Transition metal catalysts for the conversion of biomass inspired substrates
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Chapter 3

Synthesis and Structure of $M$(arene) Complexes Containing NHC-Amine Ligands

Abstract

In this chapter, we report the development of a new set of complexes of the type \([M(\text{arene})\ Cl(L)]\) (M=Ru, Ir or Rh; arene = \(p\)-cymene or Cp* (pentamethylcyclopentadienyl)), containing novel bidentate ligands \(L\) consisting of an \(N\)-heterocyclic carbene (NHC) and various primary amine moieties \((L = 1-(2\text{-aminophenyl})-3-(n\text{-alkyl})\text{imidazole-2-ylidine})\). These complexes are structurally compared to analogous complexes on the basis of NMR studies and X-ray crystal structure determinations. The investigations revealed that the combination of the small chelate ring size and resonance conjugation in the new NHC-aniline ligand \(L\) increases the electron donating capacities of the NHC compared to that of larger ring analogues. Due to the difference in oxidation state, Ir(III) and Rh(III) formed shorter M-carbene bonds compared to Ru(II), which was ascribed to the better overlap of their lower lying d-orbitals. Additionally, the conjugated properties of the aniline ring prohibited the formation of an analogous Ru(II)Cp* compound with a bidentate chelating NHC-amine moiety, since the conjugated ligand ensured a preferred coordination mode as RuCp* sandwich complex.

3.1 Introduction

In the search for active and selective catalysts, it is of great importance to explore new ligand designs and novel complexes, to investigate structural influences and to test how these new complexes can be applied. It is well known that bidentate ligands are not only able to improve the stability of complexes, but can also combine the properties of two moieties, resulting in a ligand where the “whole is greater than the sum of its parts.”\(^{[1]}\)

We envisaged to combine an \(N\)-heterocyclic carbene (NHC) moiety, providing favorable donating properties widely used in hydrogenation reactions,\(^{[2]}\) with a primary amine functionality known to function as an internal base and/or a hemi-labile moiety in a bidentate ligand. This combination could allow bifunctional substrate activation.\(^{[3-5]}\) In general, the use of NHCs and primary amine containing ligands in coordination chemistry is, thus far, poorly developed. Only a few transition metal-based catalysts based on this motive have been developed to date.\(^{[6-9]}\) We designed our NHC-primary amine containing ligand \((C_{\text{NHC}}\text{-NH}_2)\) in such a way that the NHC is linked to an aniline, creating a system where the amine is in conjugation with the imidazole through the aromatic linker, leading to stronger ligand donor capacity. Late transition metal complexes containing this electron-rich \(C_{\text{NHC}}\text{-NH}_2\) ligand were speculated to display hemi-labile and/or bifunctional behavior, which are both favorable properties when it comes to the conversion of oxygenates from biomass using hydrogenation and/or direct \(\alpha\)-alkylation.
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The first series of complexes that we designed with the C\textsuperscript{NHC}-N\textsubscript{2} ligand were based on a metal half-sandwich motif (M = Ru, Ir and Rh, see Figure 1, general structure I). During the course of our investigation the group of Cross\textsuperscript{[7]} published results using similar complexes (Figure 1, general structure II) but application is, until now, limited to transfer hydrogenation reactions.

Around the same time, the group of Morris also aimed at combining an NHC and a primary amine but developed a different type of ligand where the NHC is coupled to a benzylic amine. This entails that the structure of the ligand differs on two distinct points: the chelate ring that is formed is larger and the electronic structure lacks the conjugation with the amine function present in our ligand (Figure 1, general structure III).

![Figure 1. General structures of half-sandwich complexes synthesized in this work I, and by the groups of Cross II and Morris III.](image)

Morris performed extensive DFT studies on the performance of the catalyst in, among others, the H\textsubscript{2}-hydrogenation of ketones, which laid a firm foundation in understanding the basics of the reaction when catalysts containing the NHC-amine motif are applied. The design of our M-arene series allows for direct structural comparison with the analogous complexes of Morris and co-workers. In general, the activity of a catalyst is closely related to its structure: a small structural change can bring about large differences in activity and selectivity.

To this end, we studied the influence of three factors more closely: 1) the chelate ring size, 2) the size of the alkyl substituent on the ligand and 3) the metal. To investigate the influence of chelate ring size we needed to synthesize a Ru(p-cym) and an IrCp\textsuperscript{*} species with our C\textsuperscript{NHC}-N\textsubscript{2} ligand 4a. The influence of the size of the alkyl substituent will be looked at by coordinating ligand 4b-4d with Ru(p-cym). To check the extent of the influence of the metal, also a RhCp\textsuperscript{*} species is coordinated with ligand 4a. The synthesis and characterization of these complexes is discussed in this chapter. Furthermore, the structural and spectroscopic properties of these complexes are compared to previously reported analogous complexes.
The impact of the structural variations of the catalyst on catalytic activity in H₂-hydrogenation of ketones will be discussed in Chapter 5.

### 3.2 Synthesis, Results and Discussion

#### Ligand Synthesis

The synthesis route towards the new C\textsuperscript{NHC-NH₂} ligand is shown in Scheme 1. The 2-(2-imidazolyl)aniline was obtained by an Ullmann-type coupling of 2-fluoronitrobenzene 1, followed by hydrogenation of the aromatic nitro group of 2 to yield the imidazolium aniline 3.

The imidazolium ligand-precursors 4a-d were then obtained in good yields by N-alkylation of 3 in a sealed tube with the respective iodo- or bromoalkyl reagent in stoichiometric amounts. Formation of side products by alkylation of the free amine hardly occurred, and the ligands 4a-d were readily obtained in a pure form. The PF\textsubscript{6} imidazolium salt 4e was readily obtained by anion exchange of the halogenide 4a with an excess of KPF\textsubscript{6} in DCM. Having the new ligands 4a-e in hand, we focused on the synthesis of their metal complexes. Several synthetic routes are available to prepare NHC-metal complexes. Most of them involve either transmetallation from a preformed NHC-silver complex or deprotonation of the imidazolium salt to form the free carbene which is trapped by the desired metal precursor in a direct one-pot reaction.

![Scheme 1. Synthesis route towards C\textsuperscript{NHC-NH₂} ligands 4a-e, applying an Ullmann-type coupling, reduction of the nitro group and N-alkylation of the imidazole.](image)

A complication of the direct deprotonation route, when preparing the NHC-metal complex,
arises if the free carbene that is formed is thermodynamically not very stable. This appears to be the case for the free carbene generated from carbene precursor \(4e\). Following the reaction between \(C^{\text{NHC-NH}_2}\) ligand \(4e\) and \(\text{KOBu}\) by \(^1\text{H-NMR}\) indeed showed substantial broadening and changes in the aromatic region after 10 minutes. Since ligand exchange reactions with (kinetically inert) ruthenium complexes are generally slow, the direct deprotonation route towards ruthenium carbene complexes proved unsuitable. Therefore, we switched to the transmetallation route via the silver-NHC complexes. The synthesis of the silver complexes is described below.

