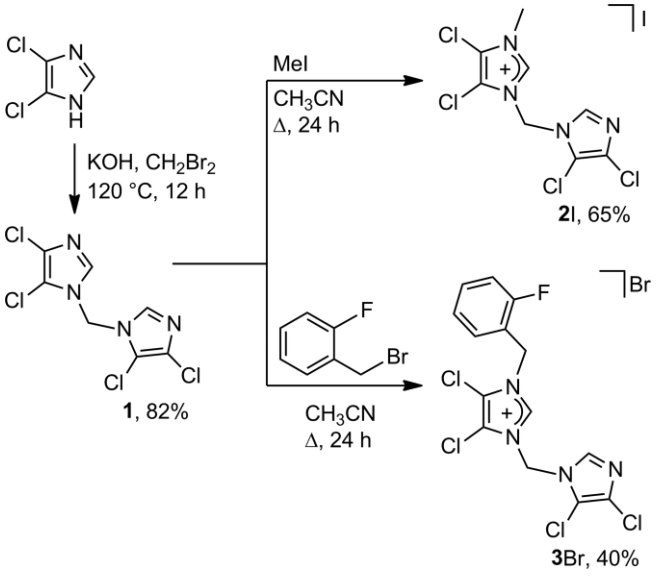
The oxidative addition of the C2–H bond of neutral azoles to selected transition metals requires, apart from a few exceptions,[13] the presence of a donor group tethered to one of the azole ring nitrogen atoms. This donor is assumed to precoordinate to the metal center and to facilitate the subsequent oxidative addition of the C2–H bond followed by reductive elimination and protonation of the ring nitrogen atom leading directly to the complex bearing a C(pNHC)^donor chelating ligand.[14]

Herein, we describe the reaction of azolium/azole compounds with $[\{Cp^*IrCl(\mu\text{-}Cl)\}_2]$ ($Cp^*=\eta^5\text{-}C_5Me_5$) in the presence of a base to give complexes with *N*-deprotonated C(pNHC)^C(NHC) ligands. The properties of the obtained complexes in the catalytic reduction of imines were subsequently studied.

## Results and Discussion

### Synthesis of Ligands 2I and 3Br

The azolium/azole compounds **2**I and **3**Br were obtained by a two-step procedure (Scheme 1).[15]




Scheme 1. Preparation of azole/azolium salts **2**I and **3**Br.

First, 4,5-dichloroimidazole was treated with KOH and $CH_2Br_2$ to give the methylene-bridged bis-azole derivative **1** in 82 % yield. The NMR spectrum of **1** perfectly matched that reported previously by Peris et al.[16]

Crystals of compound **1** suitable for an XRD study were obtained by diffusion of $Et_2O$ into a saturated solution of **1** in dichloromethane at ambient temperature. The molecular structure of **1** (Figure 3) shows no remarkable features. Bond angles and lengths in both diazaheterocycles lie in the range described previously for related azole derivatives.[17] The intra-ring N–C distances are typical for monoalkylated imidazoles. This also holds for the intra-ring N–C–N bond angles of 112.5(3) and 112.3(2)°.

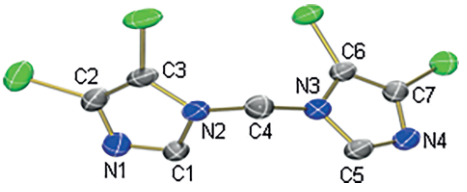
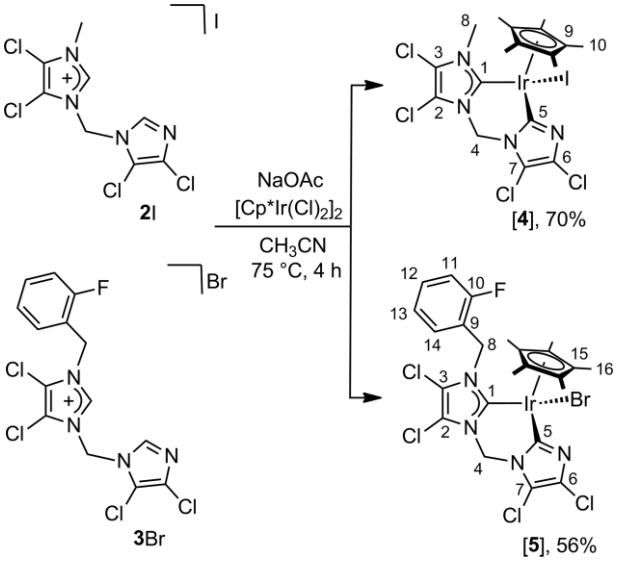



Figure 3. Molecular structure of compound **1**. Ellipsoids are given at 50 % probability (hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: N1–C1 1.315(4), N2–C1 1.361(3), N3–C5 1.370(4), N4–C5 1.316(4); C1–N1–C2 104.8(2), C1–N2–C3 106.0(2), C5–N3–C6 105.6(3), C5–N4–C7 105.0(3), N1–C1–N2 112.5(3), N3–C5–N4 112.3(2).

