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Synthesis of (NHC)Rh(cod)Cl and (NHC)RhCl(CO)$_2$ complexes – Translation of the Rh- into the Ir-scale for the electronic properties of NHC ligands

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ABSTRACT

Twenty-three different Rh complexes of the (NHC)RhCl(cod) and (NHC)RhCl(CO)$_2$ type were synthesized from [RhCl(cod)]$_2$. The electron donating nature of the NHC ligands was changed in a systematic manner. The redox potentials of the various (NHC)RhCl(cod) and the ν(CO) of the various (NHC)RhCl(CO)$_2$ were determined. A correlation of the Rh redox potentials and the Rh ν(CO), respectively, with the related data from analogous (NHC)IrCl(cod) and (NHC)IrCl(CO)$_2$ complexes established two linear relationships. The linear regression ($R^2 = 0.993$) of the Rh and the Ir redox potentials results in an equation for the redox potential transformation: $E_{1/2}(\mathrm{Ir}) = 1.016 \cdot E_{1/2}(\mathrm{Rh}) - 0.076$ V. The linear regression ($R^2 = 0.97$) of the Rh and Ir ν_{av}(CO) results in an equation for the ν_{av}(CO) transformation: $\nu_{av}(\mathrm{CO})\mathrm{Ir} = 0.8695 \cdot \nu_{av}(\mathrm{CO})\mathrm{Rh} + 250.7\ \mathrm{cm}^{-1}$. In this manner the Rh and the Ir-scale for the determination of the electron donating properties of NHC ligands are unified.

1. Introduction

The properties of metal complexes are modulated by the electronic and the steric properties of the ligands attached to the metal center [1,2]. Consequently, quantitative parameters describing such properties are essential for an understanding of the chemical reactivity of metal complexes in catalysis [3,4].

It was shown by Strohmeier and Müller [5] and by Tolman [6] that the electron-donating nature of phosphines can be conveniently probed via the ν(CO) of various metal carbonyl complexes. The relative donor strength of phosphines is independent of the metal atom for a given series of phosphine ligands. Initially (PR$_3$)Ni(CO)$_3$ complexes were considered to be the best choice and thus used to establish a series of ligand donor properties. In a landmark review Tolman defined the electronic properties of ligands through the ν(CO) (Tolman electronic parameter, TEP) and the steric properties via the space occupation around a static metal–phosphorous bond (Tolman cone angle) [7]. The high toxicity of Ni(CO)$_4$ required for the synthesis of the various LNi(CO)$_3$ complexes motivated the search for other carbonyl complexes useful in this respect. The most popular alternatives are either (NHC)Ir(CO)$_2$Cl [8–14] or (NHC)Rh(CO)$_2$X [15–29] (X = Br, I) [30–33]; even though the use of other complexes like LFe(Cp)(CO)$_2$ [34,35] or LM(CO)$_5$ (M = Cr, Mo, W) complexes [36–40] has also been reported. An obvious problem arising from the use of different scales is the lack of comparability between them [20]. This problem is aggravated by the fact that various matrices have been used for the determination of the ν(CO) via infrared spectroscopy within for a given class of metal complexes. Data derived from film measurements are not necessarily comparable with data obtained from a complex immersed in salt pellets (typically KBr).

To enable the comparison of the electronic properties of ligands evaluated via different metal complexes, Crabtree derived from experimental data the regression formula (TEP (cm^{-1}) = 0.722 [$\nu(\mathrm{CO})_{av}$] + 593 cm^{-1}) to convert the LIrCl(CO)$_2$ based data to the classic LNi(CO)$_3$ scale [10]. Recently Nolan proposed a refined regression formula (TEP (cm^{-1}) = 0.847 · $\nu(\mathrm{CO})_{av}$ + 336 cm^{-1}) drawn from an analysis [13] of a larger number of complexes LIrCl(CO)$_2$ [41].

We want to report here on the synthesis of a number of (NHC)RhCl(cod) and (NHC)RhCl(CO)$_2$ complexes, the determination of the redox potentials by cyclic voltammetry in the former and the ν(CO) by infrared spectroscopy in the latter series of complexes. The primary target of this study is to establish a regression formula to allow the translation of (NHC)RhCl(CO)$_2$-based data into the (NHC)IrCl(CO)$_2$ scale (or vice versa).

2. Results and discussion

2.1. Synthesis of the rhodium complexes

We recently reported the synthesis of (NHC)IrCl(cod) and (NHC)IrCl(CO)$_2$ complexes [8]. In the aforementioned complexes

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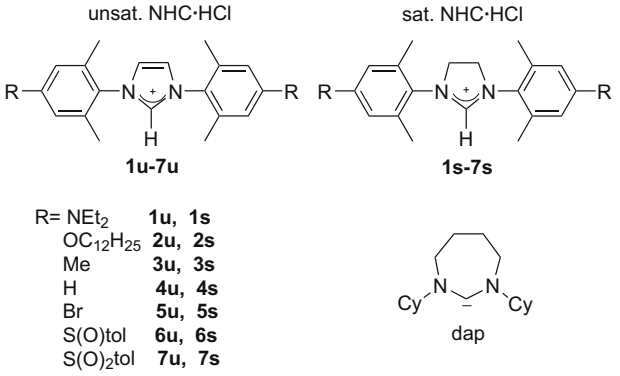
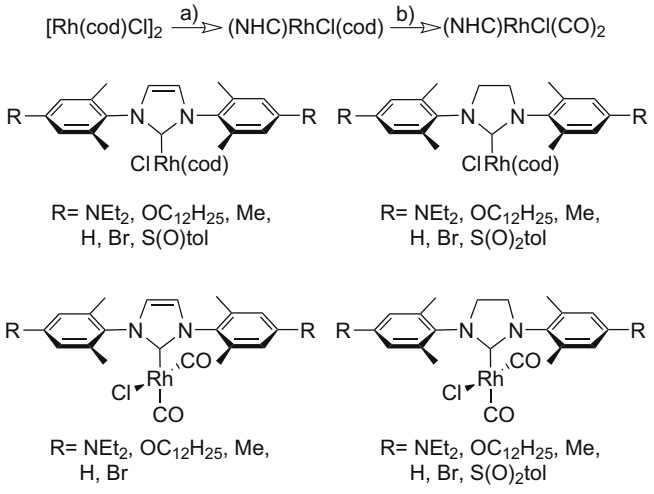


