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NHC-amide donor ligands in rhodium complexes: Syntheses and characterisation

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ABSTRACT

Rhodium(I) complexes bearing amide-functionalised NHC ligands were synthesized in high yields through various synthetic routes and from different metal precursors, showing the versatility of such systems. By changing the ancillary ligands on the rhodium from cyclooctadiene to carbonyls the coordination behaviour of the NHC-amide ligand could be influenced. When a more basic precursor was employed for complexation, bidentate behaviour with the amide in an anionic mode was observed. All reported complexes are synthesized in high yields and under ambient conditions, which shows their robustness. The monodentate rhodium(I) biscarbonyl NHC complexes were shown to be able to activate iodomethane.

Introduction

In the 1960s, the Monsanto Company developed the rhodium-catalysed process for acetic acid synthesis from methanol and carbon monoxide. The process is also catalysed by iodide, generating iodomethane *in situ* [1]. This is currently one of the largest industrially applied homogeneously catalysed reactions, with a multi-million tonne production per year. The oxidative addition of iodomethane is the rate-determining step [2], and research has focused on improving the propensity of the catalyst for this reaction by rational ligand design. Research has either focused on the use of monodentate ligands, or on the introduction of a bidentate ligand, either symmetrical or heteroditopic [3]. Other studies have dealt with the introduction of differently substituted tertiary phosphine ligands, evaluating their steric and electronic impact on the oxidative addition [4]. Often observed for rhodium complexes bearing suitably functionalized ligands is the secondary reaction of the rhodium(III) methyl complex with its carbonyl ligand to form the rhodium(III) acyl species [5].

Increase of the electron density on the rhodium metal center by using strong donor ligands has been shown to be an effective method of activating the system towards oxidative addition. Traditionally, phosphine ligands have been used to affect this. In this work, we propose to use N-heterocyclic carbene (NHC) ligands; they are strong σ-donor ligands that form strong bonds to various (transition) metals [6]. An advantage of these ligands over phosphines is their relative stability. Also, because they are less prone to dissociation from the metal, no excess ligand needs to be used in the synthesis or in the catalytic process. They have been used successfully as ligands for various processes [7].

Rhodium NHC complexes have only sparsely been used in iodomethane oxidative addition [8], one example showing conversion to the rhodium(III) alkyl species [9], while another shows exclusive acyl formation [10]. No reports are available employing bidentate NHC ligands, either homo- or heteroditopic. In our laboratories, research focuses on the development of (hetero)bidentate scaffolds for numerous applications [11]; the development of a donor-functionalized NHC-system was therefore a logical progression of our research interests. We have chosen to focus our designs on the incorporation of a secondary amide donor [12], as it could potentially be deprotonated to yield a mono-anionic bidentate ligand set [13]. In this contribution we describe the synthesis and structural properties of these systems as well as an exploratory study of their reactivity towards iodomethane.

Results and discussion

Ligand synthesis

The imidazolium salts **1** and **2** are readily synthesized [14] from 1-mesityl imidazole [15] and a chloroethyl amide, which in turn is

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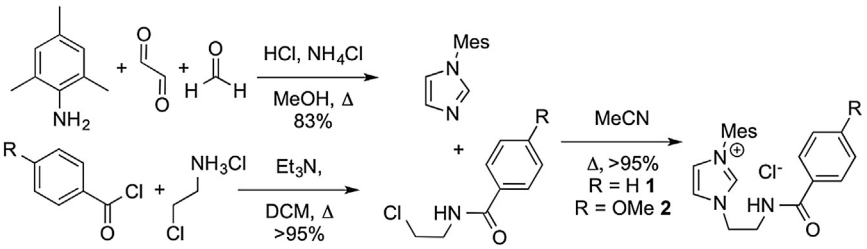


Scheme 1. Synthesis of imidazolium salts (Mes = 2,4,6-trimethylphenyl).

obtained by coupling 2-chloroethylamine hydrochloride with the appropriate aroyl chloride (Scheme 1) [16].

An interesting possibility offered by this high-yielding and simple procedure is that the robust amide-moiety could be used to link the NHC-fragment to a solid support if a heterogenized catalyst is required [17].

The mesityl imidazolium salts are characterized by a signal in the ^{1}H NMR spectra at 9.5 ppm in DMSO-d_6 and at 9.9 ppm in $CDCl_3$. The signal for the amide-hydrogen appears as a triplet around 9 ppm with a coupling of 5 Hz caused by the neighbouring methylene group. Even in the case of DMSO the splitting is clearly present, indicating that there is very slow to no exchange of the hydrogen with the water present in the deuterated solvent. Crystals of **1** suitable for X-ray crystallography were obtained by slow evaporation of a chloroform solution (Fig. 1).

The structure clearly shows the geometry of the molecule. Hydrogen bonds from the amide to the chloride and to the imidazolium proton, as well as π–π interactions constitute an intermolecular network in the solid state; no significant intramolecular interactions are present.

Silver(I) complex synthesis

From the preligands, the silver(I) complexes were synthesized first [18]. These species are routinely used to obtain the NHC without the need for stringent air- and moisture-free reaction conditions [19], and are excellent transfer agents for the carbene ligand. After reaction of the imidazolium salts with half an equivalent of silver(I) oxide in dichloromethane, the products **3** and **4** were obtained in near quantitative yields (Scheme 2).

The observed uptake of the silver(I) oxide confirms that the reaction proceeds to completion, and the ^{1}H NMR spectra clearly show the disappearance of the imidazolium C-2 hydrogen, indicating carbene-formation. Definitive proof for carbene formation is obtained from the ^{13}C NMR spectra, where the characteristic signal for the NCN carbon is observed at 181.7 ppm. This signal appeared broadened through ligand exchange in solution. Although the neutral mono-NHC complex is also a possible product, literature precedent validates the structure shown in Scheme 2 [7,20].

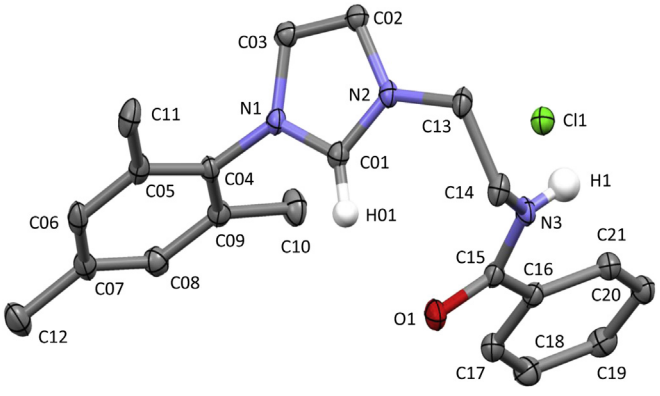


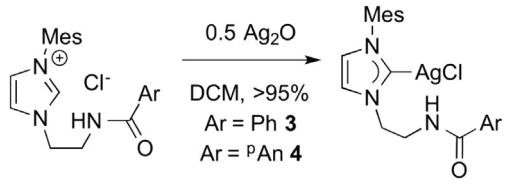
Fig. 1. Displacement ellipsoid plot of **1** (50% probability). Non-relevant hydrogen atoms are omitted for clarity.

Rhodium(I) complex synthesis

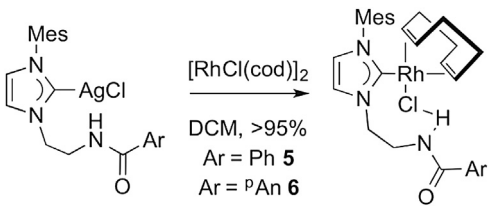
Transmetallation of the NHC to the well-known chloridorhodium(I) 1,5-cyclooctadiene (cod) dimer was performed without taking any special precautions to exclude air or moisture from the reaction mixture, obtaining the product in high yields (Scheme 3).