Subsequently, compound **1** was treated with 2 equiv. of iodomethane or 10 equiv. of 2-fluorobenzyl bromide to give selectively the imidazolium/imidazole compounds **2**I and **3**Br, respectively. The selective and very useful monoalkylation of only one azole ring of **1** has been described previously by Peris et al.[16] Formation of imidazolium salts with a pendant imidazole arm was confirmed by NMR spectroscopy. The 2-fluorobenzyl group in **3**Br was introduced because the resulting compound is insoluble in acetonitrile and can be easily isolated from this solvent by filtration. A detailed description of the synthesis of **2**I and **3**Br has been reported.[15]

The imidazolium/imidazole compounds **2**I or **3**Br were treated with 0.5 equiv. of $[\{Cp^*IrCl(\mu\text{-}Cl)\}_2]$ in the presence of 2 equiv. of NaOAc to give the iridium(III) complexes **4** and **5**, respectively (Scheme 2). The reaction proceeds most likely by an initial deprotonation of the imidazolium cation by 1 equiv. of NaOAc. The generated classical NHC donor then coordinates to the $Ir^{III}$ center to yield an NHC complex. We assume that the N–CH–N group of the pendant azole group is deprotonated by the second equivalent of NaOAc to give an azolylato ligand with an unsubstituted ring nitrogen atom, which coordinates through the N–C–N donor to the metal center. An oxidative




Scheme 2. Synthesis of complexes **4** and **5**.

addition of the C5–H bond followed by reductive elimination would lead to the *N*-protonated complex, which was not observed, and this reaction can thus be excluded. Apparently, both the imidazolium and imidazole groups of **2**I and **3**Br can be deprotonated by NaOAc. Similar behavior has been observed during the preparation of rhodium(III) NHC complexes from imidazolium/imidazole NHC precursors.[15] The presence of NaOAc is essential for the reaction to proceed, although its precise role apart from acting as a base has not been determined at this time. The role of the acetate anion in the C–H activation during *ortho*-metalation reactions has been investigated in detail,[18] and a similar mode of activation might be operational in the activation of the C–H bonds in the imidazolium/imidazole derivatives observed here.

Two doublets at $\delta$ = 6.03 ppm (d, $^2J_{H,H}$ = 12.9 Hz, 1 H, H4$_a$) and $\delta$ = 5.25 ppm (d, $^2J_{H,H}$ = 12.9 Hz, 1 H, H4$_b$) were observed in the $^1$H NMR spectrum of **4**, indicating that the H4 protons are diastereotopic (for atom numbering, see Scheme 2). This experimental observation was expected, since the coordination of the C^C chelating ligand to Ir$^{III}$ prevents rotation about the C4–N bonds and locks the two H4 protons in chemically different environments. The difference in the chemical shifts between H4$_a$ and H4$_b$ ($\Delta\delta$ = 0.78 ppm) is rather large when compared to related complexes featuring chelating methylene-bridged bis-NHC ligands.[19] A singlet for the C1 carbene carbon atom appeared at $\delta$ = 155.1 ppm in the $^{13}$C{$^1$H} NMR spectrum of **4**, and another singlet at $\delta$ = 142.9 ppm was assigned to the C5 carbene carbon atom. The chemical shift for the C1 carbene carbon atom compares well to that of the equivalent signal observed for Ir$^{III}$ NHC complexes.[17] The significant downfield shift of the resonance for the C1 carbene carbon atom compared to the resonance for the C5 carbene carbon atom illustrates that two different carbene donors are bound to the Ir$^{III}$ center. It allows a direct comparison of the different electronic properties of a classical NHC donor to those of a deprotonated pNHC unit coordinated to the same metal center.