**Synthesis of \(C^\text{NHC-NH}_2\) Silver Complexes**

Transmetallation, in which the NHC ligand is transferred from a preformed NHC-silver complex to another transition metal, is a well-established route for the preparation of a variety of different transition metal NHC complexes.\(^{10,11}\) Often this method gives cleaner and higher yields than direct metallation. Especially for palladium and rhodium, this method is frequently applied. This is illustrated by examples of coordination of NHC-amine ligands to these metals in literature.\(^{12,13}\) As mentioned before, a highly similar ligand (Figure 1, structure III) with a primary amine group was developed by Morris and colleagues.\(^{8,14}\) In this procedure, the \(\text{NH}_2\)-group was obtained by the reduction of a benzoisonitrile group linked to a NHC coordinating to the transmetallating agent. This results in an additional carbon atom between the aromatic ring and the amine. Our ligand synthesis already yields the ligand with the primary amine group and reduction of an isonitrile group is not necessary. Transmetallation via the silver(I)-carbene is a mild route without the use of strong bases which could possibly react with the amine group.

\[
\text{Ag}_2\text{O} \quad \text{MeOH} \quad \text{NH}_2 \quad \text{N} \quad \text{N} \quad \text{nBu} \quad \text{Br} \\
\text{CH}_2\text{Cl}_2 \\
\text{Ag-4a} \quad 82 \%
\]

**Scheme 2.** Synthesis of the silver(I) carbene **Ag-4a** from imidazolium ligand **4a**.

For the synthesis of silver(I)-carbene **Ag-4a**, we followed a standard procedure in which the ligand was stirred overnight in the presence of **Ag\(_2\)O** under exclusion of light (see Scheme 2). As the ligand was insoluble in DCM, a small amount of MeOH was added to the reaction mixture. An orange/brown product was obtained in moderate yield, which was mildly hygroscopic. The \(^1\text{H-NMR}\) showed no imidazolium signal which suggests the binding of the carbene to the silver. \(^{13}\text{C-NMR}\) shows a large downfield shift of the NCN carbon from 137.65
ppm in the imidazolium ligand 4a to 181.41 ppm, indicating coordination to silver in a carbene fashion. This shift is in accordance with literature examples, but the Ag-C coupling was not observed. With the C\textsubscript{NHC}-NH\textsubscript{2} ligand and its silver complex in hand, several options to coordinate the ligand with late transition metals were explored.

**Synthesis of C\textsubscript{NHC}-NH\textsubscript{2} Ruthenium Complexes**

The [Ru(p-cym)\textsubscript{2}Cl(C\textsubscript{NHC}-NH\textsubscript{2})\textsubscript{2}]PF\textsubscript{6} complex 5a was prepared by reaction of [RuCl\textsubscript{2}(p-cym)]\textsubscript{2} with Ag-4a in DCM involving transmetallation. The precursor [RuCl\textsubscript{2}(p-cym)]\textsubscript{2} already has Ru(II) in the desired oxidation state. To avoid the presence of a bromide anion in catalysis, anion exchange was performed using an excess of KPF\textsubscript{6}, producing a green complex in good yield (see scheme 3).

![Scheme 3. Synthesis of [Ru(p-cym)Cl(C\textsubscript{NHC}-NH\textsubscript{2})\textsubscript{2}]PF\textsubscript{6} complex 5a via transmetallation using Ag-4a and [RuCl\textsubscript{2}(p-cym)]\textsubscript{2}.](image)

Identification of 5a was performed by multinuclear NMR spectroscopy, high resolution mass spectrometry (HR-MS FAB) and X-ray crystal structure determination. The \textsuperscript{1}H-NMR spectrum was measured in both CD\textsubscript{2}Cl\textsubscript{2} and DMSO-\textit{d}_6, of which the latter gives a spectrum without overlapping signals. The complex gives four different signals for the aromatic protons of the p-cym ligand and one signal for the \textit{i}-propyl protons. Also, the protons of the NH\textsubscript{2}-group give two signals, each with doublet multiplicity, that shift 2 ppm downfield in the two different solvents (i.e. from \(\delta = 4.4\) and 6.5 ppm in CD\textsubscript{2}Cl\textsubscript{2} to \(\delta = 6.0\) and 8.3 ppm in DMSO-\textit{d}_6). Assuming that rotation of the p-cym moiety on NMR-time scale is slow, the splitting of the aromatic signals indicates that the surroundings of the aromatic protons make them inequivalent.

The observed splitting of the NH\textsubscript{2}-group can be ascribed to hydrogen bonding between the amino protons and the PF\textsubscript{6}\textsuperscript{-} anion or the chloride. The \textsuperscript{31}P-NMR and \textsuperscript{19}F-NMR spectra show expected signals for the PF\textsubscript{6}\textsuperscript{-} counterion with a doublet around \(\delta = 70\) ppm in the \textsuperscript{19}F-NMR spectrum and a septet around \(\delta = -144\) ppm (\(J = 712\) Hz) in the \textsuperscript{31}P-NMR spectrum. Single crystals could be grown from a DCM/EtO mixture, which were amenable to X-ray diffraction. Further details of the molecular structure will be discussed below under the section.
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Structural Comparison, where we also use the parameters obtained from the crystal structure to compare the structural characteristics of this complex with different chelate size complexes.

The [Ru(p-cym)Cl(C\textsubscript{NHC}-NH\textsubscript{2})]\textsubscript{I} complexes 5b-d, containing different alkyl substituents on the NHC, were obtained in a one-pot reaction from ligands 4b-d, using Ag\textsubscript{2}O as base but without first isolating the silver(I)-carbene complex\textsuperscript{(7)} (see Scheme 4). Anion exchange was omitted here since the goal was not to obtain the best possible catalyst but to apply these complexes in catalysis to check the influence of the size of the alkyl substituent. Complexes 5b-d have been characterized using NMR. Similar to complex 5a there are four different signals for the aromatic \textit{p}-cym protons and the splitting of NH\textsubscript{2} due to hydrogen bonding is visible, in accordance to the report of Cross\textsuperscript{(7)} where hydrogen bonding to the iodide anion is reported.

![Scheme 4. Synthesis of [Ru(p-cym)Cl(C\textsubscript{NHC}-NH\textsubscript{2})]\textsubscript{I} complexes 5b-d with varying alkyl substituents (Me, Et and \textit{n}Bu).](image)

Structural Comparison of Ru(p-cym) Complexes Containing C\textsubscript{NHC}-NH\textsubscript{2} Ligands With Differing Chelate Ring Sizes

Several structural parameters of [Ru(p-cym)Cl(C\textsubscript{NHC}-NH\textsubscript{2})]PF\textsubscript{6} 5a were obtained from the X-ray crystal structure, shown in Figure 2. These parameters were compared with analogous complexes reported previously, as discussed below. Complex 5a exhibits a tetrahedral pianostool geometry, in accordance with related literature examples. It crystallizes in the centrosymmetric triclinic space group \textit{P}-\textit{I}, with one molecule in the asymmetric unit.

These properties are similar to what was reported by Cross\textsuperscript{(7)} and to the benzyl amine complex 7 reported by Morris (see Figure adjoining Table 1), which crystallizes in the centrosymmetric orthorhombic space group \textit{Pbca} with one molecule in the asymmetric unit. Despite the chirality of both complexes 5a and 7, their crystal structures are racemic. The aromatic ring is twisted with respect to the imidazole at a dihedral angle of 33.67(9)° and the six membered chelate ring that is formed is non-planar. Amino hydrogen H1N is involved in an intermolecular hydrogen bond to a PF\textsubscript{6}\textsuperscript{-} anion. The other hydrogen atom H2N
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takes part in a bifurcated hydrogen bond: one acceptor is the chlorine of the same molecule and the second acceptor is the chlorine of a neighboring molecule. Overall this leads to a hydrogen bonded one-dimensional chain along the $b$ axis.

Figure 2. Displacement ellipsoid plot of compound 5a in the crystal, drawn at the 50% probability level. C-H hydrogen atoms and PF$_6$ anion are omitted for clarity. Only the major conformation of the disordered $n$-butyl group is shown.

We first analyzed the structural and spectroscopic differences between 5a (containing an aryl-derived 6-membered chelate-ring), and the analogous complexes 6 (containing an aliphatic 6-membered chelate-ring) and 7 (containing a benzylic 7-membered chelate-ring). Several NMR spectral data related to the chelate ring size of these complexes are summarized in Table 1. Table 2 summarizes the important crystal data of the same compounds.

