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Synthesis and characterization of chiral mono *N*-heterocyclic carbene-substituted rhodium complexes and their catalytic properties in hydrosilylation reactions

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ABSTRACT

Different chiral mono-substituted *N*-heterocyclic carbene complexes of rhodium were prepared, starting from $[Rh(COD)Cl]_2$ (COD = cyclooctadiene) by addition of free *N*-heterocyclic carbenes (NHC), or an in-situ deprotonation of the corresponding iminium salt. All new complexes were characterized by spectroscopy methods. In addition, the structures of chloro(η^4-1,5-cyclooctadiene)(1,3-di-[(1*R*,2*R*,3*R*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]hept-3-yl] imidazolin-2-ylidene)rhodium(I) (**5a**), chloro(η^4-1,5-cyclooctadiene)(1,3-di-[(1*R*,2*S*,5*R*)-2-isopropyl-5-menthylcyclohex-1-yl]imidazol-2-ylidene)rhodium(I) (**5b**) and chloro(η^4-1,5-cyclooctadiene)(1,3-di-[(2*R*,4*S*,5*S*)-2-methyl-4-phenyl-1,3-dioxacyclohex-5-yl]imidazolin-2-ylidene)rhodium(I) (**5i**) were analyzed by DFT-calculations. The enantioselective hydrosilylation of acetophenone, ethylpyruvate and *n*-propylpyruvate with diphenylsilane and hydrolysis was carried out with chiral C_2-symmetrical mono-substituted *N*-heterocyclic carbene rhodium complexes giving for the first time an enantioselective excess of up to 74% *ee* in the case of the *n*-propylpyruvate.

1. Introduction

Chirality is one of the central themes of nature, and it therefore follows that this must not be ignored whenever a synthetic compound is introduced to an organism. The tragic case of the anti-nausea drug Thalidomide is an often-used example for the need of enantio- and dia-stereoisomeric purity in synthetic products [1]. This brings us back to the research laboratory where enantioselective catalysis is a promising candidate for the preparation of enantiomerically pure compounds. The influence of homogeneous catalysis on industrial processes in recent years has attracted much attention [2]. Homogeneous catalysts have the advantage of being highly defined in their molecular structure in addition to the possibility of broad structural variety [3]. Therefore the field of stereoselective synthesis is of great interest. A particularly successful example of enantioselective catalysis in an industrial application is the synthesis of L-DOPA, a drug used for treatment of Parkinson's disease, catalyzed by a chiral bis(phosphine) rhodium complex [4], or the titanium-catalyzed formation of enantiomerically pure epoxides [5]. Conspicuously, most applications still use chiral phosphine-based catalysts [6].

Alternatively, metal complexes of imidazolin-2-ylidenes (*N*-heterocyclic carbenes, or NHCs) have attracted considerable attention as a rarely utilized class of homogeneous catalysts for this purpose [7,8]. For example, complexes of ruthenium and palladium where phosphine ligands have been replaced by NHCs show excellent catalytic properties for metathesis and C,C-coupling reactions [9]. In contrast to the corresponding phosphine complexes, ligand dissociation was not observed with these catalysts [10], and no excess of the ligand is necessary [11]. These properties make such NHC-based catalysts suitable for chiral modifications [12,13]. The first chiral *N*-heterocyclic carbenes as ligands in metal complexes were published at the beginning of the 1980s by Lappert et al. [14]. In this case, electron rich olefins, first described by Wanzlick [15], were reacted with metal precursors *in-situ* to provide metal complexes containing saturated carbenes of the imidazolidine type as ligands. These first studies were mainly of structural interest and were not focused on their usage in catalysis. Therefore a large body of work on chiral NHC complexes has been published [16] since our group reported the first example of a chiral NHC complex employed in homogeneous catalysis [17]. One drawback of these carbene ligands is the possible free rotation around the metal–carbene bond, thus effecting imperfect transfer

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of the ligand's chiral information to the substrate [18]. In the literature this problem is often combated with the use of chelating NHC ligands [13d,19,20].

We now report the synthesis of novel, non-chelating chiral-substituted imidazol-2-ylidene complexes of rhodium and their application in a comparative study of enantioselective hydrosilylation, in which chiral imidazol-2-ylidene complexes of rhodium, previously reported by our group [17,21,22] and others [13d,18,20,23] are employed.