Scheme 1. Unsaturated and saturated azolium salts used for this study.

the electronic properties of the NHC ligand were varied, while retaining the steric demand of the ligand. It was also shown, that the nature of the substituents on the N-aryl rings has a strong influence on the electron donation of the respective NHC ligand. We have now synthesized a number of analogous Rh complexes following the general procedure established for the related (NHC)IrCl(cod) and (NHC)IrCl(CO)$_2$ complexes, utilizing the known imidazolium and imidazolinium salts depicted in Scheme 1 [8].

Most of the envisaged (NHC)IrCl(cod) complexes are accessible as described in Scheme 2; typical yields for this transformation are around 80%. However, some of the NHC ligands substituted with electron-withdrawing groups (**7u** and **6s**) could not be converted into the corresponding (NHC)IrCl(cod) complexes.

The NMR spectra of the respective complexes are complicated by the fact that typically the two N-aryl flaps are inequivalent due to restricted rotation on the NMR time scale. Treatment of the various (NHC)IrCl(cod) with CO resulted in virtually quantitative replacement of cod by the CO ligand to yield the respective (NHC)IrCl(CO)$_2$ species. This conversion was successful for all cod complexes with the exception of the electron-withdrawing NHC **6u**. In the NMR spectra of the carbonyl complexes shows the expected simple spectra due to increased conformational flexibility. In general it should be noted that the Rh complexes with the less electron donating ligands **6** and **7** are much less stable than those with electron-rich NHC ligands (**1**, **2**, **3**, **4**) and decompose in solution within a few hours.



Scheme 2. Synthesis of (NHC)RhCl(cod) and (NHC)RhCl(CO)$_2$ complexes. Reagents and conditions: (a) THF, KO^{t}Bu, azolium salt, RT; (b) CH_2Cl_2, CO, RT, quantitative conversions.

2.2. X-ray crystal structure of (**1s**)RhCl(CO)$_2$

In order to firmly establish the connectivities in a Rh complex single crystals of (**1s**)RhCl(CO)$_2$ were grown. In principle, the expected structure with two different (*cis* and *trans*) CO was established. However, the crystal structure analysis of several specimen tested was always fraught with problems with respect to the CO located *cis* to the NHC ligand [42]. The analysis of the electron density map clearly revealed electron densities for less than a single CO molecule. However, the NMR and IR data clearly establish the presence of two CO ligands. Obviously in the process of crystallisation some of the *cis*-CO is lost. This phenomenon is not entirely new; facile CO loss has been reported before by Bielawski and co-workers [26] (in the process of crystallization) and by Barluenga et al. [43]; recently Herrmann studied the kinetics of this reaction in (NHC)RhCl(CO)$_2$ type complexes leading to the formation of [(NHC)Rh(μ-Cl)(CO)]$_2$ [23].

2.3. Electrochemistry

The redox potentials of the various (NHC)RhCl(cod) complexes were determined by cyclic voltammetry (Table 1). The Rh(I/II) electrochemistry – just like that of the related Ir complexes – turned out to be highly reversible for all of the twelve complexes studied. The nature of the R substituents has a significant influence on the redox potential. In the unsaturated series of NHC ligands the redox potential changes by 310 mV when replacing the most electron donating –NEt$_2$ by the strongly electron-withdrawing group –SO$_2$-tol group. The saturated NHC ligands appear to be stronger donors than the unsaturated ligands as evidenced by the 69–23 mV more cathodic redox potentials. Next we were interested to learn, whether the redox potentials of the Rh and the Ir series of complexes are correlated. Therefore the redox potentials for the corresponding complexes (with identical NHC ligands) are plotted against each other (Fig. 1). The data for the Ir series come from our recent study and were recorded under identical conditions [8].

In the given potential window an excellent linear correlation between the (NHC)IrCl(cod) and the (NHC)RhCl(cod) based redox potentials is found. This is evidenced by the very good correlation coefficient of the linear regression ($R^2 = 0.993$). Consequently, a Rh(I/II) redox potential can be reliably converted into an Ir(I/II) redox potential using the following formula: $E_{1/2}$ (Ir) = 1.016 · $E_{1/2}$ (Rh) − 0.076 V.

2.4. Infrared spectroscopy of (NHC)Rh(CO)$_2$Cl

The IR data of the Rh complexes synthesized show are indicative of little difference between the saturated and the unsaturated

Table 1
Redox potentials $E_{1/2}$ (V) and peak separation $E_a - E_c$ (mV) of the (NHC)RhCl(cod) complexes (referenced vs. Fc/Fc$^+$ $E_{1/2}$ = 0.46 V [44], 0.1 M TBAPF$_6$ in CH_2Cl_2).