The C(1)-Ru-N(3) bite angle in 5a is 79.62(6)$^\circ$, which is significantly smaller than in 6 and 7 (87.0 and 91.98$^\circ$, respectively, see Table 2). In the geometry of these complexes, the optimum angle due to the chelate ring would be 90$^\circ$, implying that complex 5a is somewhat strained. The strain causes a non-optimal orbital overlap between Ru and N(3). This can promote dissociation of the amine, which is a relevant factor to consider when these complexes are applied in catalysis reactions.

The carbene carbon of 5a resonates slightly downfield in $^{13}$C-NMR as compared to 6 and 7, indicating a more electron rich carbene. This correlates to the shorter Ru-C(1)$_{\text{Carbene}}$ bond length, suggesting a stronger Ru-carbene interaction. Compared to 7, both NH$_2$ signals of 5a in $^4$H-NMR resonate further downfield indicating that the amine becomes more acidic or more electron rich. A similar, minor shift is also visible for the imidazolium backbone protons and the aromatic ring (see Table 1), all indicative of the conjugated structure.
Table 1. Selected NMR parameters of Ru(p-cym) complexes 5a, 6 and 7.

<table>
<thead>
<tr>
<th></th>
<th>5a</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(1)-C(1) (Å)</td>
<td>2.0394(15)</td>
<td>2.041(6)</td>
<td>2.092(5)</td>
</tr>
<tr>
<td>Ru(1)-N(1) (Å)</td>
<td>2.1399(14)</td>
<td>2.114(4)</td>
<td>2.146(4)</td>
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<tr>
<td>Ru(1)-Cl (Å)</td>
<td>2.3973(4)</td>
<td>2.4140(15)</td>
<td>2.4180(13)</td>
</tr>
<tr>
<td>C(1)-Ru(1)-N(1) (°)</td>
<td>79.62(6)</td>
<td>87.0(2)</td>
<td>91.98(17)</td>
</tr>
</tbody>
</table>

Table 2. Selected structural parameters of Ru(p-cym) complexes 5a, 6 and 7.

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Structural parameters of 5a obtained from the X-ray crystal structure. Structural parameters of 6 and 7 taken from ref [9] and [8]. C(1) indicates the carbene of the NHC, N(1) indicates the NH₂.

The ¹³C-carbene signals of the complexes 5b-d, which differ in their alkyl substituents, resonate slightly further downfield at 178.21 (nBu), 176.62 (Et) and 179.09 (Me) ppm, but are otherwise similar in spectral properties to 5a. A more electron rich carbene leads to a stronger donating NHC moiety. Using the aniline ligand with a conjugated system also renders the NHC more electron rich, which is an important factor in catalytic reactions. The
influence of this and abovementioned factors on catalysis will be discussed in Chapter 5.

*Formation of a Ru-Sandwich Complex*

RuCp* analogues are logical related structures and would be similar to the successful RuCp*NHC-benzylic amine complex by Morris (Figure 2, general structure III). Several attempts to synthesize the analogous Ru(II)Cp* complex using our C^NHC-NH$_2$ ligand have proven unsuccessful. Unfortunately, using either NaH, KOrBu, Ag$_2$O or NaHMDS as the base or using the appropriate silver complex Ag-4a for transmetallation of several metal precursors, such as [RuCp*(μ$_3$-Cl)]$_4$, [RuCp*Cl$_2$]$_n$ and [RuCp*Cl(cod)] all resulted in unidentifiable mixtures of products. Apparently, the RuCp* complex with a 6-membered NHC-aniline chelate ring is very difficult to prepare and as yet, there are no reports of the synthesis of this or similar complexes. A likely reason for this behavior is the intrinsic reactivity of ruthenium towards the aromatic aniline ring. When stirring ligand 4e and the [RuCp*(μ$_3$-Cl)]$_4$ precursor in THF in the absence of base, a fine yellow precipitate formed. NMR experiments indicated the formation of complex 8, as shown in Scheme 5.

![Scheme 5. Proposed structure of RuCp* compound 8 obtained from [RuCp*(μ$_3$-Cl)]$_4$ and 4e in the absence of base.](image)

The chemical shifts of the aromatic ring of the ligand as detected in both $^1$H and $^{13}$C-NMR (around $\delta = 5.5$ ppm and $80$ ppm, respectively) of 8 are comparable to those reported for the aniline ligand in [RuCp*(η$_6$-aniline)]Cl.$^{[14]}$ The large upfield chemical shift of the amine protons in the NMR spectrum of $\delta = 8$ to $6.95$ ppm (showing only coupling to itself in COSY and no coupling to a carbon in ($^{13}$C-$^1$H) HSQC-NMR) suggests that the amine protons have become significantly more acidic compared to the free ligand 4e due to resonance of the amine lone pair with the π-system of the aromatic ring. This readily explains the observed and undesired coordination mode. The RuCp* analogue containing a benzylic amine (Figure 2, general structure III) does not share this resonance structure, and hence, in contrast to 8,$^{[14]}$ this complex is readily synthesized in its desired NHC coordination mode. The tendency of the tetrameric RuCp* moiety to coordinate to an arene in a sandwich-like fashion might explain the difficulties found when trying to form Ru-complexes with this ligand. If
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the arene coordinates first; the amine and the carbene (after deprotonation) can coordinate more or less randomly to other complexes in different ways; forming complex dimeric or cluster structures.

*Synthesis of C\textsuperscript{NH\textsubscript{2}}-NH\textsubscript{2} Rhodium and Iridium Complexes*

The analogous IrCp* and RhCp* complexes 9 and 10 were obtained in a similar manner as Ru-complex 5a, now using [IrCp*Cl\textsubscript{2}]\textsubscript{2} and [RhCp*Cl\textsubscript{2}]\textsubscript{2} as the metal precursors (see Scheme 6). Cross and Daly already reported a route to an IrCp* complex with a similar ligand (Figure 2, general structure II). The imidazolium salt was directly deprotonated with 2 equivalents of NaOtBu, resulting in a neutral amine coordination which formed when the amine coordinates to iridium and was rendered more acidic, and is subsequently deprotonated. However, this protocol was hard to reproduce and no pure complex was obtained.

![Scheme 6. Synthesis of [IrCp*Cl(C\textsuperscript{NH\textsubscript{2}}-NH\textsubscript{2})]PF\textsubscript{6} 9 and [RhCp*Cl(C\textsuperscript{NH\textsubscript{2}}-NH\textsubscript{2})]PF\textsubscript{6} 10 via transmetallation to [IrCp*Cl\textsubscript{2}]\textsubscript{2} and [RhCp*Cl\textsubscript{2}]\textsubscript{2} using Ag-4a.](image)

Instead, the transmetallation route was again chosen. Purification was performed by heating a solvent mixture (Ir: DCM/Et\textsubscript{2}O; Rh: THF/pentane) and letting it cool down to 4 °C,
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precipitating both complexes in microcrystalline fashion. Crystals suitable for X-ray diffraction were obtained from slow diffusion of these solvent mixtures (see Figure 3). Both Cp* complexes are iso-structural. Additionally, using silver as transmetallating agent also yields the complex with an NH₂ coordination instead of NH.

Structural Comparison of IrCp* Complexes Containing C\textsubscript{NHC}-NH\textsubscript{2} Ligands With Differing Chelate Ring Sizes

The structural differences between the NHC-aniline and NHC-benzylic amine ligand that was found for the Ru-complexes 5a, 6 and 7 are also visible from the NMR and crystal data of IrCp* complex 9 and analogous complex 11 reported in literature. NMR spectra related to the chelate ring size of these complexes are summarized in Table 3. Table 4 summarizes the important crystal data of the same compounds. The seven-membered ring analogues of the RhCp* complex 10 have not been described before, so no ring-size structural comparisons can be made with these species.