2. Results and discussions

2.1. Ligand synthesis

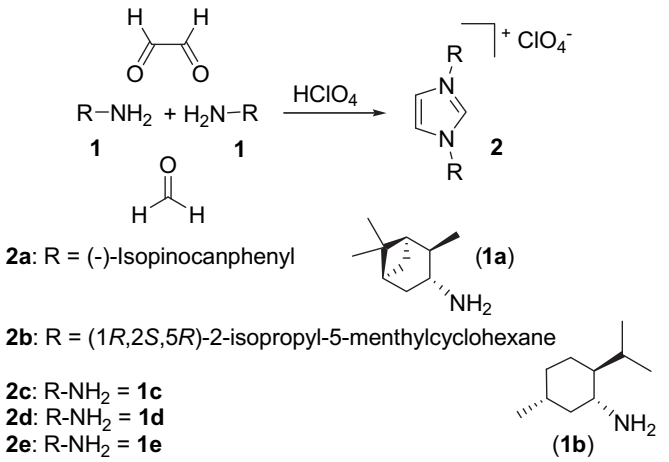
The first chiral NHCs were constructed with derivatives of natural L-amino acids under formation of a saturated backbone in the five-membered NHC ring; electron rich ligands situated approximately with middle ranged σ-donor ability for such NHCs is [24,25]. Natural amines such as L-alanine, L-leucine, L-proline, (−)-*cis*-myrtanylamine and (−)-*trans*-1,2-diaminocyclohexane were employed. For the resulting NHC ligands the chiral center is, without exception, located far from the metal center.

In order to achieve high optical induction a sterically demanding ligand next to the metal center combined with high rigidity is required [26]. One possibility is the use of cyclohexane-based substituents bearing chiral groups, which are attached to the nitrogens of the imidazoline ring. Such cyclohexane-type moieties themselves have a high steric demand, especially if appropriate substituents generating chiral centers are additionally introduced which prevent the system from ring-flipping. In this manner, the correct orientation of the substituents toward the metal center can be enforced.

The most severe problem for such cyclohexyl-substituted carbene ligands is the possibility to have more than 4 chiral centers, all of which must be delivered enantiomerically pure; thus convenient organic synthesis routes can be elusive. Therefore we looked to the chiral pool of natural products for our ligand precursors. The family of terpenes seemed quite successful for this purpose, and especially the commercial compound [1*R*,2*R*,3*R*,5*S*]-3-amino-2,6,6-trimethylbicyclo[3.1.1]heptane (**1a**), which contains a methyl group in the β-position, but its conformation is highly stabilized by the methylene bridge and can be used as a starting material. Another possibility is the family of isoprenoids such as (−)-menthol. The corresponding (−)-menthylamine (**1b**) is a very expensive commercial chemical, which can however be produced on a laboratory scale relatively cheaply starting from (−)-menthone [27].

Both amines can be converted via a known ring-closing synthesis using perchloric acid to the corresponding imidazolium salts **2a** {1,3-di[1*R*,2*R*,3*R*,5*S*]-2,6,6-trimethylbicyclo[3.1.1]hept-3-yl] imidazolium perchlorate} [28] and **2b** {1,3-di[(1*R*,2*R*,5*R*)-2-isopropyl-5-methylcyclohex-1-yl]imidazolium perchlorate} [29] (see for comparison Scheme 1). We found that the use of hypochloric acid was unsuccessful for this reaction, and with increasing steric demand of the β-substituent the yield decreased.