R=	(NHC)RhCl(cod)	$E_{1/2}$ (V)	$E_a - E_c$ (mV)
NEt$_2$	(**1u**)RhCl(cod)	0.718	76
OC$_{12}$H$_{25}$	(**2u**)RhCl(cod)	0.836	82
Me	(**3u**)RhCl(cod)	0.833	76
H	(**4u**)RhCl(cod)	0.855	82
Br	(**5u**)RhCl(cod)	0.926	74
SOtol	(**6u**)RhCl(cod)	0.923	62
NEt$_2$	(**1s**)RhCl(cod)	0.651	78
OC$_{12}$H$_{25}$	(**2s**)RhCl(cod)	0.785	92
Me	(**3s**)RhCl(cod)	0.791	76
H	(**4s**)RhCl(cod)	0.817	78
Br	(**5s**)RhCl(cod)	0.903	90
SO$_2$tol	(**7s**)RhCl(cod)	0.961	84
	(**dap**)RhCl(cod)	0.608	74

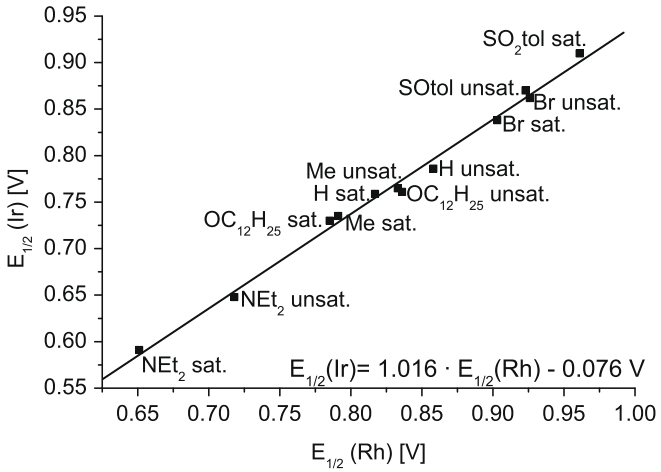


Fig. 1. Plot of the redox potentials of (NHC)IrCl(cod) vs. (NHC)RhCl(cod) (regression coefficient $R^2 = 0.993$).

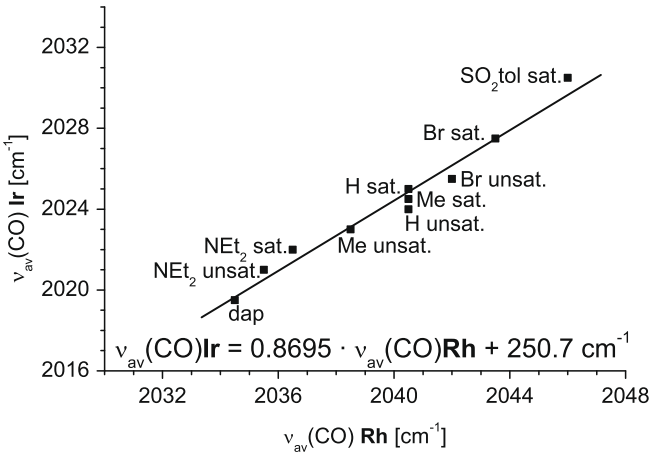


Fig. 2. Plot of the ν_{av}(CO) of (NHC)IrCl(CO)$_2$ vs. (NHC)RhCl(CO)$_2$ (regression coefficient $R^2 = 0.97$).

series of NHC ligands. The signal dispersion within the IR data is much smaller than within the redox potentials. The 10.5 cm^{-1} correspond to only 10 times the signal resolution, while this factor is ca. 60 in the cyclic voltammetry experiment (310 mV/5 mV).

To further extend the complexes to more electron-donating ligands, we have also included the ν(CO) for (dap)MCl(CO)$_2$ (M = Rh (Table 2) and M = Ir 1978, 2063 cm^{-1} (CH_2Cl_2), ν_{av}(CO) 2019.5 cm^{-1}) which were prepared by Cavell and co-workers [31]. Albrecht recently reported the synthesis and ν_{av}(CO) data for (NHC)MCl(CO)$_2$ (M = Ir, Rh)(NHC = 1,2,3-triazolylidene) [45]; the regression formula reported here is able to convert the Rh ν_{av}(CO) into Ir ν_{av}(CO) (or vice versa) with great precision.

Plotting the ν_{av}(CO) of the Rh complexes against the corresponding data from the Ir complexes allows the correlation of the two data sets. By linear regression an equation for the conversion of Rh into Ir data can be derived (Fig. 2). It is very important to note that the ν(CO) of the (NHC)IrCl(CO)$_2$ and the (NHC)RhCl(CO)$_2$ complexes were determined under precisely the same conditions. The regression coefficient $R^2 = 0.97$ for the linear regression is very good, the resulting equation for the conversion of Rh into Ir based data is: $\nu_{av}(CO)Ir = 0.8695 \cdot \nu_{av}(CO)Rh + 250.7$ cm^{-1} (or vice versa $\nu_{av}(CO)Rh = 1.116 \cdot \nu_{av}(CO)Ir - 139.7$ cm^{-1}).

In coordination chemistry redox potentials of Ru(II/III) metal complexes have been used to establish so called Lever electronic parameters (LEP) which are believed to reflect the donor capacity of ligands bound to ruthenium [46]. Correlations between the LEP and the TEP are rare [34,47]. We also attempted a correlation between the ν(CO) in (NHC)RhCl(CO)$_2$ and Rh(I/II) redox potentials of NHC)RhCl(cod). For the full data set the correlation coefficient of linear regression ($R^2 = 0.80$) is only modest, while it is good ($R^2 > 0.9$) for the two separate sets of saturated and unsaturated NHC ligands. The two correlations of the redox potentials of the separate sets of saturated and unsaturated (NHC)RhCl(cod) with the respective Hammett parameters of the R substituents are even better ($R^2 = 0.95$ unsaturated and $R^2 = 0.98$ saturated series of complexes). The same holds true for the two correlations of the ν(CO) with the respective Hammett parameters for the separate sets of saturated and unsaturated (NHC)RhCl(CO)$_2$ ($R^2 = 0.91$ unsaturated and $R^2 = 0.98$ saturated series of complexes). It should be noted in this context that infrared spectroscopy and the redox potentials look at different properties of metal complexes – even though both are related to electron density. The ν(CO) based data provide information on the electron donating capacity of a given ligand, whose electron density is transferred via the metal to the CO ligand. The redox potentials take a slightly different perspective as they represent the energy difference between the reduced metal complex and the oxidized metal complex.