Table 3. Selected NMR parameters of IrCp* complexes 9 and 11.

<table>
<thead>
<tr>
<th>1\textsuperscript{H} shift</th>
<th>9</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Im. backbone =CH</td>
<td>7.70, d,  J = 2.2 Hz</td>
<td>7.34, d,  J = 2.1 Hz</td>
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<td></td>
<td>7.38, d,  J = 2.2 Hz</td>
<td>7.32, d,  J = 2.1 Hz</td>
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<tr>
<td>H-arom</td>
<td>7.54, 7.49-7.40</td>
<td>7.75, 7.59, 7.48</td>
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<tr>
<td>NH\textsubscript{2}</td>
<td>6.12, br</td>
<td>4.38</td>
</tr>
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</table>

\textsuperscript{13}C shift

carbene                  | 160.9             | 155.8             |

NMR shifts (δ) reported in ppm. All compounds were measured in CD\textsubscript{2}Cl\textsubscript{2}. d = doublet, br = broad, J = coupling constant. Data from structure of 11 taken from ref [17].

As was observed for the Ru(p-cym) complexes 5a and 7, the C(1)-Ir-N(3) angle in our complex 9, amounting to 80.76(6)°, is much smaller than in complex 11 (90.9(2) degrees) and therefore the metallacycle is more strained. The \textsuperscript{13}C carbene shift of 9 is shifted downfield and the Ir-C distance is smaller compared to 11, both indicating a more electron rich car-
bene. There are more similarities between the Ir and Ru structural parameters in ¹H-NMR: a similar downfield shift is observed for the imidazolium backbone protons, the aromatic ring and the amine in 9, when compared to 11.

Table 4. Selected crystal data of IrCp* complexes 9 and 11.

<table>
<thead>
<tr>
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<th>9</th>
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<tr>
<td>Ir(1)-C(1) (Å)</td>
<td>2.0239(17)</td>
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<td>Ir(1)-N(1) (Å)</td>
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<td>C(1)-Ir(1)-N(1) (°)</td>
<td>80.76(6)</td>
<td>90.9(2)</td>
</tr>
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Structural parameters of 9 obtained from the X-ray crystal structure. Structural parameters of 11 taken from ref [17]. C(1) indicates the carbene of the NHC, N(1) indicates the NH₂.

The Ir-complex 9 and Rh-complex 10 both have stronger M-carbene bonds (M-C(1) are 2.0239(17) Å and 2.0296(15) Å respectively) to the NHC ligand than Ru-complex 5a (2.0394(15) Å). All three complexes are d⁶ configured but differ in oxidation state. The d-orbitals of iridium(III) and rhodium(III) lie lower in energy, and are therefore energetically better matched to allow stronger σ-bonding overlap with the sp²-hybridized donor orbital of the NHC carbene moiety, as compared to the d-orbitals of ruthenium(II). This may also explain the intrinsic reactivity of the RuCp*⁺(II) precursor towards the aniline ring of the ligand that was found for 8: the higher lying Ru d-orbitals are energetically better matched with the arene orbitals and therefore back-donation into these orbitals is likely more favorable than binding to the NHC donor, thus leading to formation of a sandwich-like coordination of the C²NHC-NH₂ ligand.

3.3 Summary and Conclusions

We succeeded in developing a novel type of C²NHC-NH₂ ligand 4a-e where an aniline ring is N-substituted to the NHC, influencing the donor properties of the ligand: compared to ligands where the primary amine does not have the option of a resonance structure of its lone pair with the π-system of the aromatic ring, the NHC of 4a-e is more electron rich and therefore displays stronger donor properties.
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The structural characteristics and features of complexes 5-11 containing the C\text{NHC-NH}_2 motif illustrate the properties of the ligand structure and its impact on complex properties. Ligands 4a-e form a smaller, six-membered, chelate and additionally exhibit conjugation of the primary amine through the ring system. This is in contrast to the NHC-benzyl amine ligand in the complexes reported by Morris, which is a larger seven-membered chelate that does not possess this conjugation. Both factors have an influence on the electronic properties of the NHC, rendering the carbene more electron rich in the C\text{NHC-NH}_2 ligand 4. This is also reflected in the M-C(1)\text{Carbene} (M = Ru, Ir) bond distances reported in the solid state, where complexes containing ligand 4 have shorter distances than complexes containing larger or non-conjugated chelate ring size ligands. NMR parameters support this statement, showing downfield shifts of the carbene carbon in \text{^13C-NMR} and of the aromatic ring and NHC backbone protons and amine protons in \text{^1H-NMR}. The smaller chelate ring creates a strained C(1)\text{Carbene}-M-N(3) angle within the complex (around 80°), which deviates from an optimal geometry (around 90°), possibly causing a non-optimal orbital overlap between the metal and the amine.

Within the series of complexes containing ligand 4 an influence of the metal oxidation state is also observed. Iridium(III) complex 9 and rhodium(III) complex 10 display shorter bonds to the carbene, due to better overlap of their lower lying d-orbitals compared to Ru(II) complex 5a. Additionally, the properties of the aniline ring prohibit the formation of a bidentate chelating analogous RuCp* compound, since the conjugated amine ensures a preferred coordination mode as a RuCp* sandwich complex 8.

Summarizing, six-membered ring chelate C\text{NHC-NH}_2 ligand 4 is a stronger donating ligand when coordinated to a metal than its analogous, non-conjugated and/or seven-membered ring chelate ligands. Additionally, the non-optimal orbital overlap caused by the smaller and somewhat strained six-membered ring chelate 4 can promote dissociation of the amine. These are important factors to consider when these complexes are applied in hydrogenation catalysis, which will be the subject of Chapter 5.

3.4 Experimental Section

General Remarks

All experiments were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. Solvents were freshly distilled under an argon atmosphere from sodium benzophenone ketyl (toluene, THF, pentane and diethyl ether) and from CaH\textsubscript{2} (CH\textsubscript{2}Cl\textsubscript{2} and MeCN). MeOH and i-prop were distilled from CaH\textsubscript{2} under a nitrogen atmosphere and
were stored over 4Å molecular sieves. Acetophenone was vacuum-distilled from P$_2$O$_5$ under a nitrogen atmosphere and was stored over 4Å molecular sieves. Deuterated solvents (CDCl$_3$ and CD$_2$Cl$_2$) were distilled from CaH$_2$ under a nitrogen atmosphere and stored over 4Å molecular sieves. Deuterated solvents (CDCl$_3$ and CD$_2$Cl$_2$) were distilled from CaH$_2$ under a nitrogen atmosphere and stored over 4Å molecular sieves. DMSO was purchased as dry solvent. 1-(2-nitrophenyl)-imidazole$^{[18]}$, imidazole aniline$^{[18]}$ and [RuCp*(μ$_3$-Cl)]$_4$$^{[19]}$ were prepared according to literature procedures. Other reagents were obtained commercially and used as received. NMR spectra were recorded on either a Bruker AMX 400 MHz, Bruker DRX 300 MHz, Varian Mercury 300 MHz or Varian INOVA 500 MHz. $^1$H and $^{13}$C{$_1$H} chemical shifts are reported in parts per million (δ, ppm) downfield from TMS, and $^{31}$P{$_1$H} chemical shifts are reported in ppm downfield from 85% H$_3$PO$_4$. Abbreviations used in the reporting of NMR spectra are b = broad, s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. High resolution mass spectra were recorded on a JEOL JMS SX/SX102A four-sector mass spectrometer coupled to a JEOL MSMP7000 data system.