The NMR spectral features of **5** strongly resemble those of **4**. In the $^1$H NMR spectrum of **5**, two doublets were found for the diastereotopic H4 protons ($\delta$ = 6.07 ppm, $^2J_{H,H}$ = 12.3 Hz and $\delta$ = 5.24 ppm, $^2J_{H,H}$ = 12.3 Hz, 1 H). The methylene protons H8, however, only give rise to a broad singlet at $\delta$ = 5.65 ppm. The $^{13}$C NMR spectrum features two resonances for the C$_{NHC}$ atoms at $\delta$ = 158.8 ppm for C1 and $\delta$ = 144.4 ppm for the more electron rich carbene carbon atom C5 of the deprotonated pNHC donor.

Crystals of the iridium(III) complex **5** suitable for an XRD study were obtained by slow diffusion of $Et_2O$ into a saturated solution of the compound in $CH_2Cl_2$ at ambient temperature. The molecular structure of **5** is shown in Figure 4.

The Ir$^{III}$ center in complex **5** is surrounded in a distorted octahedral fashion by a bromido ligand, the chelating bis-NHC ligand, and the Cp* ligand. This arrangement is best described as a piano-stool geometry with a chiral iridium center.[20] The Ir–C$_{NHC}$ distances are slightly different with the shorter one [Ir–C5 2.016(3) Å] observed for the classical NR,NR NHC donor. Rhodium complexes bearing similar C^C ligands show essentially identical M–C$_{NHC}$ distances for the two NHC donors. Comparable metric parameters in **5** resemble those of related neutral [Cp*Ir(NHC)LL′] compounds.

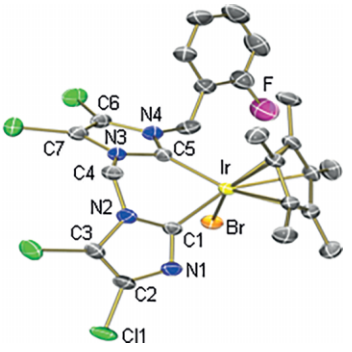



Figure 4. Molecular structure of complex **5**. Displacement ellipsoids are shown at 50 % probability and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir–Br 2.5424(5), Ir–C1 2.032(2), Ir–C5 2.016(3), range Ir–C$_{Cp*}$ 2.161(3)–2.246(3), N1–C1 1.339(4), N2–C1 1.369(4), N3–C5 1.356(4), N4–C5 1.368(4); Br–Ir–C1 86.89(9), Br–Ir–C5 88.45(8), C1–Ir–C5 84.61(13), C1–N1–C2 105.5(3), C1–N2–C3 108.7(3), C5–N3–C7 111.5(3), C5–N4–C6 109.5(3), N1–C1–N2 109.3(3), N3–C5–N4 104.6(3).

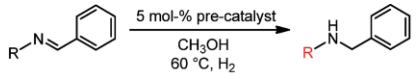
A major indication for the presence of two different NHC donors composing the C^C chelate ligand in **5** can be found in the metric parameters of the two five-membered diazaheterocycles. The NHC donor containing carbene carbon atom C5 features normal metric parameters within the heterocycle and a typical N–C$_{NHC}$–N angle of 104.6(3)°. A much larger N1–C1–N3 angle was found for the anionic azolylato donor [109.3(3)°]. This ligand also features a rather small angle at the unsubstituted ring nitrogen atom [C1–N1–C2 105.5(3)°]. The differences in the metric parameters of the two diazaheterocycles nicely demonstrate the effects of the missing substituent at ring-atom N1.

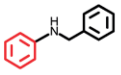
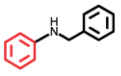
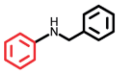
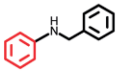
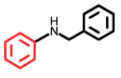
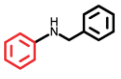
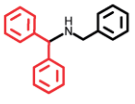
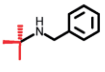
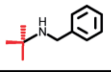
The catalytic conversion of ketones or related derivatives containing C=O bonds to the corresponding reduced compounds is a chemical transformation of great importance in organic synthesis.[21] The related transition metal catalyzed reduction of imines, however, is more difficult to perform than that of carbonyl groups, probably due to the weaker polarization of the C=N bond, which normally results in a slower process. We have described hydrogen activation with iridium complexes of type **E** (Figure 2) containing a C(pNHC)^P chelating ligand after deprotonation of the pNHC ligand. A related situation exists in the iridium complexes **4** and **5**. Here the position of the phosphine donor is taken up by the classical NHC ligand, and the pNHC ligand is already deprotonated at the ring nitrogen atom. Preliminary studies with the rhodium analogues of **4** and **5** as precatalysts revealed rather low catalytic activity in the hydrogenation of imines with dihydrogen. Since iridium complexes are established catalysts for the reduction of C=X bonds, we investigated the catalytic activity of complexes **4** and **5** in the reduction of imines.