Instead of deprotonation of the secondary donor, as is often seen with bidentate ligands in conjunction with this mildly basic rhodium precursor [21], the amide remains protonated. Initially, this was inferred from ^{1}H NMR experiments, where the signal for the amide hydrogen could still be observed. However, an upfield shift to just above 8 ppm was also noted for this signal, indicating that the proton is more strongly shielded. In addition to this effect, a clear bidentate interaction of the ligand was visible, evidenced by the splitting of the signals for the ethylene bridge hydrogens into an AA'BB' pattern. From ^{13}C NMR analysis, the signal for the carbene is observed at 182.4 ppm, with a $J_{Rh\text{-}C}$ of 52 Hz. These values are in the same range as for similar reported complexes [8].

Several coordination modes that fit these observations are possible, but definitive proof of the molecular structure was given by X-ray crystallography. Both **5** and **6** showed the same arrangement, in which the amide hydrogen shows an interaction with the rhodium-bound chlorido ligand. The two complexes crystallize differently (Figs. 2 and 3); whereas complex **5** crystallized with one molecule in the asymmetric unit, that of **6** contained two complex molecules (**a** and **b** in Table 1) and a molecule of chloroform.



Scheme 2. Synthesis of silver(I) NHC complexes.



Scheme 3. Transmetallation to chloridorhodium(I) cyclooctadiene.

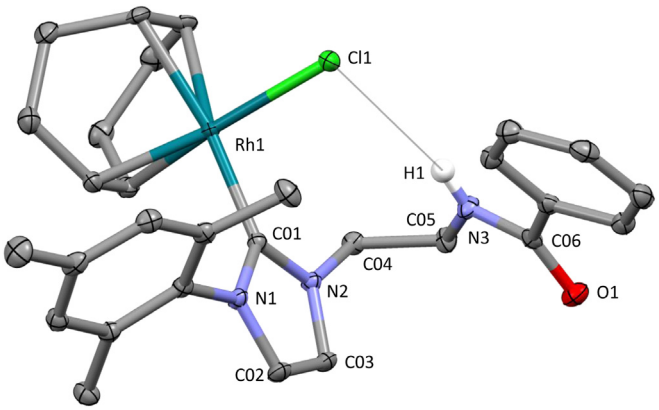


Fig. 2. Displacement ellipsoid plot of **5**, showing the intramolecular hydrogen bond (50% probability). Non-relevant hydrogen atoms and atom labels are omitted for clarity.

Both complexes have the same general distorted square planar conformation, with the most obvious feature the distorted boat-like 8-membered ring of the 'bidentate' ligand. All three hydrogen bond lengths are of similar magnitude, as are the carbene–rhodium bond lengths. The bond lengths of the rhodium center to the cyclooctadiene carbons *trans* to the NHC are significantly longer than those *trans* to the chlorido ligand; this is caused by the greater *trans*-influence of the σ-donor carbene ligand as compared to the chloride.

For application in methanol carbonylation, the rhodium complexes should bear a carbonyl ligand. When **5** and **6** were treated with CO under various conditions, no exchange of the cyclooctadiene was observed, even though this procedure is reported to be facile [8]. Alternatively, when the silver(I) NHC complexes were reacted with $[RhCl(CO)_2]_2$, a different reactivity compared to the cod-analogue was observed. Instead of the hydrogen bond interaction with the chloride, monodentate coordination of the NHC took place (Scheme 4).

This monodentate behaviour could be easily observed in the ^{1}H NMR spectra, which showed no diastereotopicity in contrast to **5** and **6**. The amide-proton is observed at 7.5 ppm, which is significantly upfield from the cod-analogues. In the ^{13}C NMR spectra, the NHC carbon is observed at 185 ppm with a $J_{Rh\text{-}C}$ of 54 Hz, which corresponds to monodentate $RhCl(CO)_2$(NHC) complexes reported in literature [8]. The carbonyl ligands of **7** and **8** show signals in IR spectroscopy at 2083 and 2004 cm^{-1} in dichloromethane and at

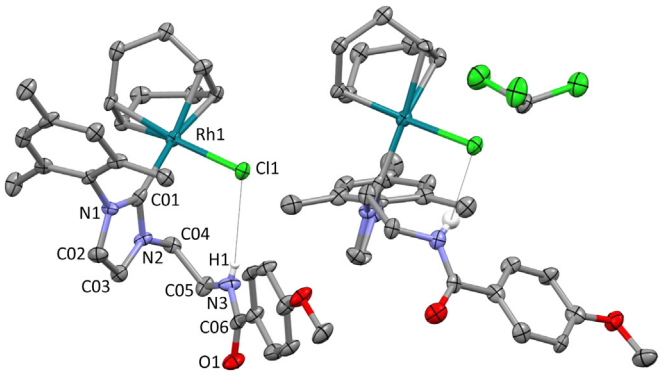


Fig. 3. Displacement ellipsoid plot of the asymmetric unit of **6**, showing the intramolecular hydrogen bond (50% probability). Non-relevant hydrogen atoms and atom labels are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for complex **5** and **6**.

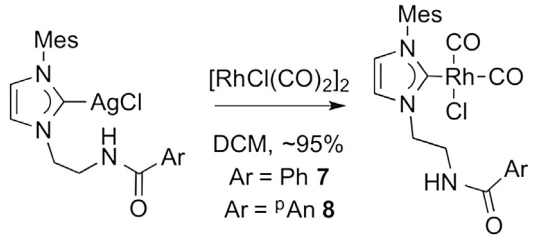
Complex	**5**	**6a**	**6b**
Rh1–C01	2.038 (2)	2.036 (8)	2.035 (8)
Rh1–Cl1	2.3958 (9)	2.3998 (19)	2.400 (2)
Rh1–C_{cod} (cis_{NHC})	2.0912 (17)	2.109 (7)	2.087 (7)
	2.1116 (18)	2.113 (6)	2.113 (7)
Rh1–C_{cod} ($trans_{NHC}$)	2.2018 (19)	2.190 (7)	2.187 (8)
	2.212 (2)	2.232 (8)	2.227 (7)
Cl1–N3	3.3806 (17)	3.395 (8)	3.346 (2)
C01–Rh1–Cl1	92.01 (5)	89.0 (2)	89.66 (19)
Cod-bite angle χ[a]	86.50 (6)	87.31 (17)	87.0 (2)
Cod-jaw angle ψ[a]	78.59 (9)	77.4 (3)	77.6 (4)

[a] For discussion on the χ bite- and ψ jaw-angles of cyclooctadiene ligands in transition metal complexes, see Ref. [22].

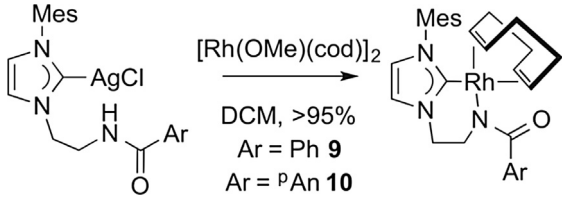
2081 and 2005 cm^{-1} in methanol, irrespective of the remote aryl substituent. With the use of a modified protocol for Tolman's Electronic Parameter (TEP) [23], the donor strength of the NHC-ligand can be determined. According to this scale, the carbene has a donor strength comparable to tricyclohexyl phosphine, without suffering from disadvantages associated with this ligand, such as ligand dissociation and decomposition by oxidation. The complexes **7** and **8** are very stable in the solid state and in solution, showing no signs of decomposition after standing in non-dried dichloromethane, methanol or methanol containing an excess of acetic acid. Also, these complexes appear to be stable in water for prolonged periods. All attempts to obtain complexes with a rhodium-amido coordination by deprotonation with mild base or chloride-abstraction with for example silver-salts were unsuccessful.