**General preparation of 1-(2-aminophenyl)-3-(n-alkyl)imidazolium halide 4a-d and imidazolium PF$_6$ (4e), based on a procedure from ref$^{[7]}$ using alkyl iodides or bromides**

Imidazole aniline (4.54 mmol) was weighed in a pressure tube and suspended in 20 ml MeCN. The appropriate alkylhalide (4.54 mmol) was added and after sealing the tube the mixture was heated to 90 °C for 4 days. The mixture was then cooled to RT, and the volatiles removed in vacuo. Purification was performed by dissolving the product in a small amount of MeOH and adding this dropwise to 200 ml Et$_2$O. Light to dark brown solids were obtained. To obtain ligand 4e, 4a (1.32 gr, 4.45 mmol) was stirred with an excess of KPF$_6$ (4.2 gr, 22.7 mmol) in 20 ml CH$_2$Cl$_2$ overnight at RT. The salts were removed by filtration over a pad of celite and the product was dried in vacuo. When an oily solid was obtained, a washing step with Et$_2$O was performed.

**Spectral data of 4a (X = Br, R = nBu), obtained from n-bromobutane as a very hygroscopic brown sticky solid in 98% yield.** $^1$H-NMR (300 MHz, CD$_2$Cl$_2$) δ = 9.56 (s, 1H, im-H), 7.56 (t, $J$ = 1.8 Hz, 1H, im =CH), 7.37 (t, $J$ = 1.8 Hz, 1H, im =CH), 7.26 (m, 1H, H$_a$), 7.14 (dd, $J$ = 7.9, 1.5 Hz, 1H, H$_b$), 6.99 (dd, $J$ = 8.2, 1.3 Hz, 1H, H$_c$), 6.77 (m, 1H, H$_d$), 5.05 (s, 2H, NH$_2$), 4.43 (t, $J$ = 7.5 Hz, 2H, NCH$_3$), 1.96 (m, 2H, CH$_2$), 1.43 (m, 2H, CH$_2$), 0.98 (t, $J$ = 7.3 Hz, 4H, CH$_3$) ppm. $^{13}$C-NMR (126 MHz, DMSO-d$_6$) δ = 144.20 (s, C$_n$NH$_2$), 137.65 (s, C=CN), 131.62 (s, C$_n$), 127.72 (s, C$_m$), 124.28 (s, C$_n$), 123.30 (s, C$_n$), 120.21 (s, C=C im), 116.96 (s, C$_n$), 116.53 (s, C=C im), 49.34 (s, CH$_3$), 31.57 (s, CH$_3$), 19.39 (s, CH$_3$), 13.89 (s, CH$_3$). FAB-MS for C$_{13}$H$_{29}$N$_3$: m/z calculated 216.1501 (100%) [M-Br]$^+$, observed 216.1494.

**Spectral data of 4b (X = I, R = nBu), obtained from n-iodobutane as a brown yellow solid in 93% yield.** $^1$H-NMR (300 MHz, CD$_2$Cl$_2$) δ = 9.28 (s, 1H, im-H), 7.54 (m, 1H, im =CH), 7.43 (t,
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Spectral data of 4c (X = I, R = Et), obtained from n-iodoethane as a brown yellow solid in 98% yield. 1H-NMR (300 MHz, CDCl₃)  δ = 9.20 (s, 1H, -CH=), 7.43 (t, J = 1.7 Hz, 1H, -CH), 7.36 (t, J = 1.8 Hz, 1H, im=CH), 7.29 (m, 1H, H₂Ar), 7.20 (d, J = 6.4 Hz, 1H, H₂Ar), 6.95 (dd, J = 8.2, 1.2 Hz, 1H, H₂Ar), 6.80 (s, 1H, H₂Ar), 6.42 (bs, 2H, NH₂), 4.50 (m, 2H, NCH₂), 1.68 (t, J = 7.4 Hz, 3H, CH₃) ppm. FAB⁺-MS (CH₂Cl₂) for C₁₆H₂₄AgN₆: m/z calculated 537.1896 (100%) [M-AgBr₂]+, observed 537.1900.

Spectral data of 4d (X = I, R = Me), obtained from iodomethane as a brown orange solid in 78% yield. 1H-NMR (300 MHz, CDCl₃)  δ = 9.29 (s, 1H, im-CH), 7.43 (t, J = 1.7 Hz, 1H, im=CH), 7.36 (t, J = 1.8 Hz, 1H, im=CH), 7.29 (m, 1H, H₂Ar), 7.11 (dd, J = 7.9, 1.4 Hz, 1H, H₂Ar), 6.88 (dd, J = 8.2, 1.2 Hz, 1H, H₂Ar), 6.80 (m, 1H, H₂Ar), 4.82 (bs, 2H, NH₂), 4.18 (s, 3H, NCH₂) ppm. FAB⁺-MS (CH₂Cl₂) for C₁₆H₂₄AgN₆: m/z calculated 174.1188 (100%) [M-I]⁺, observed 188.1185.

Spectral data of 4e (X = PF₆, R = nBu), obtained as an off-brown solid in 91% yield. 1H-NMR (300 MHz, CD₂Cl₂)  δ = 8.60 (s, 1H, im-CH), 7.48 (t, J = 1.6 Hz, 2H, im=CH), 7.36 (m, 1H, H₂Ar), 7.18 (dd, J = 7.9, 1.4 Hz, 1H, H₂Ar), 6.95 (d, J = 8.2 Hz, 1H, H₂Ar), 6.90 (m, 1H, H₂Ar), 4.32 (t, J = 7.5 Hz, 2H, NCH₂), 4.07 (bs, 2H, NH₂), 1.96 (m, 2H, CH₂), 1.45 (m, 2H, CH₂), 1.01 (t, J = 7.4 Hz, 3H, CH₃) ppm. 19F-NMR (282 MHz, CDCl₃)  δ = -72.95 (d, J = 711.3 Hz) ppm.

Preparation of Bis [1-(2-aminophenyl)-3-butyl-imidazol-2-ylidene] silver(I) dibromo argentate(I) Ag-4a

A suspension of 4a (0.32 gr, 1.1 mmol) and Ag₂O (0.25 gr, 1.1 mmol) and MeOH (2 ml) in CH₂Cl₂ (35 ml) was stirred for 30 h at 20 °C under the exclusion of light. The resulting mixture was filtered over a pad of celite and the solvent was removed under reduced pressure to yield the desired silver-carbene (0.29 gr, 66 %) as a brown/orange solid. 1H-NMR (500 MHz, DMSO-d₆)  δ = 7.65 (s, 1H, im=CH), 7.50 (s, 1H, im=CH), 7.17 (t, J = 7.7 Hz, 1H, H₂Ar), 7.07 (d, J = 8.1 Hz, 1H, H₂Ar), 6.85 (d, J = 7.5 Hz, 1H, H₂Ar), 6.63 (t, J = 7.5 Hz, 1H, H₂Ar), 6.58 (d, J = 8.1 Hz, 1H, H₂Ar), 6.43 (d, J = 7.9 Hz, 1H, H₂Ar), 3.99 (bs, 2H, NH₂), 1.75 (bs, 2H, CH₂), 1.23 (bs, 2H, CH₂), 0.88 (bs, 3H, CH₃). ¹³C-NMR (75 MHz, CD₂Cl₂)  δ = 181.41 (NCN), 142.12 (s, C₂a), 137.57 (s, C₂b), 129.80 (s, C₁b), 122.51 (s, C=C im), 120.68 (s, C=C im), 117.44 (s, C₁a), 116.49 (s, C₁b), 51.45 (s, CH₂), 32.81 (s, CH₂), 19.28 (s, CH₂), 12.97 (s, CH₂). FAB⁺-MS (CH₂Cl₂) for C₁₂₆H₁₃₄AgN₆: m/z calculated 537.1896 (100%) [M-AgBr₂]⁺, observed 537.1900.
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Preparation of \([\text{Ru}(p\text{-cym})\text{Cl}(CNIC-NH}_2])\)PF$_6$ 5a