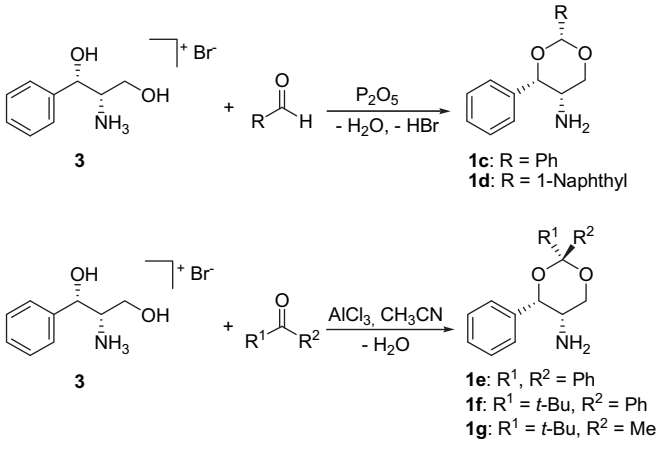
The possibility for further modifications at the carbene ligand was then investigated to modify and optimize the influence of the carbene ligand in chiral hydrosilylation. The first point would be to increase the steric bulk of the substituent in β-position to the nitrogen, for example by substitution with a phenyl group, which should provide better protection of the metal center and should restrict rotation around the nitrogen-α-carbon bond. Another point is that the bulky substituent could be coordinated in *cis*-position to the amino group, which should result in an axial position of the substituent or amino group. Therefore the heterocycle will be perpendicular to the cyclohexane plane, resulting in increased protection of the metal center. Another bulky group at the other



Scheme 1. Synthesis of chiral imidazolium salts from the chiral amines. A detailed drawing and preparation procedure for compounds **1c**–**1e** is shown in Scheme 2.

β-position of the ring will stabilize the desired conformation and will prevent the rotation of the substituent at the nitrogen to increase the steric hindrance at the metal center. An alternative possibility to generate such sterically protected amines is the use of substituted 1,3-dioxanes, which later could serve as building blocks for chiral imidazolium salts.

In this regard, the (1*S*,2*S*)-2-amino-1-phenyl-1,3-propanediol (**3**) (see Scheme 2) serves as an inexpensive starting material that is produced commercially as a side product during the production of chloramphenicol [(1*R*,2*R*)-2-dichloracetamino-1-(4-nitrophenyl)-1,3-propanediol] the first synthetically produced *broad-spectrum* antimycoticum [30]. The side product, (1*S*,2*S*)-2-amino-1-phenyl-1,3-propanediol (**3**), is therefore very cheap and available in large quantities. The amine has two chiral centers, they can react with an aldehyde or ketone resulting in a six-membered ring. This compound has many advantages, as was realized by Weinges in the asymmetric Strecker-synthesis [31]. Unfortunately the common method for the preparation of cyclic acetals cannot be used for 2-amino-1-phenyl-1,3-propanediols, as the functional groups can undergo side reactions. For example the benzylic hydroxyl group can lose water by an elimination reaction, or the amino group can react with the carbonyl group to an imine or as a β-amino alcohol to an oxazolidine derivative. Weinges published two procedures where the reaction was carried out at room temperature by suppression of the possible water elimination with simultaneous protection of the amino group by a Lewis acid [32].



Scheme 2. Synthesis of chiral 1,3-dioxanes (**1c**–**1g**).

Aldehydes that are liquids at room temperature and are not able to undergo aldol-condensation can be used directly as the solvent itself, if the (1*S*,2*S*)-2-amino-1-phenyl-1,3-propanediol (**3**), which is protected as its hydrobromide salt, is sufficiently soluble in it. With P_2O_5 as the condensation agent, the chiral amines **1c** and **1d** could be synthesized according to Scheme 2.

Though the amino group is protected, there is a large amount of imine produced during the reaction. In the case of **1c**, the benzaldehyde is distilled off and a basic hydrolysis and workup of the P_2O_5 was carried out. The residue was treated with a steam strip, in which most of the imine was hydrolyzed and the aldehyde could be removed. The remaining imine (about 15%) can be separated quantitatively via column chromatography, but its presence does not negatively effect the ring closure in the next reaction step. Because of the very high boiling point of the aldehyde in the case of **1d**, it could not be distilled off and therefore an extraction workup of the product with dilute acetic acid from the ether phase was required. The following neutralization precipitates the imines as solids which, after separation, can be hydrolyzed selectively with acetic acid or formic acid in a THF/water mixture.

Ketones that can undergo an aldol condensation or are solids at room temperature had to be treated in a different manner. In this case, dry aluminum chloride was used as a condensation agent in dry acetonitrile; after alkali hydrolysis of the aluminum chloride, **1e**–**g** could be extracted with dilute acetic acid from the diethyl ether phase (Scheme 2). In all cases the yields were relatively low and rarely over 10%.