From these experiments, it was clear that use of the aforementioned precursors did not lead to carbonyl-bearing bidentate NHC–N complexes. Therefore, recourse was taken to a more basic rhodium-precursor; [Rh(OMe) (cod)]$_2$. This precursor should be able to deprotonate the amide donor *in situ* and the exchange of the chloride ligand for the methoxide moiety should therefore facilitate the bidentate coordination. After the NHC silver complexes **3** and **4** were subjected to this precursor under the same mild reaction conditions, it became clear that the desired reactivity exists (Scheme 5).

For both complexes **9** and **10**, the absence of a signal for the amide proton was noted in ^{1}H NMR spectroscopy, as well as a



Scheme 4. Synthesis of chloridorhodium biscarbonyl NHC complexes.



Scheme 5. Synthesis of bidentate Rh(NHC-N) (cod) complexes.

significant downfield shift for the signals of the *ortho*-aryl and ethylene linker hydrogens, indicating the anionic character of the amide. The bidentate character of the ligand is clearly visible, as in **5** and **6**, which indicates that the deprotonated amido-nitrogen coordinates to the rhodium center. Alternatively, when the basic rhodium precursor was reacted with imidazolium salts **1** and **2** *directly*, hydrogen bond-containing complexes **5** and **6** were obtained in good yields, obviating the need for the intermediate silver complex [24]. This pathway highlights the rich reactivity of these compounds with respect to different transition metal precursors. As with **5** and **6**, treatment of the bidentate complexes did not show exchange of the cyclooctadiene ligand; only starting material (**9** or **10**) was recovered.

From the results discussed above, it appeared that it was necessary to combine the basic functionality of the alkoxide ligand with the presence of carbonyl ligands in the rhodium precursor. However, for rhodium carbonyl complexes, literature involving bridging alkoxy-species is sparse, and deals with *in situ* characterisation only [25]. When the available protocol was employed with our ligand system, only the monodentate complexes **7** and **8** were isolated in yields of 74–77% (Scheme 6).

Clearly, the remaining presence of the chloride in the reaction mixture hampers the isolation of the desired products. Despite our efforts with various rhodium precursors and reaction conditions [26], we were not successful in isolating complexes in which the bidentate coordination mode of the NHC-amide ligand was present together with carbonyl ligands.

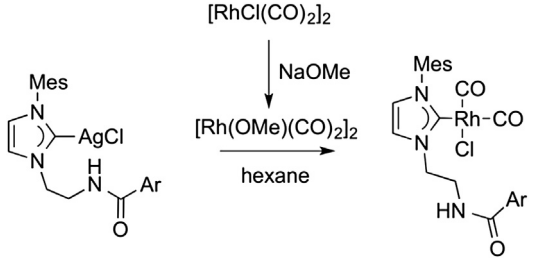
Exploratory iodomethane oxidative addition studies

As the carbonyl-ligand containing complexes are designed with use in methanol carbonylation in mind, they were tested in a model reaction often performed in our laboratory: the oxidative addition of iodomethane to yield the rhodium(III) alkyl complex **B** (Scheme 7).

This is the first step in the catalytic cycle, and is usually also the rate-determining one [1]. Often, the subsequent migratory insertion of a carbonyl ligand, leading to the rhodium(III) acyl species **C**, can also be observed [5]. Both steps are equilibria, although the ligands used determine to what side they lie. The behaviour of newly developed catalysts in this transformation gives valuable insights in their viability for the whole process. When a solution of complex **7** or **8** was reacted with iodomethane, 'direct' conversion to complex **C** was observed as evidenced by a broad and complex signal around 1650 cm^{-1} in IR, which corresponds to an acyl ligand [9]. Further research into the activity and selectivity of these complexes is in process.

Conclusion

The ligands described in this work show versatile coordination chemistry; they bind as monodentate ligands in rhodium dicarbonyl complexes, but the amide donor engages in a hydrogen bond interaction with the rhodium-bound chloride instead when cyclooctadiene is present. When a rhodium precursor with more basic ligands is used, the coordination can be switched to bidentate behaviour depending on the NHC source. Unequivocal evidence of the structure of the different complex classes was obtained by combining the results of various analytical techniques. It has to be noted that all the complexes were shown to be extremely robust and resilient against air and moisture, making their applicability highly feasible. Additionally, the diverse and tunable coordination behaviour could significantly enhance the functionality of the complexes. When the rhodium NHC dicarbonyl complexes were employed in a model reaction to probe their potential usefulness in methanol carbonylation, formation of rhodium(III) acyl species was observed, proving the developed complexes as viable targets.



Scheme 6. Attempted synthesis of biscarbonyl bidentate rhodium complex.

Experimental section

NMR spectroscopic data were acquired on a Bruker Advance II 600 MHz spectrometer. ^{1}H NMR data are listed in the order: chemical shift (δ, reported in ppm and referenced to the residual solvent peak of DMSO-d_6 [$\delta = 2.50$ ppm], CD_2Cl_2 [$\delta = 5.32$ ppm] or $CDCl_3$ [$\delta = 7.26$ ppm]), multiplicity, coupling constant (J, in Hz), number of protons, assignment. Proton decoupling experiments were used to assist in the assignment of proton signals. Proton decoupled ^{13}C NMR data are listed in the order: chemical shift (δ, reported in ppm and referenced to the residual solvent peak of DMSO-d_6 [$\delta = 39.5$ ppm], CD_2Cl_2 [$\delta = 77.0$ ppm] or $CDCl_3$ [$\delta = 77.0$ ppm]), multiplicity, coupling constant (J, in Hz) where appropriate, number of carbons, assignment. HMQC experiments were performed to assist in the allocation of signals. FT-IR spectra were recorded on a Bruker Tensor 27 spectrophotometer equipped with a temperature sensor accurate within 0.3 °C in the range of 3000–600 cm^{-1} *via* the ATR or in a NaCl cell. Elemental analyses were performed in duplicate on a Leco Truspec Micro. 1-mesityl imidazole [15] and N-(2-chloroethyl)-benzamide [16] are known compounds and were synthesized according to literature procedures. All other chemicals were used as received from the supplier.

N-(2-chloroethyl)-4-methoxybenzamide

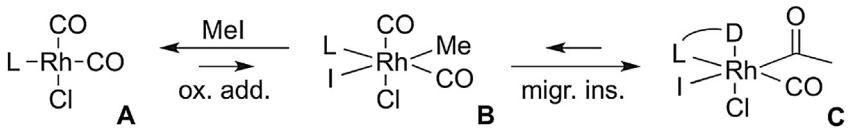
The product was obtained as a white microcrystalline solid in a yield of >95%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (d, $^{3}J(HH) = 8.8$ Hz, 2H, aryl-H), 6.93 (d, $^{3}J(HH) = 8.8$ Hz, 2H, aryl-H), 6.52 (broad s, 1H, NH), 3.85 (s, 3H, OCH_3), 3.80-3.70 (m, 4H, 2 CH_2). ^{13}C NMR (151 MHz, $CDCl_3$): δ 167.2 (CO), 162.4 (p-aryl-C), 128.8 (m-aryl-CH), 126.3 (i-aryl-C), 113.8 (o-aryl-CH), 55.4 (OCH_3), 44.2 ($ClCH_2$), 41.6 ($NHCH_2$).

Synthesis of imidazolium salts

1 mmol 1-mesityl imidazole and 1 mmol of 2-chloroethyl amide were suspended in 10 mL acetonitrile, which was refluxed for a period of 48 h. The pure product precipitated from the reaction mixture and was collected by filtration.