A solution of Ag-4a (0.27 gr, 0.66 mmol) in DCM (15 ml) was added to a solution of [RuCl$_2$(p-cym)]$_2$ (0.19 gr, 0.30 mmol) and KPF$_6$ (0.36 gr, 1.98 mmol) in DCM (20 ml) and was stirred at RT for 3 h during which the solution became dark green with grey silver halides suspended in it. The mixture was filtered over a pad of celite and the volume of filtrate was reduced to 3 ml. 20 ml pentane was added which resulted in a precipitation of a dark green solid. Repeated precipitation from DCM with EtO furnished the desired light green complex (0.19 gr, 96%). $^1$H-NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ = 7.78 (m, 1H, $H_{\text{cym}}$), 7.65 (d, $J = 2.2$ Hz, 1H, im=CH), 7.43 (d, $J = 2.2$ Hz, 1H, im=CH), 7.48-7.37 (m, 3H, $H_{\text{cym}}$), 6.52 (d, $J = 8.9$ Hz, 1H, NH$_2$), 5.83 (d, $J = 5.9$ Hz, 1H, $H_{\text{cym}}$-p-cym), 5.71 (d, $J = 6.1$ Hz, 1H, $H_{\text{cym}}$-p-cym), 5.09 (m, 2H, $H_{\text{cym}}$-p-cym), 4.38 (d, $J = 10.6$ Hz, 1H, NH$_2$), 4.29 (t, $J = 8.1$ Hz, 2H, NCH$_2$), 2.05 - 1.80 (m, 3H, CH$_3$ and CH$_2$-p-cym), 1.74 (s, 3H, CH$_3$-p-cym), 1.52 (m, 2H, CH$_3$), 1.05 (t, $J = 7.3$ Hz, 3H, CH$_3$), 0.93 (dd, $J = 16.6, 6.9$ Hz, 6H, CH$_3$-i-Pr) ppm. $^{13}$C-NMR (75 MHz, CD$_2$Cl$_2$) $\delta$ = 177.22 (s, NCl), 134.26 (s, $C_{\text{ar}}$), 132.06 (s, $C_{\text{ar}}$), 128.80 (s, $C_{\text{ar}}$), 127.68 (s, $C_{\text{ar}}$), 123.71 (s, $C_{\text{ar}}$), 121.81 (s, C=C im), 121.67 (s, C=C im), 120.14 (s, $C_{\text{ar}}$), 109.37 (s, $C_{\text{ar}}$-p-cym), 101.81 (s, $C_{\text{ar}}$-p-cym), 89.06 (s, $C_{\text{ar}}$-p-cym), 83.89 (s, $C_{\text{ar}}$-p-cym), 83.73 (s, $C_{\text{ar}}$-p-cym), 81.96 (s, $C_{\text{ar}}$-p-cym), 51.52 (s, CH$_2$), 33.01 (s, CH$_3$), 30.78 (s, CH$_3$-p-cym), 23.33 (s, CH$_3$-p-cym), 20.19 (s, CH$_3$-p-cym), 19.85 (s, CH$_3$-p-cym), 17.83 (s, CH$_3$), 13.62 (s, CH$_3$) ppm. $^{19}$F-NMR (121 MHz, CD$_2$Cl$_2$) $\delta$ = -144.06 (septet, $J = 711.9$ Hz) ppm. FAB$^+$-MS (CH$_2$Cl$_2$) for $C_{23}$H$_{31}$ClN$_2$Ru: m/z calculated 486.1253 (100%) [M-PF$_6$]$^+$, observed 486.1248.

Preparation of \([\text{Ru}(p\text{-cym})\text{Cl}((R\text{-CNIC-NH})_2)]\)PF$_6$ 5b-5d based on a modified procedure from ref.[7]

[Ru(p-cym)Cl$_2$]$_2$ (97 mg, 0.16 mmol), the appropriate imidazolium salt (4b-d) (0.32 mmol) and Ag$_2$O (37 mg, 0.16 mmol) were weighed in a Schlenk and dissolved in 15 ml DCM and stirred under absence of light at 33°C overnight. The solvent was removed in vacuo and together with KI (0.53 gr, 3.17 mmol), it was redissolved in 20 ml acetone and stirred at reflux for 1 hr. The solvent was removed in vacuo, the crude product redissolved in 20 ml DCM, filtered over a pad of celite and concentrated under vacuum. The complex was purified by repeatedly dissolving in a DCM/EtO mixture and cooling to 4°C to obtain the pure complex.

Spectral data for 5b ($R = $Me)

5b Was obtained as a dark brown crystalline solid in 33% yield. $^1$H-NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ = 10.08 (d, $J = 9.9$ Hz, 1H, NH$_2$), 8.60 (d, $J = 6.8$ Hz, 1H, $H_{\text{cym}}$), 7.62 (s, 1H, im=CH), 7.36 (s, 1H, $H_{\text{cym}}$), 7.42 - 7.18 (m, 3H, $H_{\text{cym}}$), 6.24 (d, $J = 5.4$ Hz, 1H, $H_{\text{cym}}$-p-cym), 5.85 (d, $J = 5.7$ Hz, 1H, $H_{\text{cym}}$-p-cym), 5.32 (d, $J = 5.4$ Hz, 1H, $H_{\text{cym}}$-p-cym), 5.19 (d, $J = 5.7$ Hz, 1H, $H_{\text{cym}}$-p-cym), 4.06 (s, 1H, NH$_2$), 4.01 (s, 3H, CNH$_3$), 1.90 (m, 1H, CH$_2$-p-cym), 1.77 (s, 3H, CH$_3$-p-cym), 0.86 (dd, $J = 19.8, 6.8$ Hz, 6H, CH$_3$-i-Pr) ppm. $^{13}$C-NMR (75 MHz, CD$_2$Cl$_2$) $\delta$ = 179.09 (s, NCl), 135.61 (s, $C_{\text{ar}}$), 132.53 (s, $C_{\text{ar}}$), 128.26 (s, $C_{\text{ar}}$), 126.85 (s, $C_{\text{ar}}$), 125.78 (s, $C_{\text{ar}}$), 123.72 (s, C=C im), 120.98 (s, C=C im), 119.41 (s, $C_{\text{ar}}$), 107.37 (s, $C_{\text{ar}}$-p-cym), 102.08 (s,
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$C_{29}p$-cym), 89.87 (s, $C_{31}p$-cym), 83.88 (s, $C_{32}p$-cym), 83.83 (s, $C_{33}p$-cym), 83.11 (s, $C_{34}p$-cym), 38.94 (s, $CH_2$), 30.62 (s, $CH_{2-p}$-cym), 23.35 (s, $CH_{2-p}$-cym), 20.15 (s, $CH_{3-p}$-cym), 18.00 (s, $CH_{1-p}$-cym) ppm.