The prepared 5-amino-4-phenyl-1,3-dioxanes **1c**–**1g** are viscous yellow oils which precipitate when left open to the atmosphere, in the cases of the larger substituents phenyl and 1-naphthyl. During the acetal-formation, compounds **1c**, **1d**, **1f**, **1g** may form two diastereomers. The absolute configuration at the second carbon atom was determined by probing the nuclear Overhauser effect and no further diastereomers were observed [32]. The acetal formation is highly stereoselective because the most sterically bulky substituent in α-position is forced to be in equatorial position.

The *syn*-axial interactions in 1,3-dioxane are much stronger compared to cyclohexane, due to the shorter CO-bonds (relative to the CC-bonds in cyclohexane), which results in a stronger folding in the acetal region and simultaneously less space between the axial substituents. Subsequently it was ascertained that in the case of polar substituents not only the steric *van der Waals* interactions are present, but also interactions with the two oxygens, which show a preference in the 5-position for an axial coordination [33]. For the 5-amino-4-phenyl-1,3-dioxanes (**1c**–**1g**) this effect is highly favored, because intramolecular hydrogen bridges with the axially-orientated amino group can also be formed. Additionally, the conformation is fixed for these (4*S*,5*S*)-5-amino-4-phenyl-1,3-dioxanes by the substituents in position 4 and 5. These results are supported by the ^{1}H NMR spectra, where the methylene group in position 6 shows an ABX-spin system with large geminal (J_{AB} = 11–12 Hz) and small vicinal (J_{Ax}, J_{Bx} = 1–2 Hz) coupling constants. The amino group in an equatorial position with two axial protons would result in a nearly 180° dihedral angle and the coupling constant should be approximately J_{aa} = 9–13 Hz.

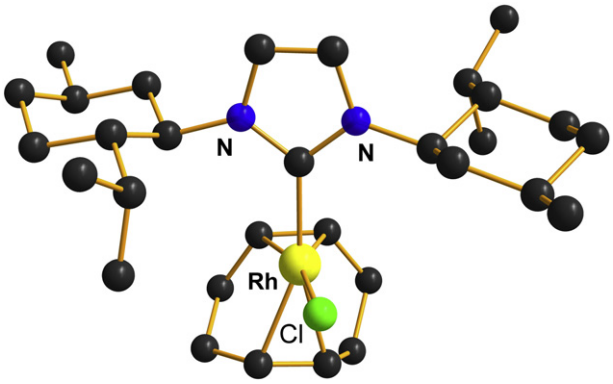
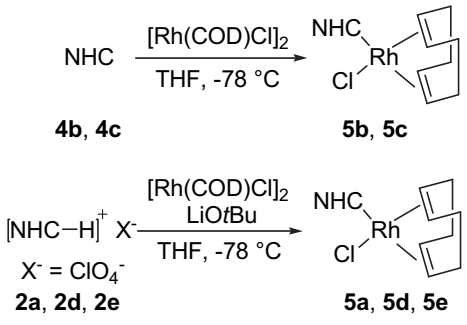


Fig. 1. Ball and Stick model of compound **5b** in the solid state [29]. Hydrogen atoms are omitted for clarity.

Since cyclic acetals serve as common protecting groups [34] in basic media and are usually cleaved under acidic conditions, it was only possible to form the corresponding imidazolium salts **2c**–**2e** analogously to **2a** and **2b**, by using $HClO_4$ as the corresponding acid required for ring closure reaction (Scheme 1). In 1997 Enders et al. published a similar unsymmetrical triazolium compound with only one 2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl group [23]. The synthesis of **2c** and **2d** [28,35] is complicated by solubility problems which can be avoided by adding water and/or methylene chloride to the reaction. If methylene chloride is added the product can be precipitated afterward by addition of diethyl ether to the reaction mixture. This reaction method failed for the amines **1f** and **1g**.

Starting from the free carbenes **4b** [29] and **4c** the corresponding chiral mono(carbene) rhodium(I) complexes **5b** [29] and **5c** were prepared (Scheme 3). To a solution of the binuclear bis[μ-chloro(η^4-1,5-cyclooctadiene)rhodium(I)] in THF was added a THF solution of the free carbenes **4b** and **4c**. The two complexes **5b** [chloro(η^4-1,5-cyclooctadiene)(1,3-di[(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohex-1-yl]imidazolin-2-ylidene)rhodium(I)] [29] and **5c** [chloro(η^4-1,5-cyclooctadiene)-(1,3-di[(2*R*,4*S*,5*S*)-2,4-diphenyl-1,3-dioxocyclohex-5-yl]imidazolin-2-ylidene)rhodium(I)] were obtained after purification in good yields. Both complexes can be recrystallized from a methylene chloride/diethyl ether solution.