(1-(2-benzamido)-ethylene-3-mesityl)-imidazolium chloride ***1***

The product was obtained as an off-white solid in a yield of >95%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.51 (s, 1H, NCHN), 8.95 (t, $^{3}J(HH) = 5.0$ Hz, 1H, NH), 8.11 (s, 1H, CH), 7.87 (s, 1H, CH), 7.82 (d, $^{3}J(HH) = 7.2$ Hz, 2H, *o*-Ph-H), 7.51 (t, $^{3}J(HH) = 7.1$ Hz, 1H, p-Ph-H), 7.45 (m, 2H, m-Ph-H), 7.07 (s, 2H, m-Mes-H), 4.48 (t, $^{3}J(HH) = 5.0$ Hz, 2H, NCH_2), 3.79 (dt, $^{3}J(HH) = 5.0$ Hz, $^{3}J(HH) = 5.0$ Hz, 2H, $NHCH_2$), 2.27 (s, 3H, p-Mes-CH_3), 1.90 (s, 6H, o-



Scheme 7. Observed reactivity between iodomethane and rhodium.

Mes-CH_3). ^{13}C NMR (151 MHz, DMSO-d_6): δ 167.1 (CO), 140.6 (p-Mes-C), 138.1 (NCN), 134.8 (o-Mes-C), 134.1 (p-Ph-CH), 131.9 (i-Mes-C), 131.6 (i-Ph-C), 129.6 (m-Mes-CH), 128.7 (o-Ph-CH), 127.7 (m-Ph-CH), 124.2 (CH), 124.1 (CH), 49.9 (NCH_2), 39.5 ($NHCH_2$), 21.0 (p-Mes-CH_3), 17.2 (o-Mes-CH_3).

(1-(2-(4-methoxybenzamido))-ethylene-3-mesityl)-imidazolium chloride ***2***

The product was obtained as an off-white solid in a yield of >95%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.87 (s, 1H, NCHN), 9.12 (t, ^{3}J(HH) = 5.0 Hz, 1H, NH), 8.02 (d, ^{3}J(HH) = 8.7 Hz, 2H, aryl-H), 7.95 (s, 1H, CH), 7.02 (s, 1H, CH), 6.85 (s, 2H, Mes-H), 6.82 (d, ^{3}J(HH) = 8.7 Hz, 2H, aryl-H), 5.00 (t, ^{3}J(HH) = 5.2 Hz, 2H, NCH_2), 4.05 (dt, ^{3}J(HH) = 5.2 Hz, ^{3}J(HH) = 5.0 Hz, 2H, $NHCH_2$), 3.77 (s, 3H, OCH_3), 2.25 (s, 3H, p-Mes-CH_3), 1.78 (s, 6H, o-Mes-CH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ 167.4 (CO), 162.2 (p-aryl-C), 141.2 (p-Mes-C), 138.1 (NCHN), 134.2 (o-Mes-C), 130.5 (i-Mes-C), 129.7 (m-Mes-CH), 129.6 (o-aryl-CH), 125.3 (i-aryl-C), 123.7 (CH), 123.0 (CH), 113.5 (m-aryl-CH), 55.3 (OCH_3), 49.2 (NCH_2), 38.9 ($NHCH_2$), 21.0 (p-Mes-CH_3), 17.1 (o-Mes-CH_3).

Synthesis of silver(I) NHC complexes

To a suspension of 0.1 mmol imidazolium salt in 10 mL dichloromethane was added 0.05 mmol silver(I) oxide. The reaction mixture was stirred at room temperature for 16 h, after which it was filtered over a pad of celite. The resulting colourless solution was then concentrated *in vacuo* to yield the pure product.

Chlorido[(1-(2-benzamido)-ethylene-3-mesityl)-imidazol-2-ylidene]silver(I) ***3***

The product was obtained as a colourless oil in a yield of >95%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 9.0-8.0 (broad s, 1H, NH), 7.92 (d, ^{3}J(HH) = 6.9 Hz, 2H, o-Ph-H), 7.44 (t, ^{3}J(HH) = 7.1 Hz, 1H, p-Ph-H), 7.4-7.3 (m, 3H, m-Ph, CH), 6.86 (broad s, 3H, Mes-H, CH), 4.44 (t, ^{3}J(HH) = 5.9 Hz, 2H, NCH_2), 3.96 (dt, ^{3}J(HH) = 5.7 Hz, ^{3}J(HH) = 5.5 Hz, 2H, $NHCH_2$), 2.34 (s, 3H, p-Mes-CH_3), 1.69 (s, 6H, o-Mes-CH_3). ^{13}C NMR (151 MHz, CD_2Cl_2): δ 181.7 (NCN), 167.3 (CO), 138.9 (p-Mes-C), 135.5 (i-Mes-C), 134.9 (o-Mes-C), 133.9 (p-Ph-H), 131.3 (i-Ph-H), 128.9 (m-Mes-CH), 128.2 (o-Ph-CH), 127.5 (m-Ph-CH), 122.5 (CH), 121.8 (CH), 50.9 (NCH_2), 40.0 ($NHCH_2$), 20.8 (p-Mes-CH_3), 17.1 (o-Mes-CH_3). ^{13}C NMR (151 MHz, CD_2Cl_2): δ 181.8 (NCN), 167.3 (CO), 138.9 (p-Mes-C), 135.5 (i-Mes-C), 134.9 (o-Mes-C), 133.9 (i-Ph-C), 131.3 (p-Ph-CH), 128.9 (m-Mes-CH), 128.2 (o-Ph-CH), 127.5 (m-Ph-CH), 122.5 (CH), 121.8 (CH), 50.9 (NCH_2), 40.0 ($NHCH_2$), 20.8 (p-Mes-CH_3), 17.1 (o-Mes-CH_3).

Chlorido[(1-(2-(4-methoxybenzamido))-ethylene-3-mesityl)-imidazol-2-ylidene]silver(I) ***4***

The product was obtained as a pale oil in a yield of >95%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 9.0-8.0 (broad s, 1H, NH), 7.92 (d, ^{3}J(HH) = 8.5 Hz, 2H, aryl-H), 7.37 (d, ^{3}J(HH) = 1.7 Hz, 1H, CH), 6.88 (d, ^{3}J(HH) = 1.7 Hz, 1H, CH), 6.87 (d, ^{3}J(HH) = 8.5 Hz, 2H, aryl-H), 6.86 (s, 2H, Mes-H), 4.47 (t, ^{3}J(HH) = 6.3 Hz, 2H, NCH_2), 3.96 (dt, ^{3}J(HH) = 6.3 Hz, ^{3}J(HH) = 6.3 Hz, 2H, $NHCH_2$), 3.84 (s, 3H, OCH_3), 2.34 (s, 3H, p-Mes-CH_3), 1.70 (s, 6H, o-Mes-CH_3). ^{13}C NMR (151 MHz, CD_2Cl_2): δ 181.6 (broad, NCN), 166.9 (CO), 162.2 (p-aryl-C), 139.0 (p-Mes-C), 135.5 (i-Mes-C), 134.9 (o-Mes-C), 129.3 (m-Mes-CH), 129.0 (o-aryl-CH), 126.2 (i-aryl-C), 122.6 (CH), 121.8 (CH), 112.4 (m-aryl-CH), 55.3 (OCH_3), 51.1 (NCH_2), 40.0 ($NHCH_2$), 20.8 (p-Mes-CH_3), 17.2 (o-Mes-CH_3).