Table 2
ν(CO)(*cis*, *trans*) and ν_{av}(CO) of the (NHC)RhCl(CO)$_2$ complexes (in CH_2Cl_2).

R=	(NHC)RhCl(CO)$_2$	ν(CO) (cm^{-1})	ν_{av}(CO) (cm^{-1})
NEt_2	(**1u**)RhCl(CO)$_2$	1995, 2076	2035.5
$OC_{12}H_{25}$	(**2u**)RhCl(CO)$_2$	1998, 2082	2040
Me	(**3u**)RhCl(CO)$_2$	1996, 2081	2038.5
H	(**4u**)RhCl(CO)$_2$	1998, 2083	2040.5
Br	(**5u**)RhCl(CO)$_2$	2000, 2084	2042
NEt_2	(**1s**)RhCl(CO)$_2$	1996, 2079	2036.5
$OC_{12}H_{25}$	(**2s**)RhCl(CO)$_2$	1998, 2082	2040
Me	(**3s**)RhCl(CO)$_2$	1997, 2084	2040.5
H	(**4s**)RhCl(CO)$_2$	1998, 2083	2040.5
Br	(**5s**)RhCl(CO)$_2$	2000, 2087	2043.5
SO_2Ar	(**7s**)RhCl(CO)$_2$	2002, 2090	2046
	(**dap**)RhCl(CO)$_2$	1994, 2075	2034.5

3. Summary and conclusions

Based on the synthesis and the infrared spectroscopic and electrochemical study of a large number of (NHC)Rh- and (NHC)Ir-complexes we have determined a regression formula to convert the ν_{av}(CO) from (NHC)RhCl(CO)$_2$ complexes into ν_{av}(CO) from (NHC)IrCl(CO)$_2$: $\nu_{av}(CO)\mathbf{Ir} = 0.8695 \cdot \nu_{av}(CO)\mathbf{Rh} + 250.7$ cm^{-1}. This equation will allow the comparison of NHC electronic parameters determined with (NHC)IrCl(CO)$_2$ and (NHC)RhCl(CO)$_2$, which happen to be the most prominent references for the evaluation of ligand electronic parameters.

Due to the obnoxious properties of Ni(CO)$_4$ it is unlikely that in the future a significant number of new LNi(CO)$_3$ complexes will be reported, to provide data for the classical TEP scale. Based on the increased stability of the LIrCl(CO)$_2$ and LIrCl(cod) complexes (as compared to the corresponding rhodium complexes) it is our opinion, that iridium complexes appear to be most suitable reference compounds for the evaluation of the electron donating properties of various ligands. Several (NHC)Rh-complexes suffer from limited stability in solution, especially with less electron donating NHC ligands. The determination of the redox potentials by cyclic voltammetry is highly a sensitive tool towards small changes in the electronic situation. The classic approach by monitoring the ν(CO) via infrared spectroscopy is more flexible as an intrinsic property of a single compound is recorded, but compared to the electrochemical approach it is much less sensitive to changes in the electron donation of ligands.

4. Experimental

All chemicals were purchased as reagent grade from commercial suppliers and used without further purification, unless otherwise noted. THF was distilled over potassium and benzophenone under an argon atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX 500 at 500 and 125.75 MHz, respectively, or on Bruker DRX 300 at 300 or 75.07 MHz. The chemical shifts are referenced to tetramethylsilane (^{1}H, ^{13}C NMR = 0.0 ppm). Abbreviations for NMR data: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet. IR spectra of the metal carbonyls were recorded on a Perkin–Elmer 1600 IR spectrometer in CH_2Cl_2 solution as $100 \cdot 10^{-6}$ m films between KBr plates. TLC was performed by using silica gel 60 F254 (0.2 mm) on aluminum plates. For preparative chromatography, E. Merck silica gel 60 (0.063–0.20 mesh) was used. Electrochemistry: The standard electrochemical instrumentation consisted of an EG&G 273 A-2 potentiostat. A three-electrode configuration was employed. The working electrode was a Pt disk (diameter 1 mm) sealed in soft glass with a Pt wire as counter electrode. The pseudo reference electrode was an Ag wire. All cyclic voltammograms were recorded in dry CH_2Cl_2 under an atmosphere of Ar. As supporting electrolyte NBu_4PF_6 (0.1 M) was used. Potentials were calibrated internally against the formal potential of ferrocene (0.46 V vs. Ag/AgCl) [44]. All azolium salts were available from a previous study [8].

5. General procedure for the synthesis of [(NHC)RhCl(cod)] complexes

[Rh-(μ-Cl)(cod)]$_2$ (1.0 eq.) and KO^{t}Bu (2.2 eq.) were placed in a Schlenk tube, dissolved in thf (25 mL) under an atmosphere of Ar and stirred for 45 min at room temperature. To this mixture was added the corresponding azolium salt (2.2 eq.). The reaction mixture was stirred for 2 h at room temperature, filtered and the filtrate evaporated in vacuo. (workup A) The residue was washed with pentane (3 mL) and dried in vacuo. (workup B) The residue was dissolved in cyclohexane/ethyl acetate and purified by column chromatography using cyclohexane/ethyl acetate as an eluent.