The catalytic reductions were performed with *N*-benzylideneaniline as substrate (Table 1). When carried out in aprotic solvents ($CH_2Cl_2$, $CH_3CN$, THF, toluene) only low conversions were observed with precatalysts **4** and **5**. In methanol, however, improved catalytic activity was found.

In a typical experiment, *N*-benzylideneaniline was dissolved in MeOH and the precatalyst was added to the solution. Subse-

Table 1. Reduction of iminies catalyzed by **4** and **5**.[a]




| Entry | Pre-catalyst | Reaction product | Time [h] | $H_2$ [bar] | Yield [%][b] |
|---|---|---|---|---|---|
| 1 | **[4]** |  | 3 | 3 | 82 |
| 2 | none |  | 3 | 3 | 0 |
| 3 | **[4]** |  | 15 | 1 | 85 |
| 4 | **[4]** |  | 48 | none | 0 |
| 5 | $[Cp^*Ir(Cl)_2]_2$ |  | 3 | 3 | 5 |
| 6 | **[5]** |  | 3 | 3 | 75 |
| 7 | **[4]** |  | 3 | 3 | 80 |
| 8 | **[4]** |  | 3 | 3 | 7 |
| 9 | **[4]** |  | 32 | 3 | 85 |

[a] Conditions: 60 °C, catalyst 5 mol-%, substrate 20 mg, solvent 3 mL. [b] Yield of isolated product determined by column chromatography on silica gel with $CH_2Cl_2$ or acetone as eluent.

quently, the reaction vessel was filled with $H_2$ until a pressure of 3 bar was reached. After the selected reaction time, the reaction products were isolated and characterized by column chromatography. The iridium(III) complexes **4** and **5** gave after a reaction time of 3 h yields of 82 and 75 %, respectively, of the secondary amine (Table 1, entries 1 and 6).

We assume that the reduction of *N*-benzylideneaniline catalyzed by **4** or **5** involves the initial formation of an IrH–NH complex, as was found in the reaction of deprotonated **E** with dihydrogen.[9] This complex can then transfer a proton and a hydride in a cooperative manner to the substrate. While this proposal is based on previous observations with related complexes, it has not been confirmed experimentally at this time. Contrary to metal–ligand bifunctional catalysts featuring primary or secondary amines,[6] no base is necessary for the activation of **4** or **5** due to the presence of a basic deprotonated pNHC ligand in these complexes.

The reduction of *N*-benzylideneaniline does not proceed in the absence of iridium complex **4** or **5** (Table 1, entry 2). $[\{Cp^*IrCl(\mu\text{-}Cl)\}_2]$ is only marginally catalytically active (Table 1, entry 5). Clearly the precatalysts **4** or **5** are essential for the catalytic transformation. In addition, no catalytic transformation occurred in the absence of $H_2$ (Table 1, entry 4). However, solvent participation cannot be excluded at this point, as the catalytic reaction proceeds only in MeOH and not in aprotic solvents.

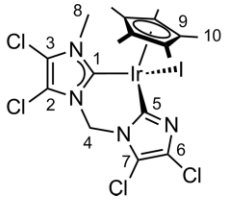
Encouraged by the catalytic conversions achieved for *N*-benzylideneaniline, we subsequently tried to reduce other imines or olefins using complex **4** as precatalyst. Both *N*-benzyl-2-methylpropan-2-amine and *N*-benzyl-1,1-diphenylmethanamine could be obtained from the corresponding imines. However, catalyst **4** was inactive for the reduction of styrene, as would be expected. The outcome of the imine reduction depends on the steric demand of the substrate. Due to its steric bulk, the hydrogenation of *N*-benzylidene-*tert*-butylamine (Table 1, entries 8 and 9) is more difficult than the reduction of the other imines selected for substrate screening.