Synthesis of rhodium(I) NHC complexes from silver(I) NHC complexes

To 10 mL of a 10 mM silver(I) NHC solution was added 0.5 equivalent of the rhodium dimer precursor. Immediately, a yellow suspension is formed. After 1 h of stirring, the reaction mixture is filtered over a pad of celite, after which the pure product is obtained by concentration of the solution.

Chlorido[(η^4-1,5-cyclooctadiene) ((1-(2-benzamido)-ethylene-3-(2,4,6-trimethylphenyl))-imidazol-2-ylidene)rhodium(I)] ***5***

The product was obtained as a yellow microcrystalline solid in a yield of 97%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.20 (d, ^{3}J(HH) = 6.8 Hz, 1H, NH), 7.94 (d, ^{3}J(HH) = 7.1 Hz, 2H, o-Ph-H), 7.42 (t, ^{3}J(HH) = 7.4 Hz, 1H, p-Ph-H), 7.35 (dt, ^{3}J(HH) = 7.4 Hz, ^{3}J(HH) = 7.1 Hz, 2H, m-Ph-H), 7.15 (d, ^{3}J(HH) = 1.9 Hz, 1H, CH), 7.05 (broad s, 1H, Mes-H), 6.93 (broad s, 1H, Mes-H), 6.73 (d, ^{3}J(HH) = 1.9 Hz, 1H, CH), 5.99 (ddd, ^{3}J(HH) = 13.6 Hz, ^{3}J(HH) = 11.7 Hz, ^{2}J(HH) = 5.2 Hz, 1H, NCH_2), 4.83 (m, 2H, cod-CH), 4.56 (m, 1H, $NHCH_2$), 4.42 (ddd, ^{3}J(HH) = 13.6 Hz, ^{3}J(HH) = 5.2 Hz, ^{2}J(HH) = 2.8 Hz, 1H, NCH_2), 3.81 (dddd, ^{3}J(HH) = 14.3 Hz, ^{3}J(HH) = 5.0 Hz, ^{2}J(HH) = 2.8 Hz, ^{3}J(HH) = 6.8 Hz, 1H, $NHCH_2$), 3.53 (m, 1H, cod-CH), 3.02 (m, 1H, cod-CH), 2.45 (m, 1H, cod-CH_2), 2.37 (s, 3H, p-Mes-CH_3), 2.17 (s, 3H, o-Mes-CH_3), 2.15 (m, 1H, cod-CH_2), 2.03 (m, 1H, cod-CH_2), 1.97 (m, 1H, cod-CH_2), 1.85 (s, 3H, o-Mes-CH_3), 1.82 (m, 1H, cod-CH_2), 1.67 (m, 1H, cod-CH_2), 1.6–1.4 (m, 2H, cod-CH_2). ^{13}C NMR (151 MHz, $CDCl_3$): δ 182.4 (d, ^{2}J(RhC) = 52 Hz, NCN), 168.2 (CO), 138.7 (p-Mes-C), 136.9 (i-Mes-C), 135.9 (o-Mes-C), 134.0 (o-Mes-C), 133.7 (i-Ph-C), 131.3 (m-Mes-CH), 129.6 (m-Mes-CH), 128.3 (p-Ph-CH), 128.1 (o-Ph-CH), 127.6 (m-Ph-CH), 124.0 (CH), 119.8 (CH), 97.8 (d, ^{2}J(RhC) = 6.9 Hz, cod-CH), 97.2 (d, ^{2}J(RhC) = 7.3 Hz, cod-CH), 69.4 (d, ^{2}J(RhC) = 15 Hz, cod-CH), 67.3 (d, ^{2}J(RhC) = 14 Hz, cod-CH), 48.6 (NCH_2), 38.1 ($NHCH_2$), 34.7, 30.9, 29.6, 27.6 (cod-CH_2), 21.1 (p-Mes-CH_3), 19.3 (o-Mes-CH_3), 17.9 (o-Mes-CH_3). Anal. Calcd. for $C_{29}H_{35}N_3ORhCl$ (579.97): C, 60.06; H, 6.08; N, 7.25. Found: C, 60.37; H, 6.36; N, 6.94.

Chlorido[(η^4-1,5-cyclooctadiene) ((1-(2-(4-methoxybenzamido))-ethylene-3-(2,4,6-trimethylphenyl))-imidazol-2-ylidene) rhodium(I)] ***6***

The product was obtained as a yellow microcrystalline solid in a yield of 96%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.06 (d, ^{3}J(HH) = 6.7 Hz, 1H, NH), 7.94 (d, ^{3}J(HH) = 8.9 Hz, 2H, aryl-H), 7.14 (d, ^{3}J(HH) = 1.9 Hz, 1H, CH), 7.06 (broad s, 1H, Mes-H), 6.94 (broad s, 1H, Mes-H), 6.86 (d, ^{3}J(HH) = 8.9 Hz, 2H, aryl-H), 6.73 (d, ^{3}J(HH) = 1.9 Hz, 1H, CH), 5.99 (ddd, ^{3}J(HH) = 13.7 Hz, ^{3}J(HH) = 11.9 Hz, ^{2}J(HH) = 5.1 Hz, 1H, NCH_2), 4.81 (broad s, 2H, cod-CH), 4.55 (m, 1H, $NHCH_2$), 4.40 (ddd, ^{3}J(HH) = 13.7 Hz, ^{3}J(HH) = 12.9 Hz, ^{2}J(HH) = 5.1 Hz, 1H, NCH_2), 3.80 (s, 3H, OCH_3), 3.78 (m, 1H, $NHCH_2$), 3.53 (m, 1H, cod-CH), 3.03 (m, 1H, cod-CH),

2.45 (m, 1H, cod-CH_2), 2.37 (s, 3H, p-Mes-CH_3), 2.19 (s, 3H, o-Mes-CH_3), 2.16 (m, 1H, cod-CH_2), 2.04 (m, 1H, cod-CH_2), 1.97 (m, 1H, cod-CH_2), 1.85 (s, 3H, o-Mes-CH_3), 1.84 (m, 1H, cod-CH_2), 1.66 (m, 2H, cod-CH_2), 1.53 (m, 1H, cod-CH_2), 1.49 (m, 1H, cod-CH_2). ^{13}C NMR (151 MHz, $CDCl_3$): δ 182.4 (d, ^{1}J(RhC) = 53 Hz, NCN), 167.7 (CO), 162.0 (p-aryl-C), 138.0 (p-Mes-C), 136.9 (i-Mes-C), 135.9 (o-Mes-C), 134.0 (o-Mes-C), 129.6 (m-Mes-CH), 129.4 (o-aryl-CH), 128.3 (m-Mes-CH), 126.2 (i-aryl-C), 123.9 (CH), 119.8 (CH), 113.3 (m-aryl-CH), 97.8 (d, ^{1}J(RhC) = 6.9 Hz, cod-CH), 97.2 (d, ^{1}J(RhC) = 7.3 Hz, cod-CH), 69.4 (d, ^{1}J(RhC) = 14 Hz, cod-CH), 67.2 (d, ^{1}J(RhC) = 14 Hz, cod-CH), 55.3 (OCH_3), 48.7 (NCH_2), 38.1 ($NHCH_2$), 34.7, 30.9, 29.6, 27.6 (cod-CH_2), 21.1 (p-Mes-CH_3), 19.4 (o-Mes-CH_3), 17.9 (o-Mes-CH_3). Anal. Calcd. for $C_{30}H_{37}N_3O_2RhCl$ (609.99): C, 59.07; H, 6.11; N, 6.89. Found: C, 59.32; H, 6.28; N, 6.79.