*[(**1u**)RhCl(cod)].* [Rh(μ-Cl)(cod)]$_2$ (50 mg, 0.1 mmol, 1 eq.); KO^{t}Bu (25 mg, 0.223 mmol, 2.2 eq.); *N*,*N*′-bis(2,6-dimethyl-4-diethylaminophenyl)imidazolium chloride (102 mg, 0.223 mmol, 2.2 eq.). (workup A). Yield: 112 mg (88%) of a light green powder. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.21 (t, 12H, CH_3), 1.53–1.56 (m, 4H, cod CH_2), 1.85–1.90 (m, 4H, cod CH_2), 2.06 (s, 6H, CH_3), 2.39 (s, 6H, CH_3), 3.34–3.40 (m, 8H, CH_2), 3.43 (m, 2H, cod CH), 4.51 (m, 2H, cod CH), 6.45 (m, 2H, arom.), 6.51 (m, 2H, arom.), 6.93 (s, 2H, NCHCHN). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.6, 18.7, 20.4, 28.4 (cod), 32.8 (cod), 44.4, 67.3 (cod), 95.3 (cod), 110.1, 111.7, 123.8, 127.7, 135.3, 138.3, 147.7, 184.3 (J_{Rh-C} = 53 Hz). HRMS-EI *m*/*z*: calcd. for $C_{35}H_{50}N_4Cl_1Rh_1$: 664.2776; found: 664.2758.

*[(**2u**)RhCl(cod)].* [Rh(μ-Cl)(cod)]$_2$ (50 mg, 0.1 mmol, 1 eq.); KO^{t}Bu (25 mg, 0.223 mmol, 2.2 eq.); *N*,*N*′-bis(2,6-dimethyl-4-dodecyloxyphenyl)imidazolium chloride (152 mg, 0.223 mmol, 2.2 eq.). (workup A). Yield: 170 mg (96%) of a yellow powder. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.81 (t, 6H, CH_3), 1.21 (m, 32H, CH_2), 1.39–1.44 (m, 4H, cod CH_2), 1.48–1.52 (m, 4H, CH_2), 1.72–1.77 (m, 4H, cod CH_2), 1.81–1.86 (m, 4H, CH_2), 2.03 (s, 6H, CH_3), 2.34 (s, 6H, CH_3), 3.24 (bs, 2H, cod CH), 3.94 (m, 4H, OCH_2), 4.47 (bs, 2H, cod CH), 6.65 (s, 2H, arom.), 6.69 (s, 2H, arom.), 6.87 (s, 2H, NCHCHN). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.1, 18.4, 20.3, 22.7, 26.1, 28.4, 29.3, 29.4 (cod), 29.6, 29.7, 31.9, 32.8 (cod), 67.6 (cod), 68.1, 96.1 (cod), 113.6, 114.0, 123.7, 131.7, 135.9, 139.2, 158.9, 184.3 (J_{Rh-C} = 53 Hz).

*[(**3u**)RhCl(cod)].* [Rh(μ-Cl)(cod)]$_2$ (50 mg, 0.1 mmol, 1 eq.); KO^{t}Bu (25 mg, 0.223 mmol, 2.2 eq.); *N*,*N*′-bis(2,4,6-trimethylphenyl)imidazolium chloride (76 mg, 0.223 mmol, 2.2 eq.). (workup A). Yield: 100 mg (90%) of a yellow powder. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.54–1.56 (m, 4H, cod CH_2), 1.81–1.89 (m, 4H, cod CH_2), 2.11 (s, 6H, CH_3), 2.39 (s, 6H, CH_3), 2.40 (s, 6H, CH_3), 3.29 (m, 2H, cod CH), 4.52 (m, 2H, cod CH), 6.95 (s, 2H, NCHCHN), 7.00 (s, 2H, arom.), 7.06 (s, 2H, arom.). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.1, 19.8, 21.1, 28.4 (cod), 32.7 (cod), 67.8 (cod) 96.2 (cod), 123.5, 128.1, 129.7, 134.4, 136.3, 137.6, 138.7, 183.6 (J_{Rh-C} = 53 Hz). HRMS-EI *m*/*z*: calcd. for $C_{29}H_{36}N_2Cl_1Rh_1$: 550.1618; found: 550.1598.

*[(**4u**)RhCl(cod)].* [Rh(μ-Cl)(cod)]$_2$ (50 mg, 0.1 mmol, 1 eq.); KO^{t}Bu (25 mg, 0.223 mmol, 2.2 eq.); *N*,*N*′-bis(2,6-dimethylphenyl)imidazolium chloride (70 mg, 0.223 mmol, 2.2 eq.). (workup A). Yield: 80 mg (76%) of a yellow powder. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.53–1.55 (m, 4H, cod CH_2), 1.82–1.85 (m, 4H, cod CH_2), 2.16 (s, 6H, CH_3), 2.46 (s, 6H, CH_3), 3.28 (m, 2H, cod CH), 4.52 (m, 2H, cod CH), 7.01 (s, 2H, NCHCHN), 7.22 (m, 3H, arom.), 7.32–7.35 (m, 3H, arom.). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.2, 19.9, 28.4 (cod), 32.7 (cod), 67.8 (cod), 96.3 (cod), 123.4, 127.5, 129.0, 134.7, 138.1, 138.6, 183.6 (J_{Rh-C} = 53 Hz). HRMS-EI *m*/*z*: calcd. for $C_{27}H_{32}N_2Cl_1Rh_1$: 522.1305; found: 522.1341.