## Conclusions

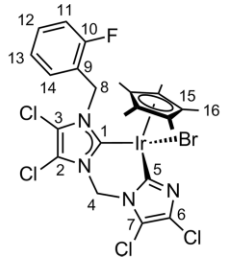
Iridium(III) complexes **4** and **5** bearing a C^C bis-carbene chelating ligand composed of a classic NHC and an anionic imidazolylato donor were obtained by the reaction of methylene-linked imidazolium/imidazole compounds with $[\{Cp^*IrCl(\mu\text{-}Cl)\}_2]$ in the presence of NaOAc. The base NaOAc is capable of deprotonating the imidazolium group as well as the neutral imidazole. Complexes **4** and **5** are moderately active catalysts in the reduction of various imines with dihydrogen. It is assumed that the complexes act as bifunctional catalysts in the activation and transfer of dihydrogen by the initial formation of a hydride complex bearing a $C_{NHC}$^$C_{pNHC}$ chelating ligand.

## Experimental Section

**General:** All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques. Glassware was oven-dried at 120 °C. Solvents were distilled by standard procedures prior to use. $^1H$ and $^{13}C\{^1H\}$ NMR spectra were recorded at 298 K with Bruker AVANCE I 400, Bruker AVANCE III 400, and Bruker AVANCE II 200 spectrometers. Chemical shifts $\delta$ are expressed in ppm downfield from tetramethylsilane by using the residual protonated solvent as an internal standard. All coupling constants are expressed in Hertz. Mass spectra were obtained with an Orbitrap LTQ XL (Thermo Scientific) spectrometer. 4,5-Dichloroimidazole, iodomethane, 2-fluorobenzyl bromide, *N*-benzylideneaniline, *N*-benzylidene-*N*-(diphenylmethyl)amine and *N*-benzylidene-*tert*-butylamine were used as received from commercial sources. $[\{Cp^*IrCl(\mu\text{-}Cl)\}_2]$[22] and the ligand precursors **2**I[15] and **3**Br[15] were prepared as described previously. Satisfactory microanalytical data for **4** and **5** could not be obtained due to the sensitivity of the compounds or the fluorine content of **5**. A complete set of NMR spectra is provided in the Supporting Information instead. For assignment of the NMR resonances, see the numbering schemes in the molecular plots.



**Complex 4:** Compound [**2**]I (50 mg, 0.12 mmol) was dissolved in $CH_3CN$ (10 mL) and NaOAc (19 mg, 0.23 mmol) was added to the solution. The reaction mixture was then stirred for 10 min. Subsequently, [{Cp*IrCl(μ-Cl)}$_2$] (46 mg, 0.058 mmol) was added. The resulting suspension was stirred for 4 h at 75 °C. Thereafter, the mixture was filtered through Celite to give a clear solution. The filtrate was concentrated to about 1 mL, and cold diethyl ether (5 mL) was added to precipitate a red solid. The solid was isolated by filtration, washed with diethyl ether (3 × 10 mL) and dried in vacuo, yield 63 mg (0.084 mmol, 70 %). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 6.03 (d, $^2J_{H,H}$ = 12.9 Hz, 1 H, H4$_a$), 5.25 (d, $^2J_{H,H}$ = 12.9 Hz, 1 H, H4$_b$), 3.79 (s, 3 H, H8), 1.93 ppm (s, 15 H, H10). $^{13}$C{$^1$H} NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 155.1 (C1), 142.9 (C5), 128.0 (C6), 117.9 (C3), 115.3 (C2), 110.1 (C7), 94.0 (C9), 56.4 (C4), 39.8 (C8), 10.5 ppm (C10). HRMS (ESI, positive ions): *m/z* = 752.9162 (calcd. for [**4** + H]$^+$ 752.9166).