Chlorido[cis-dicarbonyl((1-(2-benzamido)-ethylene-3-(2,4,6-trimethylphenyl))-imidazol-2-ylidene)rhodium(I)] ***7***

The product was obtained as a yellow solid in a yield of 94%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 (d, ^{3}J(HH) = 8.1 Hz, 2H, o-Ph-H), 7.56 (t, ^{3}J(HH) = 5.2 Hz, 1H, NH), 7.47 (t, ^{3}J(HH) = 7.4 Hz, 1H, p-Ph-H), 7.39 (dd, ^{3}J(HH) = 8.1 Hz, ^{3}J(HH) = 7.4 Hz, 2H, m-Ph-H), 7.28 (d, ^{3}J(HH) = 1.7 Hz, 1H, CH), 6.97 (s, 2H, Mes-H), 6.90 (d, ^{3}J(HH) = 1.7 Hz, 1H, CH), 4.79 (t, ^{3}J(HH) = 5.8 Hz, 2H, NCH_2), 4.18 (dt, ^{3}J(HH) = 5.8 Hz, ^{3}J(HH) = 5.2 Hz, 2H, $NHCH_2$), 2.36 (s, 3H, p-Mes-CH_3), 1.98 (s, 6H, o-Mes-CH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ 184.8 (d, ^{2}J(RhC) = 54 Hz, NCN), 182.0 (d, ^{2}J(RhC) = 75 Hz, CO), 175.3 (d, ^{2}J(RhC) = 53 Hz, CO), 168.0 (CO), 139.5 (p-Mes-C), 135.1 (i-Mes-C), 133.5 (o-Mes-C), 131.6 (p-Ph-CH), 131.1 (i-Ph-C), 129.3 (m-Mes-CH), 128.3 (o-Ph-CH), 127.3 (m-Ph-CH), 123.7 (CH), 121.9 (CH), 49.1 (NCH_2), 38.6 ($NHCH_2$), 21.2 (p-Mes-CH_3), 18.1 (o-Mes-CH_3). Anal. Calcd. for $C_{23}H_{23}N_3O_3RhCl$ (527.81): C, 52.34; H, 4.39; N, 7.96. Found: C, 52.71; H, 4.76; N, 7.81.

Chlorido[cis-dicarbonyl((1-(2-(4-methoxybenzamido))-ethylene-3-(2,4,6-trimethylphenyl))-imidazol-2-ylidene)rhodium(I)] ***8***

The product was obtained as a beige solid in a yield of 96%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, ^{3}J(HH) = 4.4 Hz, 2H, aryl-H), 7.45 (t, ^{3}J(HH) = 2.6 Hz, 1H, NH), 7.27 (d, ^{3}J(HH) = 0.9 Hz, 1H, CH), 6.97 (s, 2H, Mes-H), 6.89 (d, ^{3}J(HH) = 0.9 Hz, 1H, CH), 6.87 (d, ^{3}J(HH) = 4.4 Hz, 2H, aryl-H), 4.77 (t, ^{3}J(HH) = 2.9 Hz, 2H, NCH_2), 4.15 (dt, ^{3}J(HH) = 2.9 Hz, ^{3}J(HH) = 2.6 Hz, 2H, $NHCH_2$), 3.83 (s, 3H, OCH_3), 2.36 (s, 3H, p-Mes-CH_3), 1.99 (s, 6H, o-Mes-CH_3). ^{13}C NMR (151 MHz, $CDCl_3$): δ 184.8 (d, ^{2}J(RhC) = 54 Hz, NCN), 182.0 (d, ^{2}J(RhC) = 76 Hz, CO), 175.2 (d, ^{2}J(RhC) = 44 Hz, CO), 167.5 (CO), 162.2 (p-aryl-C), 139.5 (p-Mes-C), 135.1 (i-Mes-C), 135.0 (o-Mes-C), 129.3 (m-Mes-CH), 129.1 (o-aryl-CH), 125.9 (i-aryl-C), 123.7 (CH), 121.9 (CH), 113.5 (m-aryl-CH), 55.4 (OCH_3), 49.1 (NCH_2), 38.5 ($NHCH_2$), 21.1 (p-Mes-CH_3), 18.1 (o-Mes-CH_3). Anal. Calcd. for $C_{24}H_{25}N_3O_4RhCl$ (557.83): C, 51.67; H, 4.52; N, 7.53. Found: C, 52.02; H, 4.91; N, 7.15.

(η^4-1,5-cyclooctadiene)[(1-(2-benzamidato)-ethylene-3-(2,4,6-trimethylphenyl))-imidazol-2-ylidene-κ^2C,N]rhodium(I) ***9***

The product was obtained as an orange solid in a yield of 94%. ^{1}H NMR (600 MHz, CD_2Cl_2): 8.49 (d, ^{3}J(HH) = 6.9 Hz, 2H, o-Ph-H), 7.38 (t, ^{3}J(HH) = 7.3 Hz, 1H, p-Ph-H), 7.31 (dt, ^{3}J(HH) = 7.3 Hz, ^{3}J(HH) = 6.9 Hz, 2H, m-Ph-H), 7.21 (d, ^{3}J(HH) = 1.7 Hz, 1H, CH), 7.12 (broad s, 1H, Mes-H), 7.02 (broad s, 1H, Mes-H), 6.75 (d, ^{3}J(HH) = 1.7 Hz, 1H, CH), 5.45 (m, 1H, NCH_2), 4.76 (m, 1H, N—CH_2), 4.42 (m, 1H, NCH_2), 3.65 (m, 1H, cod-CH), 3.59 (m, 1H, N—CH_2), 3.47 (m, 2H, cod-CH), 2.73 (m, 1H, cod-CH), 2.46 (m, 1H, cod-CH_2), 2.44 (s, 3H, p-Mes-CH_3), 2.10 (m, 1H, cod-CH_2), 2.00 (s, 3H, o-Mes-CH_3), 1.98 (m, 1H, cod-CH_2), 1.91 (s, 3H, o-Mes-CH_3), 1.80 (m, 1H, cod-CH_2), 1.59 (m, 1H, cod-CH_2), 1.52 (m, 1H, cod-CH_2), 1.29 (m, 1H, cod-CH_2), 1.20 (m, 1H, cod-CH_2). ^{13}C NMR (151 MHz, CD_2Cl_2): δ 179.1 (d, ^{3}J(RhC) = 53 Hz, NCN), 172.6 (CO), 136.3 (o-Mes-C), 135.7 (i-Mes-C), 135.2 (o-Mes-C), 129.0 (m-Mes-CH), 128.8 (p-Ph-CH), 128.5 (m-Mes-CH), 128.3 (o-Ph-CH), 126.7 (m-Ph-CH), 121.7 (CH), 120.8 (CH), 96.7 (d, ^{3}J(RhC) = 8.9 Hz, cod-CH), 89.1 (d, ^{3}J(RhC) = 8.1 Hz, cod-CH), 71.6 (d, ^{3}J(RhC) = 11 Hz, cod-CH), 71.0 (d, ^{3}J(RhC) = 13 Hz, cod-CH), 51.9 (NCH_2), 45.6 (N—CH_2), 34.1 (cod-CH_2), 31.7 (cod-CH_2), 29.9 (cod-CH_2), 28.0 (cod-CH_2), 20.9 (p-Mes-CH_3), 17.9 (o-Mes-CH_3), 17.3 (o-Mes-CH_3). Anal. Calcd. for $C_{29}H_{34}N_3ORh$ (543.51): C, 64.09; H, 6.31; N, 7.73. Found: C, 63.73; H, 6.36; N, 7.94.