*[(**5u**)RhCl(cod)].* [Rh(μ-Cl)(cod)]$_2$ (50 mg, 0.1 mmol, 1 eq.); KO^{t}Bu (25 mg, 0.223 mmol, 2.2 eq.); *N*,*N*′-bis(2,6-dimethyl-4-bromophenyl)-imidazolium chloride (149 mg, 0.223 mmol, 2.2 eq.). (workup A). Yield: 170 mg (87%) of a green powder. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.17–1.23 (m, 4H, cod CH_2), 1.79–1.85 (m, 4H, cod CH_2), 2.06 (s, 6H, CH_3), 2.35 (s, 6H, CH_3), 3.16 (m, 2H, cod CH), 4.51 (m, 2H, cod CH), 6.90 (s, 2H, NCHCHN), 7.31 (s, 2H, arom.), 7.34 (s, 2H, arom.). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 16.7, 17.1, 18.9, 27.4 (cod), 31.7 (cod), 67.1 (cod), 96.2 (cod) 121.8, 122.5, 129.4, 130.9, 135.6, 136.6, 139.2, 183.4 (J_{Rh-C} = 53 Hz).

*[(**6u**)RhCl(cod)].* [Rh(μ-Cl)(cod)]$_2$ (19 mg, 0.04 mmol, 1 eq.); KO^{t}Bu (10 mg, 0.08 mmol, 2.2 eq.); *N*,*N*′-bis(2,6-dimethyl-4-tolylsulfinylphenyl)imidazolium chloride (50 mg, 0.08 mmol, 2.2 eq.). (workup A). Yield: 43 mg (72%) of a yellow powder. Rapid decomposition in solution: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.33 (s, 12H, CH_3), 2.10 (m, 4H, cod CH_2), 2.20 (m, 4H, cod CH_2), 2.35 (s, 6H, CH_3), 3.00 (m, 2H, cod CH), 4.35 (m, 2H, cod CH_2), 6.91 (m, 2H, arom.), 7.50–7.54 (m, 10H, arom.).

*[(**1s**)RhCl(cod)].* [Rh(μ-Cl)(cod)]$_2$ (50 mg, 0.1 mmol, 1 eq.); KO^{t}Bu (25 mg, 0.223 mmol, 2.2 eq.); *N*,*N*′-bis(2,6-dimethyl-4-diethylaminophenyl)imidazolinium chloride (102 mg, 0.223 mmol, 2.2 eq.). (workup B). Yield: 130 mg (97%) of a light green powder. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.11 (t, 12H, CH_3), 1.40–1.48 (m, 4H, cod CH_2), 1.71–1.78 (m, 4H, cod CH_2), 2.21 (s, 6H, CH_3), 2.51 (s, 6H, CH_3), 3.25–3.35 (m, 8H, NCH_2), 3.56 (m, 2H, cod CH), 3.69–3.82 (m, 4H, NCH_2CH_2N), 4.38 (s, 2H, cod CH), 6.36 (m, 2H, arom.), 6.42 (m, 2H, arom.). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.6, 19.0, 20.5, 28.2 (cod), 32.7 (cod), 44.4, 51.8, 67.0 (cod), 96.3 (cod), 110.6, 112.2, 127.7, 136.0, 139.3, 147.2, 213.3 (J_{Rh-C} = 47 Hz). HRMS-EI *m*/*z*: calcd. for $C_{35}H_{52}N_4Cl_1Rh_1$: 666.2932; found: 666.2931.

*[(**2s**)RhCl(cod)].* [Rh(μ-Cl)(cod)]$_2$ (50 mg, 0.1 mmol, 1 eq.); KO^{t}Bu (25 mg, 0.223 mmol, 2.2 eq.); *N*,*N*′-bis(2,6-dimethyl-4-dodecyloxyphenyl)imidazolinium chloride (152 mg, 0.223 mmol, 2.2 eq.). (workup A). Yield: 160 mg (89%) of a yellow powder. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.81 (t, 6H, CH_3), 1.20 (m, 32H, CH_2), 1.37–1.42 (m, 4H, cod CH_2), 1.43–1.48 (m, 4H, cod CH_2), 1.70–1.75 (m, 8H, CH_2), 2.24 (s, 6H, CH_3), 2.53 (s, 6H, CH_3), 3.31 (bs, 2H, cod CH), 3.71–3.82 (m, 4H, NCH_2CH_2), 3.87–3.95 (m, 4H, OCH_2), 4.42 (bs, 2H, cod CH), 6.62 (d, 2H, arom.), 6.66 (d, 2H, arom.). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.1, 18.6, 20.4, 22.7, 26.0, 28.2, 29.3 (cod), 29.4, 29.6, 29.7, 31.9, 32.7 (cod), 51.5, 67.3 (cod), 68.1, 97.2 (cod), 113.9, 114.2, 131.8, 136.6, 140.1, 158.3, 213.5 (J_{Rh-C} = 48 Hz). HRMS-EI *m*/*z*: calcd. for $C_{51}H_{82}N_2Cl_1Rh_1$: 890.5084; found: 890.5025.

*[(**3s**)RhCl(cod)]*. [Rh(μ-Cl)(cod)]$_2$ (25 mg, 0.05 mmol, 1 eq.); KO^{t}Bu (13 mg, 0.11 mmol, 2.2 eq.); *N*,*N*′-bis(2,4,6-trimethylphenyl)-imidazolinium chloride (38 mg, 0.11 mmol, 2.2 eq.). (workup A). Yield: 52 mg (95%) of a yellow powder. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.50–1.54 (m, 4H, cod CH_2), 1.77–1.80 (m, 4H, cod CH_2), 2.33 (d, 12H, CH_3), 2.60 (s, 6H, CH_3), 3.36 (m, 2H, cod CH), 3.82–3.89 (m, 4H, NCH_2CH_2N), 4.48 (m, 2H, cod CH), 6.97 (s, 2H, arom.), 7.02 (s, 2H, arom.). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.3, 20.0, 21.0, 28.1 (cod), 32.6 (cod), 51.4, 67.5 (cod), 97.2 (cod), 128.4, 130.0, 135.2, 136.3, 137.9, 138.5, 212.8 (J_{Rh-C} = 49 Hz). HRMS-EI *m*/*z*: calcd. for $C_{29}H_{38}N_2Cl_1Rh_1$: 552.1775; found: 552.1760.