Spectral data for $5c$ ($R = Et$). $5c$ was obtained as a brown microcrystalline powder in 29% yield. 'H-NMR (300 MHz, CD$_2$Cl$_2$) δ = 8.81 – 8.63 (m, 1H, $H_{2-p}$), 8.56 (d, $J = 11.2$ Hz, 1H, NH$_2$), 7.77 (d, $J = 2.2$ Hz, 1H, im=CH), 7.46 (d, $J = 2.1$ Hz, 1H, im=CH), 7.37 (dt, $J = 6.8$, 4.0 Hz, 3H, $H_{Ar}$), 6.31 (d, $J = 6.0$ Hz, 1H, $H_{Ar}$, p-cym), 5.79 (d, $J = 6.0$ Hz, 1H, $H_{Ar}$, p-cym), 5.22 (dd, $J = 10.5$, 6.1 Hz, 2H, $H_{Ar}$-p-cym), 4.33 (ddq, $J = 35.5$, 14.6, 7.4 Hz, 2H, NCH$_2$), 4.17 (d, $J = 11.3$ Hz, 1H, NH$_2$), 2.14 (m, 1H, CH$_{p}$/cym) 2.09 (s, 3H, CH$_3$-p-cym), 1.58 (t, $J = 7.3$ Hz, 3H, CH$_3$), 0.92 (dd, $J = 6.9$, 4.1 Hz, 6H, CH$_3$i-Pr) ppm. $^{13}$C-NMR (75 MHz, CD$_2$Cl$_2$) δ = 176.62 (s, NCN), 135.80 (s, $C_{32}$), 132.57 (s, $C_{33}$), 128.22 (s, $C_{34}$), 127.28 (s, $C_{35}$), 123.13 (s, $C_{36}$), 122.39 (s, C=Cl im), 121.57 (s, C=Cl im), 120.53 (s, $C_{37}$), 110.48 (s, $C_{38}$-p-cym), 102.22 (s, $C_{39}$-p-cym), 89.51 (s, $C_{40}$-p-cym), 84.02 (s, $C_{41}$-p-cym), 82.76 (s, $C_{42}$-p-cym), 82.22 (s, $C_{43}$-p-cym), 48.61 (s, CH$_3$), 31.50 (s, CH$_{2-p}$-p-cym), 23.67 (s, CH$_{3-p}$-p-cym), 20.44 (s, CH$_{3-p}$-p-cym), 19.75 (s, CH$_{3-p}$-p-cym), 15.69 (s, CH$_{3}$-p-cym).

Spectral data for $5d$ ($R = nBu$). $5d$ was obtained in a dark brown microcrystalline solid in 46% yield. 'H-NMR (300 MHz, CD$_2$Cl$_2$) δ = 10.14 (bs, 1H, NH$_2$), 8.57 (s, 1H, im=CH), 7.72 (s, 1H, im=CH), 7.36 (m, 4H, $H_{Ar}$), 6.16 (d, $J = 5.5$ Hz, 1H, $H_{Ar}$-p-cym), 5.81 (d, $J = 5.9$ Hz, 1H, $H_{Ar}$-p-cym), 5.28 (d, $J = 5.5$ Hz, 1H, $H_{Ar}$-p-cym), 5.18 (d, $J = 5.8$ Hz, 1H, $H_{Ar}$-p-cym), 4.31 (t, $J = 7.1$ Hz, 2H, NCH$_2$), 4.01 (bs, $J = 9.1$ Hz, 1H, NH$_2$), 1.91 (m, 3H, CH$_3$ + CH$_{p}$-p-cym), 1.50 (m, $J = 7.4$ Hz, 2H, CH$_3$), 1.03 (t, $J = 7.3$ Hz, 3H, CH$_3$), 0.87 (dd, $J = 25.8$, 6.9 Hz, 6H, CH$_3$i-Pr) ppm. $^{13}$C-NMR (75 MHz, CD$_2$Cl$_2$) δ = 178.21 (s, NCN), 135.78 (s, $C_{32}$), 132.57 (s, $C_{33}$), 128.10 (s, $C_{34}$), 126.90 (s, $C_{35}$), 123.58 (s, $C_{36}$), 123.14 (s, C=Cl im), 121.36 (s, C=Cl im), 120.18 (s, $C_{37}$), 107.75 (s, $C_{38}$-p-cym), 101.25 (s, $C_{39}$-p-cym), 89.54 (s, $C_{40}$-p-cym), 84.20 (s, $C_{41}$-p-cym), 83.89 (s, $C_{42}$-p-cym), 82.79 (s, $C_{43}$-p-cym), 51.48 (s, CH$_3$), 33.10 (s, CH$_{2-p}$-p-cym), 30.58 (s, CH$_{3}$), 23.37 (s, CH$_{3}$), 20.23 (s, 2 x CH$_3$-p-cym), 17.90 (s, CH$_3$-p-cym), 13.70 (s, CH$_3$) ppm. FAB-MS (CH$_2$Cl$_2$) for $C_{23}H_{31}$In$_2$Ru: m/z calculated 578.0613 (100%) [M-I]$, observed 578.0608.

Preparation of $[RuCp^*(\eta^5-1-(2-aminophenyl)-3-(n-butyl)imidazolium)PF_6]Cl$ complex 8 $[RuCp^*(\mu_\eta^1-Cl)]$ (109 mg, 0.1 mmol) and 4e (145 mg, 0.4 mmol) were weighed in a Schlenk, dissolved in 10 ml THF and stirred overnight at RT. The brown/yellow precipitate was filtered off, washed with a small amount of cold THF and dried in vacuo (yield 44%). COSY and HSQC NMR spectroscopy have been used in the identification of the peaks. 'H-NMR (300 MHz, CD$_2$Cl$_2$) δ = 10.03 (bs, 1H, im-H), 7.64 (s, 1H, im=CH), 7.60 (s, 1H, im=CH), 6.95 (bs, 2H, NH$_2$), 6.39 (m, 2H, $H_{Ar}$), 5.64 (s, 3H, $H_{Ar}$), 4.41 (bs, 2H, NCH$_2$), 2.03 (m, 2H, CH$_3$), 1.98 (s, 15H, $CH_3$), 1.49 (m, 2H, CH$_3$), 1.02 (t, $J = 7.2$ Hz, CH$_3$) ppm. $^{13}$C-NMR (282 MHz, CD$_2$Cl$_2$) δ = -72.27 (d, $J = 711.9$ Hz) ppm. $^{19}$F-NMR (282 MHz, CD$_2$Cl$_2$) δ = 138.49 (s, NCN), 123.52 (s,
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Preparation of [IrCp*Cl(C=C=im)] PF₆ 9

[IrCp*Cl]₂(0.25 mmol, 199 mg) and KPF₆ (1.25 mmol, 230 mg) in 8 ml DCM was added to a solution of Ag-4a (0.25 mmol, 201 mg) in 7 ml DCM and stirred at RT under the exclusion of light for 2 hr. The resulting reaction mixture was filtered over a pad of celite and the solvent was evaporated in vacuo. The complex was purified by dissolving in a DCM/Et₂O mixture (2 ml/5 ml) and cooling to 4°C to obtain the complex in a crystalline fashion (yield 51%). ¹H-NMR (300 MHz, CD₂Cl₂) δ = 7.70 (d, J = 2.2 Hz, 1H, im=CH), 7.54 (m, 2H, H₅), 7.49 – 7.40 (m, 2H, H₅), 7.38 (d, J = 2.2 Hz, 1H, im=CH), 6.12 (bs, 2H, NH₂), 4.26 (m, 1H, NCH₃), 3.97 (m, 1H, NCH₃), 1.88 (m, 2H, CH₂), 1.46 (s, 17H, η⁵-C₅Me₅). ¹³C-NMR (75 MHz, CD₂Cl₂) δ = 160.97 (s, N=C), 133.81 (s, C₆H₅), 128.12 (s, C₆H₅), 127.89 (s, C₆H₅), 122.82 (s, C=C=im), 121.84 (s, C=C=im), 121.66 (s, C₆H₅), 119.71 (s, C₆H₅), 90.13 (s, η⁵-C₅Me₅), 50.81 (s, NCH₃), 33.21 (s, CH₃), 13.59 (s, CH₃), 8.13 (s, η⁵-C₅Me₅) ppm. ¹⁹F-NMR (282 MHz, CD₂Cl₂) δ = -72.06 (d, J = 711.7 Hz) ppm. FAB+MS for C₂₃H₃₂ClN₃Ir: m/z calculated 578.1907 (100%) [M-Cl-PF₆]⁺, observed 578.1907.