(η^4-1,5-cyclooctadiene)[(1-(2-(4-methoxybenzamidato))-ethylene-3-(2,4,6-trimethylphenyl))-imidazol-2-ylidene-κ^2C,N]rhodium(I) ***10***

The product was obtained as an orange solid in a yield of 93%. δ ^{1}H NMR (600 MHz, CD_2Cl_2): δ 8.51 (d, ^{3}J(HH) = 8.7 Hz, 2H, o-Ar-H), 7.20 (d, ^{3}J(HH) = 1.7 Hz, 1H, CH), 7.11 (broad s, 1H, Mes-H), 7.02 (broad s, 1H, Mes-H), 6.82 (d, ^{3}J(HH) = 8.7 Hz, 2H, m-Ar-H), 6.74 (d, ^{3}J(HH) = 1.7 Hz, 1H, CH), 5.45 (ddd, ^{3}J(HH) = 22.0 Hz, ^{3}J(HH) = 12.8 Hz, ^{2}J(HH) = 3.8 Hz, 1H, NCH_2), 4.77 (m, 1H, N—CH_2), 4.41 (m, 1H, NCH_2), 3.84 (s, 3H, OCH_3), 3.65 (m, 1H, cod-CH), 3.57 (m, 1H, N—CH_2), 3.46 (m, 2H, cod-CH), 2.87 (m, 1H, cod-CH), 2.44 (s, 3H, p-Mes-CH_3), 2.31 (m, 1H, cod-CH_2), 2.03 (m, 1H, cod-CH_2), 2.00 (s, 3H, o-Mes-CH_3), 1.96 (m, 1H, cod-CH_2), 1.87 (s, 3H, o-Mes-CH_3), 1.82 (m, 1H, cod-CH_2), 1.53 (m, 2H, cod-CH_2), 1.40 (m, 1H, cod-CH_2), 1.24 (m, 1H, cod-CH_2). ^{13}C NMR (151 MHz, CD_2Cl_2): δ 180.0 (d, ^{2}J(RhC) = 54 Hz, NCN), 172.2 (CO), 160.4 (p-Ar-C), 139.2 (p-Mes-C), 136.5 (i-Mes-C), 135.7 (o-Mes-C), 134.3 (o-Mes-C), 130.0 (o-Ar-CH), 129.3 (m-Mes-CH), 128.5 (m-Mes-CH), 126.3 (i-Ar-C), 121.6 (CH), 120.8 (CH), 111.7 (m-Ar-CH), 96.8 (d, ^{2}J(RhC) = 8.6 Hz, cod-CH), 89.3 (d, ^{2}J(RhC) = 7.4 Hz, cod-CH), 71.5 (d, ^{2}J(RhC) = 12 Hz, cod-CH), 71.0 (d, ^{2}J(RhC) = 12 Hz, cod-CH), 55.2 (OCH_3), 51.9 (NCH_2), 45.6 (N—CH_2), 34.2, 31.6, 30.0, 28.0 (cod-CH_2), 20.9 (p-Mes-CH_3), 17.8 (o-Mes-CH_3), 17.3 (o-Mes-CH_3). Anal. Calcd. for $C_{30}H_{36}N_3O_2Rh$ (573.53): C, 62.82; H, 6.33; N, 7.33. Found: C, 62.49; H, 6.25; N, 6.99.

Synthesis of chloridorhodium cyclooctadiene NHC complexes ***5*** *and* ***6*** *from imidazolium salts*

To a suspension of 0.1 mmol imidazolium salt in dichloromethane was added 0.5 equivalent of $[Rh(OMe)(cod)]_2$. The resulting suspension was stirred overnight. The obtained yellow solution was filtered over a pad of celite, and concentrated *in vacuo* to yield the pure products **5** and **6** in a yield of 89 and 92%, respectively.

X-ray structure determination for compounds ***1***, ***5*** *and* ***6***

The X-ray intensity data were collected at 100(2) K on a Bruker X8 ApexII 4K Kappa CCD diffractometer equipped with an Oxford Crystream cooling unit, using graphite monochromated MoKα radiation. Images were collected at 20 s (**1**), 10 s (**5**) and 60 s (**6**) exposure time per image respectively. Data collection strategies were calculated with the program APEX2 [27]. Data reduction and cell refinement were performed with the SAINT-Plus package [27]. The data were corrected for absorption using the SADABS program [28]. Using the program suite WinGX [29], the structures were solved by Patterson interpretation and phase expansion using SHELXL97, and refined with full-matrix least squares on F2 using SHELXL97 [30]. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were fixed at calculated positions except for the NH hydrogen-atoms, which were located in the Fourier maps and refined; all of them were given an overall isotropic thermal parameter. Additional details regarding data collection are provided in the CIF files. Full crystallographic data have been deposited at the Cambridge Crystallographic Data Centre.

Crystal data for (1-(2-benzamido)-ethylene-3-mesityl)-imidazolium chloride ***1***

$[C_{21}H_{24}N_3O]Cl$, M = 369.88, triclinic, space group $P\bar{1}$, $a = 7.0950(5)$ Å, $b = 7.8294(6)$ Å, $c = 17.3969(14)$ Å, $\alpha = 98.292(4)^\circ$, $\beta = 90.401(4)^\circ$, $\gamma = 98.021(4)^\circ$, V = 946.53(13) Å^3, $Z = 2$, $\mu = 0.22$ mm^{-1}, $F(000) = 392.0$, $T = 100(2)$ K, 10878 measured reflections, 4032 independent ($R_{int} = 0.040$), $R_1 = 0.0442$, $wR_2 = 0.1139$ for $I > 2\sigma(I)$.

Crystal data for chlorido[(η^4-1,5-cyclooctadiene) ((1-(2-benzamido)-ethylene-3-(2,4,6-trimethylphenyl))-imidazol-2-ylidene)rhodium(I)] ***5***

$RhC_{29}H_{35}ClN_3O$, M = 579.96, triclinic, space group $P\bar{1}$, $a = 8.5310$ (5) Å, $b = 12.3359$ (7) Å, $c = 12.9324$ (8) Å, $\alpha = 94.8118$ (17)°, $\beta = 98.5242$ (18)°, $\gamma = 103.4192$ (18)°, V = 1299.26 (13) Å^3, $Z = 2$, $\mu = 0.79$ mm^{-1}, $F(000) = 600.0$, $T = 100(2)$ K, 15237 measured reflections, 6166 independent ($R_{int} = 0.021$), $R_1 = 0.0234$, $wR_2 = 0.0601$ for $I > 2\sigma(I)$.

Crystal data for chlorido[(η^4-1,5-cyclooctadiene) ((1-(2-(4-methoxy-benzamido))-ethylene-3-(2,4,6-trimethylphenyl))-imidazol-2-ylidene rhodium(I)] ***6***

$2(C_{30}H_{37}ClN_3O_2Rh) \cdot CHCl_3$, M = 1339.34, triclinic, space group $P\bar{1}$, $a = 13.2793$ (15) Å, $b = 13.7014$ (15) Å, $c = 17.1427$ (17) Å, $\alpha = 90.783$ (6)°, $\beta = 106.881$ (6)°, $\gamma = 98.826$ (6)°, V = 2943.7 (6) Å^3, $Z = 2$, $\mu = 0.84$ mm^{-1}, $F(000) = 1380.0$, $T = 100(2)$ K, 36281 measured reflections, 13825 independent ($R_{int} = 0.117$), $R_1 = 0.0714$, $wR_2 = 0.2305$ for $I > 2\sigma(I)$.

General procedure for oxidative addition IR experiments

In two separate volumetric flasks, dichloromethane solutions of the rhodium NHC complex (10 mmol/L) and iodomethane (1 mol/L) were prepared. After mixing 250 μL of each solution in a NaCl-cell, the reaction was followed by FT-IR.