The solid state structure of complex **5b** [29] was examined crystallographically and theoretically at PBE-D/TZVP level (see for computational details the theoretical section). A plot of the solid state structure of **5b** is given in Fig. 1, the most important bonding parameters are listed in Table 1.



Scheme 3. Synthesis of NHC complexes **5a**–**5e**.

Table 1
Most important bonding parameters of the calculated versus experimental structure of **5b**. Selected bond lengths [Å] and bond angles [deg]. Cg1 and Cg2 define the midpoints of the double bonds in the COD ligand, C2 is the carbene carbon.

Bonding parameter	Experimental value [29]	Theoretical value
Rh–Cl	2.3832(5)	2.396
Rh–Cg1	1.991	2.011
Rh–Cg2	2.093	2.110
Rh–C2	2.052(2)	2.030
Cl–Rh–Cg1	174.3	172.2
Cl–Rh–Cg2	90.13	90.3
Cl–Rh–C2	89.89(4)	89.5
Cg1–Rh–Cg2	86.98	86.9
Cg1–Rh–C2	93.34	94.2

The computational data are in perfect agreement with the results of the X-ray study. The experimental and quantum chemical investigations reveal the same trend. The solid state structure of complex **5b** [29] shows a square planar coordination of the central metal atom, which is not unusual for this type of complex [36]. As in comparable known complexes, the distance of the rhodium to the double bond of the COD-ring *trans* to the carbene ligand is significantly longer (0.1 Å) as compared to the double bond *trans* to the chloro-ligand, due to the *trans*-effect. The metal–carbene distance (2.052(2) Å, experimental value in Table 1) is only slightly longer than other carbene ligands with less steric hindrance, for example as in the unsubstituted 1,3-dicyclohexylimidazolin-2-ylidene ligand (2.021 Å) [37], or other small substituted imidazolin-2-ylidene ligands (1.998–2.037 Å) [11,38,39]. The same region of bond distances around 2.049–2.067 Å are only known from imidazolin-2-ylidene ligands substituted with bulky mesityl or diisopropylphenyl groups in 1,3-position [40]. The six-membered ring substituents are nearly perpendicular to the carbene framework and are oriented 180° to one another. This structural assignment is also in accord with the results from the quantum chemical calculations and experimental NMR data from the original publication, where all carbon atoms are inequivalent both at low temperature (233.15 K) and room temperature [29]. An orientation of the alkyl group in β-position of the substituent to the rhodium atom, which would give stronger and direct asymmetric shielding at the metal center, was not obtained.

In complex **5b** it was possible to lock all relevant rotation axes and to create a relatively rigid structure, which is an indispensable requirement for asymmetric catalysis. The hindered free rotation around the rhodium–carbene carbon and nitrogen-α-carbon bond was proven in the NMR spectrum. In fact, complex **5b** has only C_1-symmetry; thus all carbon atoms of the imidazoline ring, the methyl substituents and the olefinic ligand are magnetically inequivalent. The same was also observed for the hydrogen atoms, except for the regions where free rotation is possible in the molecule, such as for the methyl groups. In the $^{13}C\{^1H\}$ NMR spectrum couples of signals were found with chemical shifts between $\Delta\delta = 0.1$–1.6 ppm. For the ^1H NMR spectrum pairs of signals were found for the backbone of the imidazoline ring, at the α-carbon atoms, and the olefinic protons of the COD ligand, in addition to overlapping multiplets in the aliphatic region. The carbene carbon, which shows only one signal in the $^{13}C\{^1H\}$ NMR spectrum, has a characteristically downfield chemical shift of $\delta = 180.2$ ppm and a coupling constant to the rhodium atom of $J = 51.5$ Hz, and appears in a region similar to less sterically hindered rhodium complexes [24,41].