**Complex 5:** Compound [**3**]Br (75 mg, 0.16 mmol) was dissolved in $CH_3CN$ (10 mL), and NaOAc (26 mg, 0.31 mmol) was added to the solution. The reaction mixture was then stirred for 10 min. Thereafter [{Cp*IrCl(μ-Cl)}$_2$] (63 mg, 0.079 mmol) was added. The resulting suspension was stirred for 4 h at 75 °C. Subsequently, the mixture was filtered through Celite to give a clear solution. The filtrate was concentrated to about 1 mL, and cold diethyl ether (5 mL) was added to precipitate a red solid. The solid was collected by filtration and washed with diethyl ether (3 × 10 mL). After drying of the solid in vacuo, complex **5** was obtained as a red solid, yield 71 mg (0.089 mmol, 56 %). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ = 7.33–7.28 (m, 1 H, H12), 7.14–7.04 (m, 2 H, H11 and H13), 6.96–6.90 (m, 1 H, H14), 6.07 (d, $^2J_{H,H}$ = 12.3 Hz, 1 H, H4$_a$), 5.65 (br. s, 2 H, H8), 5.24 (d, $^2J_{H,H}$ = 12.3 Hz, 1 H, H4$_b$), 1.75 ppm (s, 15 H, H16). $^{13}$C{$^1$H} NMR (100 MHz, $CD_2Cl_2$): $\delta$ = 160.1 (d, $^1J_{C,F}$ = 246.7 Hz, C10), 158.8 (C1), 144.4 (C5), 129.8 (d, $^3J_{C,F}$ = 8.5 Hz, C12), 128.8 (d, $^3J_{C,F}$ = 3.2 Hz, C14), 126.1 (C6), 124.4 (d, $^4J_{C,F}$ = 3.7 Hz, C13), 123.3 (d, $^2J_{C,F}$ = 12.9 Hz, C9), 117.9 (C3), 116.3 (C2), 115.3 (d, $^2J_{C,F}$ = 21.8 Hz, C11), 109.5 (C7), 93.6 (C15), 56.5 (C4), 48.5 (C8), 9.8 ppm (C16). HRMS (ESI, positive ions): *m/z* = 800.9496 (calcd. for [**5** + H]$^+$ 800.9506) and *m/z* = 822.9323 (calcd. for [**5** + Na]$^+$ 822.9331).

**X-ray Crystallography:** X-ray diffraction data were collected with a Bruker APEX-II CCD diffractometer by using graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). Empirical absorption corrections by means of the program SADABS[23] were applied to the raw data for **1** (0.704 ≤ *T* ≤ 0.879) and **5** (0.164 ≤ *T* ≤ 0.242). Structure solutions were found with SHELXS[24] in both cases, and the refinement was carried out with SHELXL[24] by using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions and were refined as riding atoms.

**Crystal Data for 1:** $C_7H_4N_4Cl_4$, *M* = 285.94, yellow block, 0.15 × 0.15 × 0.12 mm, monoclinic, $P2_1/c$, *a* = 11.605(4), *b* = 8.168(3), *c* = 11.793(4) Å, $\beta$ = 106.434(4)°, *V* = 1072.2(6) Å$^3$, *Z* = 4, $2\theta_{max}$ 58.0°, $\mu$ = 1.072 mm$^{-1}$, *T* = 100(2) K, 6513 measured reflections, 2567 independent reflections ($R_{int}$ = 0.037), 1617 observed reflections [$I \geq 2\sigma(I)$], all independent reflections used in refinement against $|F^2|$, *R* = 0.0391, *wR* = 0.1048, $R_{all}$ = 0.0837, $wR_{all}$ = 0.134.

**Crystal Data for 5:** $C_{24}H_{23}N_4BrCl_4FIr$, *M* = 800.37, yellow prism, 0.20 × 0.15 × 0.15 mm, monoclinic, $P2_1/c$, *a* = 15.718(2), *b* = 14.800(2), *c* = 12.474(2) Å, $\beta$ = 112.691(2)°, *V* = 2677.3(6) Å$^3$, *Z* = 4, $2\theta_{max}$ 59.0°, $\mu$ = 6.907 mm$^{-1}$, *T* = 100(2) K, 29244 measured reflections, 7020 independent reflections ($R_{int}$ = 0.0444), 5904 observed reflections [$I \geq 2\sigma(I)$], all independent intensities used in refinement against $|F^2|$, *R* = 0.0275, *wR* = 0.0597, $R_{all}$ = 0.0366, $wR_{all}$ = 0.0628.

CCDC 1486012 (for **1**) and 14866013 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

## Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) (IRTG 1444, SFB 858).

**Keywords:** Homogeneous catalysis · Reduction · Carbene ligands · Iridium · Chelates

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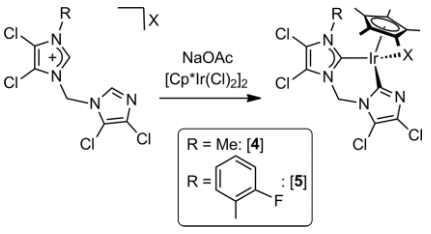
Received: July 26, 2016
Published Online: ■




Iridium(III) complexes **4** and **5** bearing C^C bis-carbene chelating ligands composed of a classical NHC and an anionic imidazolylato donor were obtained from imidazolium/imidazole compounds and $[\{Cp^*IrCl(\mu\text{-}Cl)\}_2]$ in the presence of NaOAc. Complexes **4** and **5** are moderately active catalysts in the reduction of various imines with dihydrogen.

**DOI: 10.1002/ejic.201600922**