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Appendix A. Supplementary material

CCDC 912655, 912656 and 912657 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] P.M. Maitlis, A. Haynes, G.J. Sunley, M.J. Howard, J. Chem. Soc. Dalton Trans. (1996) 2187.
[2] N. Lassauque, T. Davin, D.H. Nguyen, R.J. Adcock, Y. Coppel, C. Le Berre, P. Serp, L. Maron, P. Kalck, Inorg. Chem. 51 (2012) 4.
[3] a) X.F. Wu, H. Neumann, ChemCatChem 4 (2012) 447;
b) D.K. Dutta, B. Deb, G. Hua, J.D. Woollins, J. Mol. Catal. A 353–354 (2012) 7;
c) R.J. Adcock, D.H. Nguyen, S. Ladeira, C. Le Berre, P. Serp, P. Kalck, Inorg. Chem. 51 (2012) 8670;
d) G.L. Williams, C.M. Parks, C.R. Smith, H. Adams, A. Haynes, A.J.H.M. Meijer, G.J. Sunley, S. Gaemers, Organometallics 30 (2011) 6166;
e) J. Rankin, A.C. Benyei, A.D. Poole, D.J. Cole-Hamilton, J. Chem. Soc. Dalton Trans. (1999) 3771;
f) L. Gonsalvi, H. Adams, G.J. Sunley, E. Ditzel, A. Haynes, J. Am. Chem. Soc. 124 (2002) 13597;
g) L. Gonsalvi, J.A. Gaunt, H. Adams, A. Castro, G.J. Sunley, A. Haynes, Organometallics 22 (2003) 1047.
[4] A. Brink, A. Roodt, G. Steyl, H.G. Visser, Dalton Trans. 39 (2010) 5572.
[5] a) J.A. Venter, J.G. Leipoldt, R. van Eldik, Inorg. Chem. 30 (1991) 2207;
b) S. Warsink, F.G. Fessha, W. Purcell, J.A. Venter, J. Organomet. Chem. 726 (2013) 14.
[6] a) F.E. Hahn, M.C. Jahnke, Angew. Chem. Int. Ed. 47 (2008) 3122;
b) T. Droege, F. Glorius, Angew. Chem. Int. Ed. 49 (2010) 6940.
[7] a) P. Hauwert, R. Boerleider, S. Warsink, J.J. Weigand, C.J. Elsevier, J. Am. Chem. Soc. 132 (2010) 16900;
b) S. Warsink, R.M. Drost, M. Lutz, A.L. Spek, C.J. Elsevier, Organometallics 29 (2010) 3109.
[8] a) W. Gil, A.M. Trzeciak, Coord. Chem. Rev. 255 (2011) 473;
b) J.M. Praetorius, C.M. Crudden, Dalton Trans. 37 (2008) 4079;
c) M.S. Datt, J.J. Nair, S. Otto, J. Organomet. Chem. 690 (2005) 3422;
d) A.R. Chianese, X. Li, M.C. Janzen, J.W. Faller, R.H. Crabtree, Organometallics 22 (2003) 1663.
[9] H.C. Martin, N.H. James, J. Aitken, J.A. Gaunt, H. Adams, A. Haynes, Organometallics 22 (2003) 4451.
[10] J.M. Wilson, G.J. Sunley, H. Adams, A. Haynes, J. Organomet. Chem. 690 (2005) 6089.
[11] a) A. Roodt, H.G. Visser, A. Brink, Cryst. Rev. 17 (2011) 241;
b) M. Schutte, G. Kemp, H.G. Visser, A. Roodt, Inorg. Chem. 50 (2011) 12486;
c) M. Schutte, A. Roodt, H.G. Visser, Inorg. Chem. 51 (2012) 11996.
[12] a) H. Jong, B.O. Patrick, M.D. Fryzuk, Can. J. Chem. 86 (2008) 803;
b) W.B. Cross, C.G. Daly, Y. Boutadla, K. Singh, Dalton Trans. 40 (2011) 9722.
[13] a) L. Busetto, M.C. Cassani, C. Femoni, M. Mancinelli, A. Mazzanti, R. Mazzoni, G. Solinas, Organometallics 30 (2011) 5258;
b) C.-Y. Liao, K.-T. Chan, J.-Y. Zeng, C.-H. Hu, C.-Y. Tu, H.M. Lee, Organometallics 26 (2007) 1692;
c) Y. Unger, T. Strassner, J. Organomet. Chem. 713 (2012) 203.
[14] P.L. Arnold, S.H. Mungur, A.J. Blake, C. Wilson, Angew. Chem. Int. Ed. 42 (2003) 5981.
[15] J. Liu, J. Chen, J. Zhao, Y. Zhao, L. Li, H. Zhang, Synthesis (2003) 2661.
[16] W.-J. Yoo, C.-J. Li, J. Am. Chem. Soc. 128 (2006) 13064.
[17] a) D.B. Bagal, R.A. Watile, M.V. Khedkar, K.P. Dhake, B.M. Bhanage, Catal. Sci. Technol. 2 (2012) 354;
b) G. Lázaro, M. Iglesias, F.J. Fernández-Alvarez, P.J. Sanz Miguel, J.J. Pérez-Torrente, L.A. Oro, ChemCatChem 5 (2013) 1133.
[18] a) H.M.J. Wang, I.J.B. Lin, Organometallics 17 (1998) 972;
b) H.-L. Su, L.M. Pérez, S.-H. Lee, J.H. Reibenspies, H.S. Bazzi, D. Bergbreiter, Organometallics 31 (2012) 4063;
c) A. Biffis, M. Cipani, C. Tubaro, M. Basato, M. Costante, E. Bressan, A. Venzo, C. Graiff, New. J. Chem. 37 (2013) 4175;
d) E. Caytan, S. Roland, Organometallics 33 (2014) 2115.
[19] J.C. Garrison, W.J. Youngs, Chem. Rev. 105 (2005) 3978.
[20] P. de Frémont, N.M. Scott, E.D. Stevens, T. Ramnial, O.C. Lightbody, C.L.B. Macdonald, J.A.C. Clyburne, C.D. Abernethy, S.P. Nolan, Organometallics 24 (2005) 6301.
[21] a) S. Warsink, A. Roodt, Acta Cryst. E 68 (2012) m1053;
b) G.J.S. Venter, G. Steyl, A. Roodt, Acta Cryst. E 68 (2012) m666.
[22] a) T.N. Hill, A. Roodt, G. Steyl, Polyhedron 50 (2012) 82;
b) T.N. Hill, A. Roodt, G. Steyl, Acta Cryst. B 69 (2013) 36.
[23] a) S. Wolf, H. Plenio, J. Organomet. Chem. 694 (2009) 1487;
b) R.A. Kelly III, H. Clavier, S. Giudice, N.M. Scott, E.D. Stevens, J. Bordner, I. Samardjiev, C.D. Hoff, L. Cavallo, S.P. Nolan, Organometallics 27 (2008) 202.
[24] a) C. Köcher, W.A. Herrmann, J. Organomet. Chem. 532 (1997) 261;
b) S. Gülcemal, Appl. Organomet. Chem. 26 (2012) 246.
[25] A. Vizi-Orosz, G. Pályi, L. Markó, J. Organomet. Chem. 57 (1973) 379.
[26] A. Bittermann, D. Baskakov, W.A. Herrmann, Organometallics 28 (2009) 5107.
[27] Bruker, APEX2, SAINT-plus, Bruker AXS Inc, Madison, Wisconsin, USA, 2007.
[28] G.M. Sheldrick, SADABS, University of Göttingen, Germany, 2008.
[29] L.J. Farrugia, J. Appl. Cryst. 32 (1999) 837.
[30] G.M. Sheldrick, Acta Cryst. A 64 (2008) 112.