*[(**4s**)RhCl(cod)]*. [Rh(μ-Cl)(cod)]$_2$ (50 mg, 0.1 mmol, 1 eq.); KO^{t}Bu (25 mg, 0.223 mmol, 2.2 eq.); *N*,*N*′-bis(2,6-dimethylphenyl)imidazolinium chloride (70 mg, 0.223 mmol, 2.2 eq.). (workup A). Yield: 80 mg (84%) of a yellow powder. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.49–1.53 (m, 4H, cod CH_2), 1.73–1.77 (m, 4H, cod CH_2), 2.37 (s, 6H, CH_3), 2.66 (s, 6H, CH_3), 3.35 (m, 2H, cod CH), 3.87–3.94 (m, 4H, NCH_2CH_2N), 4.47 (m, 2H, cod CH), 7.16–7.17 (m, 3H, arom.), 7.21–7.24 (m, 3H, arom.). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.5, 20.1, 28.1 (cod), 32.6 (cod), 51.3, 67.6 (cod), 97.5 (cod), 127.8, 128.3, 129.3, 135.6, 138.8, 139.0, 212.9 (J_{Rh-C} = 48 Hz). HRMS-EI *m*/*z*: calcd. for $C_{27}H_{34}N_2Cl_1Rh_1$: 524.1462; found: 524.1447.

*[(**5s**)RhCl(cod)]*. [Rh(μ-Cl)(cod)]$_2$ (50 mg, 0.1 mmol, 1 eq.); KO^{t}Bu (25 mg, 0.223 mmol, 2.2 eq.); *N*,*N*′-bis(2,6-dimethyl-4-bromophenyl)-imidazolinium chloride (150 mg, 0.223 mmol, 2.2 eq.). (workup B). Yield: 150 mg (86%) of a green powder. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.56–1.59 (m, 4H, cod CH_2), 1.80–1.83 (m, 4H, cod CH_2), 2.33 (s, 6H, CH_3), 2.61 (s, 6H, CH_3), 3.30 (m, 2H, cod CH), 3.82–3.89 (m, 4H, NCH_2CH_2N), 4.55 (m, 2H, cod CH), 7.33 (d, 2H, arom.), 7.37 (d, 2H, arom.). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.3, 20.0, 28.2 (cod), 32.6 (cod), 51.2, 67.9 (cod), 98.4 (cod), 121.9, 130.6, 132.2, 137.7, 141.1, 213.7 (J_{Rh-C} = 49 Hz). HRMS-EI *m*/*z*: calcd. for $C_{27}H_{32}N_2Br_2Cl_1Rh_1$: 679.9671; found: 679.9641.

*[(**7s**)RhCl(cod)]*. [Rh(μ-Cl)(cod)]$_2$ (20 mg, 0.04 mmol, 1 eq.); KO^{t}Bu (10 mg, 0.09 mmol, 2.2 eq.); *N*,*N*′-bis(2,6-dimethyl-4-tosylphenyl)imidazolinium chloride (56 mg, 0.09 mmol, 2.2 eq.). (workup A). Yield: 58 mg (88%) of a yellow powder. Rapid decomposition in solution: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.20–1.36 (m, 4H, codCH_2), 2.28–2.36 (m, 12H, CH_3), 2.59 (s, 6H, CH_3), 3.00 (s, 2H, cod CH), 3.65–3.85 (m, 4H, NCH_2CH_2N), 4.23 (s, 2H, cod CH), 7.19–7.24 (m, 3H, arom.), 7.66–7.78 (m, 9H, arom.)., 172.4, 215.3 (J_{Rh-C} = 49 Hz).

6. General procedure for the synthesis of [(NHC)RhCl(CO)$_2$] complexes

The corresponding [(NHC)RhCl(cod)] complex was dissolved in CH_2Cl_2 (10 mL) and CO was bubbled through the solution for 15 min. The solvent was evaporated, the residue suspended in pentane (10 mL) and filtered leaving a yellow solid.

*[(**1u**)RhCl(CO)$_2$]*. [(**1u**)RhCl(cod)] (50 mg, 0.08 mmol). Yield: 45 mg (92%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.21 (t, 12H, CH_3), 2.18 (s, 12H, $ArCH_3$), 3.38 (q, 8H, CH_2), 6.42 (s, 4H, arom.), 7.05 (s, 2H, NCHCHN). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.6, 19.1, 44.2, 110.6, 124.1, 126.3, 136.2, 148.0, 178.1 (J_{Rh-C} = 45 Hz), 183.1 (J_{Rh-C} = 75 Hz), 185.4 (J_{Rh-C} = 54 Hz).

*[(**2u**)RhCl(CO)$_2$]*. [(**2u**)RhCl(cod)] (60 mg, 0.07 mmol). Yield: 33 mg (56%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.88 (t, 6H, CH_3), 1.28 (s, 32H, CH_3), 1.47 (m, 4H, CH_2), 1.80 (m, 4H, CH_2), 2.21 (s, 12H, CH_3), 3.98 (t, 4H, OCH_2), 6.71 (s, 4H, arom.), 7.08 (s, 2H, NCHCHN). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.1, 18.8, 22.7, 26.1, 29.3, 29.6, 31.9, 68.0, 114.0, 123.9, 130.5, 136.8, 159.3, 178.3 (J_{Rh-C} = 45 Hz), 182.8 (J_{Rh-C} = 74 Hz), 184.9 (J_{Rh-C} = 54 Hz).