Similar results were found for complex **5c**. In accordance with the C_1-symmetry of the complex nearly all carbon atoms are magnetically inequivalent, and in the $^{13}C\{^1H\}$ NMR spectrum all carbon atoms appear as pairs: the imidazoline backbone at $\delta = 122.5$; 121.6 ppm, the acetal carbon atoms at $\delta = 102.2$; 102.0 ppm, the β-carbon atoms at $\delta_{Ph} = 81.9$; 80.1; $\delta_H = 73.0$; 72.4 ppm and the α-carbon atoms at $\delta = 58.2$ and 55.9 ppm. An exception is the trivalent carbene carbon atom at $\delta = 183.0$ ppm with a coupling constant of $J = 52.9$ Hz to rhodium(I).

Because of the overlapping of the signals in the aromatic region, it is difficult to predict if the phenyl rings can freely rotate. This should not be possible because of the interactions with the COD ligand. For the acetal phenyl rings and their positions it is not known why free rotation should not be possible, consequently a reduced dataset was obtained. In the ^1H NMR spectrum the chemical shifts for the COD and the protons of the dioxanyl ring also appear as pairs. With exception of the downfield-shifted protons at the α-carbon atoms the signal sets are very similar to the imidazolium salt **2c**. For the ABX-signal sets of the β-methyl groups an asymmetry was observed, i.e., one proton pair is more influenced than the other by the sterically hindered coordination with a geminal ($J_{AB} \approx 12$ Hz) and a vicinal (J_{Ax}, $J_{Bx} = 0$–3 Hz) coupling constant. It is on this basis that the inversion of the six-membered ring from a chair to a twist conformation can be excluded for further informations see the Supporting Information.

The chiral monocarbene complexes **5a**, **5d**, and **5e** were obtained by *in-situ* deprotonation of the corresponding imidazolium salts with lithium-*tert*-butanolate (Scheme 3). To a THF solution of the bis [μ-chloro(η^4-1,5-cyclooctadiene)rhodium(I)] complex was added 3 eq. lithium-*tert*-butanolate, and after 30 min 1.2 eq. of the imidazolium salt **2a** [35], **2d**, and **2e** were added. The carbene complexes **5a**, **5d**, and **5e** were obtained after 3 days of stirring and purification in very high yields. Enders published three unsymmetrical rhodium(I) triazolinylidene complexes, where the triazolinylidene ligand was substituted with one 2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl group [23]. The rhodium complexes were used in asymmetric hydrosilylation reactions with high enantiomerical selectivities (19–44% *ee*).

Complex **5d** shows a similar $^{13}C\{^1H\}$ NMR spectrum compared to **5c** with a chemical shift of $\delta = 182.7$ ppm for the carbene carbon and a rhodium(I) coupling constant of $J = 53$ Hz. Remarkably all 32 aromatic carbon atoms were found as single signals, which shows that all rotations are blocked – an unusually rigid structure for a monodentate NHC ligand. In the ^1H NMR spectrum the signals appear as pairs, except in the aromatic and aliphatic region were an overlap was found. For example the COD ligand, the acetal protons ($\delta = 6.53$ and 6.47 ppm), the protons of the α-positioned carbon atoms ($\delta = 6.05$ and 5.94 ppm), and the in β-position methine groups ($\delta = 5.66$ and 5.56 ppm). The asymmetry of the split ABX-signals of the β-positioned methylene groups is not significantly revealed in the chemical shifts ($\delta_A = 4.75$, and 4.63 and $\delta_B = 4.48$ and 4.35 ppm, respectively), with a large geminal ($J_{AB} \approx 12$ Hz) and a small vicinal coupling. It could not be further resolved due to effects mentioned above.

Complex **5e**, which has only four chiral centers, has the further consequence that in the backbone of the dioxanyl ring an additional phenyl substituent compared to complex **3c** shows a similar basic structure as the latter one in the $^{13}C\{^1H\}$ and ^1H NMR spectra. The carbene carbon atom has a chemical shift of $\delta = 182.5$ ppm and a rhodium(I) coupling constant of $J = 52.9$ Hz.