Preparation of [RhCp*Cl(C=C=NH₂)] PF₆ 10

[RhCp*Cl]₂(0.095 mmol, 59 mg), KPF₆ (0.95 mmol, 175 mg) and Ag-4a (0.19 mmol, 77 mg) were weighed in a schlenk and dissolved in 10 ml DCM. The solution was stirred at RT for 24 hr under the exclusion of light. The mixture was then filtered over a pad of celite and the solvent was evaporated in vacuo till 1 ml and precipitated with Et₂O. The complex was purified by dissolving in a THF/pentane mixture (2 ml/6 ml) and cooling to 4°C to obtain the complex in a crystalline fashion (yield 62%). ¹H-NMR (300 MHz, CD₂Cl₂) δ = 7.73 (d, J = 2.2 Hz, 1H, im=CH), 7.57-7.42 (m, 4H, H₅), 7.45 (d, J = 2.4 Hz, 1H, im=CH), 5.19 (bs, 2H, NH₂), 4.26 (m, 1H, NCH₃), 4.02 (m, 1H, NCH₃), 1.87 (m, 2H, CH₂), 1.42 (s, 17H, η⁵-C₅Me₅), 1.02 (t, J = 7.4 Hz, 2H, CH₂) ppm. ¹³C-NMR (75 MHz, CD₂Cl₂) δ = 173.02 (d, J = 53 Hz, NCN), 133.12 (s, C₆H₅), 132.11 (s, C₆H₅), 128.46 (s, C₆H₅), 127.57 (s, C₆H₅), 123.63 (s, C=C=im), 122.32 (s, C=C=im), 121.84 (s, C₆H₅), 120.98 (s, C₆H₅), 97.62 (d, J = 98 Hz, η⁵-C₅Me₅), 51.04 (s, NCH₃), 32.79 (s, CH₃), 20.03 (s, CH₃), 13.59 (s, CH₃), 8.13 (s, η⁵-C₅Me₅) ppm. ¹⁹F-NMR (282 MHz, CD₂Cl₂) δ = -72.19 (d, J = 711.9 Hz) ppm. Anal. Calcd. for C₂₃H₃₂ClF₆N₃PrH:C 43.58; H, 5.09; N, 6.63. Found: C, 42.15; H, 4.97; N, 6.49. FAB+MS for C₂₃H₃₂ClN₃Rh: m/z calculated 488.1340 (100%) [M-PF₆]⁺, observed 488.1335.
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X-ray crystal structure determinations

Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator ($\lambda = 0.71073 \text{ Å}$) up to a resolution of $(\sin \theta/\lambda)_{\text{max}} = 0.65 \text{ Å}^{-1}$. Software packages used for the intensity integration were Saint[20] (compound 6) and Eval15[21] (compounds 7 and 8). Absorption correction and scaling was performed with SADABS.[22]

The structures were solved with SHELXS-97[23] and refined with SHELXL-97[23] against $F^2$ of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions (6) or located in difference Fourier maps (7 and 8). N-H hydrogen atoms were refined freely with isotropic displacement parameters, C-H hydrogen atoms were refined with a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[24] CCDC 931590 (compound 6), 931591 (compound 7), and 931592 (compound 8) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Compound 5a $[[\text{Ru}(p\text{-cym})\text{Cl(CNHC-NH}_2\text{)]PF}_6]]$: $[\text{C}_{23}\text{H}_{31}\text{ClN}_3\text{Ru}](\text{PF}_6)$, Fw = 631.00, green block, 0.22 x 0.15 x 0.06 mm$^3$, T = 150(2) K, triclinic, P-1 (no. 2), a = 11.6256(5), b = 13.2108(4), c = 9.3584(4) Å, $\alpha = 109.7203(12)$, $\beta = 95.4923(13)$, $\gamma = 95.6165(13)$ º, V = 1333.73(10) Å$^3$, Z = 2, D$_x$ = 1.571 g/cm$^3$, $m = 0.81$ mm$^{-1}$. 33032 Reflections were measured, 6075 reflections were unique ($R_{\text{int}} = 0.019$), of which 5564 were observed ($I > 2\sigma(I)$). The PF$_6$ ions were located on inversion centers. One PF$_6$ and the n-butyl group were refined with a disorder model. 364 Parameters were refined with 110 restraints (distance and angle restraints for the disordered groups, ISOR instructions for the disordered F atoms). R1/wR2 [$I > 2\sigma(I)$]: 0.0201 / 0.0493. R1/wR2 [all refl.]: 0.0239 / 0.0512. S = 1.047. Residual electron density between 0.36 and 0.38 e/Å$^3$.

Compound 9 $[[\text{IrCp}^*\text{Cl(CNHC-NH}_2\text{)]PF}_6]]$: $[\text{C}_{23}\text{H}_{32}\text{ClIrN}_3\text{]}(\text{PF}_6)\cdot \text{CH}_2\text{Cl}_2$, Fw = 808.06, yellow block, 0.38 x 0.24 x 0.10 mm$^3$, T = 100(2) K, monoclinic, P2$_1$/n (no. 14), a = 23.3692(3), b = 8.49180(14), c = 15.3294(3) Å, $\beta = 98.781(1)$ º, V = 2925.60(15) Å$^3$, Z = 4, D$_x$ = 1.835 g/cm$^3$, $m = 4.95$ mm$^{-1}$. 47947 Reflections were measured, 6707 reflections were unique ($R_{\text{int}} = 0.018$), of which 5564 were observed ($I > 2\sigma(I)$). The CH$_2$Cl$_2$ molecule was refined with a disorder model. 370 Parameters were refined with 7 restraints (distance and angle restraints for the disordered CH$_2$Cl$_2$). R1/wR2 [$I > 2\sigma(I)$]: 0.0142 / 0.0309. R1/wR2 [all refl.]: 0.0156 / 0.0314. S = 1.038. Residual electron density between 0.76 and 0.66 e/Å$^3$.

Compound 10 $[[\text{RhCp}^*\text{Cl(CNHC-NH}_2\text{)]PF}_6]]$: $[\text{C}_{23}\text{H}_{32}\text{ClN}_3\text{Rh}](\text{PF}_6)\cdot \text{C}_4\text{H}_8\text{O}$, Fw = 705.95, yellow block, 0.60 x 0.22 x 0.12 mm$^3$, T = 150(2) K, monoclinic, P2$_1$/n (no. 14), a = 8.49180(14), b = 23.3692(3), c = 15.3294(3) Å, $\beta = 98.781(1)$ º, V = 3006.42(8) Å$^3$, Z = 4, D$_x$ = 1.560 g/
39596 Reflections were measured, 6886 reflections were unique (Rint = 0.017), of which 6480 were observed [\(I > 2\sigma(I)\)]. The THF molecule was refined with a disorder model. 421 Parameters were refined with 70 restraints (distance, angle and ISOR restraints for the disordered THF). R1/wR2 [\(I > 2\sigma(I)\)]: 0.0212 / 0.0529. R1/wR2 [all refl.]: 0.0230 / 0.0538. S = 1.040. Residual electron density between 0.50 and 0.49 e/Å³.

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3.5 References

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