*[(**3u**)RhCl(CO)$_2$]*. [(**3u**)RhCl(cod)] (50 mg, 0.09 mmol). Yield: 43 mg (96%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.21 (s, 12H, CH_3), 2.37 (s, 6H, CH_3), 7.01 (s, 4H, arom.), 7.11 (s, 2H, NCHCHN). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.5, 21.2, 123.7, 129.3, 135.1, 135.3, 139.4, 177.7 (J_{Rh-C} = 45 Hz), 182.8 (J_{Rh-C} = 74 Hz), 184.9 (J_{Rh-C} = 54 Hz).

*[(**4u**)RhCl(CO)$_2$]*. [(**4u**)RhCl(cod)] (50 mg, 0.1 mmol). Yield: 44 mg (93%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.27 (s, 12H, CH_3), 7.16 (s, 2H, NCHCHN), 7.20 (s, 2H, arom.), 7.23 (s, 2H, arom.), 7.34 (m, 2H, arom.). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.6, 123.6, 128.6, 129.6, 135.7, 137.5, 177.6 (J_{Rh-C} = 45 Hz), 182.7 (J_{Rh-C} = 74 Hz), 184.7 (J_{Rh-C} = 54 Hz).

*[(**5u**)RhCl(CO)$_2$]*. [(**5u**)RhCl(cod)] (50 mg, 0.07 mmol). Yield: 44 mg (95%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.23 (s, 12H, CH_3), 7.14 (s, 2H, NCHCHN), 7.38 (t, 4H, arom.). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.5, 123.6, 123.7, 131.6, 136.5, 137.7, 178.3 (J_{Rh-C} = 45 Hz), 182.6 (J_{Rh-C} = 73 Hz), 184.4 (J_{Rh-C} = 54 Hz).

*[(**1s**)RhCl(CO)$_2$]*. [(**1s**)RhCl(cod)] (50 mg, 0.07 mmol). Yield: 45 mg (97%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.19 (t, 12H, CH_3), 2.40 (s, 12H, $ArCH_3$), 3.35 (q, 8H, CH_2), 3.93 (s, 4H, NCH_2CH_2N), 6.39 (s, 4H, arom.). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.8, 19.3, 44.2, 52.1, 111.0, 126.1, 137.0, 147.5, 183.4 (J_{Rh-C} = 76 Hz), 185.5 (J_{Rh-C} = 53 Hz), 206.0 (J_{Rh-C} = 41 Hz).

*[(**2s**)RhCl(CO)$_2$]*. [(**2s**)RhCl(cod)] (60 mg, 0.07 mmol). Yield: 33 mg (56%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.88 (t, 6H, CH_3), 1.20 (m, 36H, CH_2), 1.39 (m, 4H, CH_2), 1.71 (m, 4H, CH_2), 2.36 (s, 12H, CH_3), 3.88 (t, 4H, NCH_2CH_2N), 6.60 (s, 4H, arom.). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.1, 19.0, 22.7, 26.1, 29.3, 29.4, 29.5, 29.6, 29.6, 29.7, 31.9, 51.8, 67.7, 67.9, 114.3, 130.3, 137.7, 158.8, 183.1 (J_{Rh-C} = 76 Hz), 185.0 (J_{Rh-C} = 54 Hz), 206.2 (J_{Rh-C} = 42 Hz).

*[(**3s**)RhCl(CO)$_2$]*. [(**3s**)RhCl(cod)] (50 mg, 0.09 mmol). Yield: 34 mg (75%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.32 (s, 6H, CH_3), 2.43 (s, 12H, CH_3), 4.00 (s, 4H, NCH_2CH_2N), 6.97 (s, 4H, arom.). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.6, 51.6, 129.6, 134.9, 136.1, 135.6, 183.0 (J_{Rh-C} = 75 Hz), 185.0 (J_{Rh-C} = 53 Hz), 205.5 (J_{Rh-C} = 41 Hz).

*[(**4s**)RhCl(CO)$_2$]*. [(**4s**)RhCl(cod)] (50 mg, 0.1 mmol). Yield: 30 mg (63%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.48 (s, 12H, CH_3), 4.04 (s, 4H, NCH_2CH_2N), 7.15 (m, 2H, arom.), 7.18 (m, 2H, arom.), 7.24 (d, 2H, arom.). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.6, 51.4, 122.7, 131.5, 136.4, 137.7, 181.9 (J_{Rh-C} = 74 Hz), 183.8 (J_{Rh-C} = 53 Hz), 204.6 (J_{Rh-C} = 42 Hz).

*[(**5s**)RhCl(CO)$_2$]*. [(**5s**)RhCl(cod)] (50 mg, 0.07 mmol). Yield: 46 mg (99%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.44 (s, 12H, CH_3), 4.00 (s, 4H, NCH_2CH_2N), 7.32 (s, 4H, arom.). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.1, 18.6, 22.3, 51.4, 122.7, 131.8, 136.5, 182.8 (J_{Rh-C} = 74 Hz), 184.5 (J_{Rh-C} = 54 Hz) 206.2 (J_{Rh-C} = 41 Hz).

*[(**7s**)RhCl(CO)$_2$]*. [(**7s**)RhCl(cod)] (50 mg, 0.06 mmol). Yield: 44 mg (96%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.43 (s, 6H, CH_3), 2.49 (s, 12H, CH_3), 3.99 (s, 4H, NCH_2CH_2N), 7.34, 7.36 (AA′, m, 4H, arom.), 7.71 (s, 4H, arom.), 7.85, 7.87 (BB′, m, 4H, arom.).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.12.047.

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