Complex **5a** shows an extra ordinary solubility in all organic solvents, except in *n*-pentane, analogous to chloro(η^4-1,5-cyclooctadiene)(1,3-dicyclohexylimidazolin-2-ylidene) rhodium(I). The crystallization of this compound was therefore very difficult and single crystals suitable for solid state X-ray analysis could not be obtained. The substituents at the imidazoline ring of compound **5a** two relatively small and compact pinane groups, which have only an *anti*-positioned methyl group in β-position, thus only a small steric interaction with the COD ligand and a low rotation barrier is

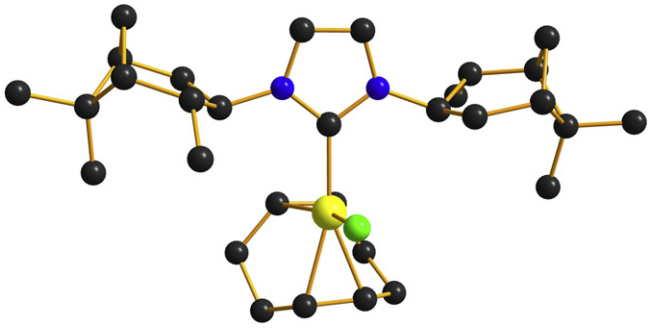
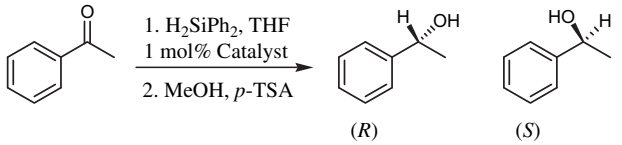


Fig. 2. Ball and Stick model of the most stable conformer of compound **5a** at a computational level of PBE-D/TZVP, hydrogens are omitted for clarity.



Scheme 4. Catalytic hydrosilylation of acetophenone and hydrolysis resulting in 1-phenylethanol.

expected [42]. Surprisingly we found in the $^{13}C\{^1H\}$ NMR spectrum two complete signal sets, where all carbon atoms were magnetically inequivalent, demonstrating that free rotation is not possible in this complex anymore. The reason for this phenomenon could not be definitively resolved here, whether the *β-trans* positioned methyl group, the axial methyl groups at the quarternized carbon atom, or the methylene bridge, which provides a rigid ring. The divalent carbon atom has a chemical shift in the same region as the complexes mentioned above (δ = 182.2 ppm) and a rhodium coupling constant of J = 51.3 Hz. As expected, ^1H NMR spectrum shows no characteristic differences for the inequivalent protons. The two *β-trans* positioned methyl groups can be selected as an example with chemical shifts of δ = 1.33 and 1.24 ppm.

Additionally, we performed DFT-calculations on complex **5a**, to obtain a better understanding of the conformation of the carbene ligand in this complex. The most stable conformation obtained by DFT calculations is depicted in Fig. 2, the methylene moieties of the two substituents at the imidazoline ring are found to be pointing away from the metal center. The other less stable conformations are (3.2 and 4.4 kcal/mol higher in energy compared to the most stable conformer depicted in Fig. 2) the conformer where the methylene moieties are oriented at an angle of 180° with one another, and where both methylene moieties are pointing to the metal center, respectively.

All monocarbene complexes **5a**–**5e** are air-stable in the solid state as well as in solution. Given that high purity is necessary for catalytic applications, in all cases purification was carried out using a 100:1 mixture of methylene chloride/methanol as eluent on a silica column.

2.2. Catalytic hydrosilylation

The chiral carbene complexes **5a**–**5e** were tested for their efficacy in the asymmetric hydrosilylation of ketones. In this reaction the carbonyl compound is typically reacted with diphenylsilane in the presence of a catalyst. In the literature copper complexes substituted with phosphines or NHCs are also used as effective catalysts for this reaction [43]. At the end of the reaction methanol is added in the presence of catalytic amounts of *p*-toluenesulfonic acid to obtain the chiral alcohol (see Scheme 4). Because of the high reactivity of the silane, the reaction can be carried out under low temperatures and in short time. In a side reaction the formation of an enol ether is possible, which will be cleaved after hydrolysis back to the ketone and reduce the yield of this reaction. According to a study carried out by Lappert et al. if acetophenone is used, this enol ether reaction can account for around 30% of the conversion, depending on the catalyst used and temperature [44]. In principle this problem is under control at low temperatures, where the disproportionation of the silane to disilane plays a reduced role. The reactions presented in Tables 2–4 are not optimized and only the temperature was varied. The usual conditions for this reaction were used to obtain datasets, which can be compared with other previous published systems [17]. The quantity of these experiments was chosen to be 3 and 4.5 mmol of the carbonyl compound. The catalyst (**5a**–**5e**) (1 mol%) was added at low temperatures as a THF solution, afterward an equimolar amount of diphenylsilane was added. The reaction was quenched by addition of a 2% *p*-toluenesulfonic acid/methanol solution, and the solvent was removed under vacuum. The determination of the enantiomeric access was carried out on a chiral GC-column.

In general it is proposed that the catalysts, with a general square planar structure used before by Nile [45] and Lappert, stays intact during the whole catalytic cycle and no de-coordination of the COD ligand occurs. Corresponding to a postulated mechanism observed in our group an oxidative addition of the silane at the square planar rhodium(I) complex occurs to form an octahedral moiety, where the COD ligand sterically blocks one side of the complex with high efficiency [17]. A similar coordination mode was published earlier by the group of Nishiyama for the enantionselective hydrosilylation using a bis(oxazolinyl)pyridine rhodium(I) complex [46]. Therefore the coordination of the substrate occurs mainly from the side where the chiral information is located, which could explain why an optical induction was observed.

To compare with other published results acetophenone was used as the initial substrate, yielding optically active 1-phenylethanol. The obtained conversions and enantiomerical excesses are summarized in Table 2.

In complex **5b**, the *β-cis*-positioned isopropyl groups in the cyclohexyl ring are positioned 180° to each other, and the steric interaction with the phenyl group of the substrate kinetically favors the *Si*-side. A methyl group in the same position is not enough to exert chiral induction, as in complex **5a** shown, where only the racemate was obtained. The fact that for complex **5b** an increase from −20 °C to room temperature corresponds to a decrease of the enantiomeric excess by half clearly shows the dominant role of the steric interactions. The enantiomeric excess of 38% at −20 °C and 20% at room temperature are the highest known values for rhodium complexes with non-chelating C_2-symmetrical ligands compared

Table 2
Catalytic hydrosilylation of acetophenone with diphenylsilane and hydrolysis resulting in 1-phenylethanol.

Catalyst	Temperature [°C]	Reaction time [h]	Conversion [%]	Yield [%][a]	*ee* [%]
5a	−20	48	9	7	–
5b	−20	48	29	11	38 (*R*)
5b	25	4.5	18	11	20 (*R*)
5c	−20	48	46	44	14 (*R*)
5d	−20	48	53	49	8 (*S*)
5e	−20	48	34	22	5 (*R*)

[a] Isolated yield after a distillation via a ball condenser.

Table 3
Catalytic hydrosilylation of ethylpyruvate with diphenylsilane and hydrolysis.

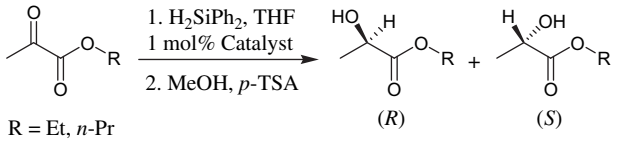
Catalyst	Temperature [°C]	Reaction time [h]	Conversion [%]	Yield [%][a]	*ee* [%]
5a	−20	48	9	4	4 (*S*)
5b	−20	48	62	27	29 (*S*)
5c	−20	48	92	55	72 (*R*)
5c	25	2.5	95	35	60 (*R*)
5d	−20	48	62	33	67 (*R*)

[a] Isolated yield after a distillation via a ball condenser.

Table 4
Catalytic hydrosilylation of *n*-propylpyruvate with diphenylsilane and hydrolysis.

Catalyst	Temperature [°C]	Reaction time [h]	Conversion [%]	Yield [%][a]	*ee* [%]
5b	25	4.5	7	6	9 (*S*)
5c	−20	48	98	66	74 (*R*)
5c	25	1.5	81	49	60 (*R*)
5d	−20	48	51	33	64 (*R*)
5d	25	4	88	48	57 (*R*)
5e	−20	48	49	38	58 (*R*)

[a] Isolated yield after a distillation via a ball condenser.



Scheme 5. Catalytic hydrosilylation of pyruvic acid and hydrolysis resulting in pyruvic acid esters.

with the literature [11,17,22]. For non C_2-symmetrical rhodium complexes with a non-chelating NHC ligand the same or slightly higher *ee*s [20–44%] have been obtained in the past [20d,21b,c]. The highest enantioselectivities are obtained for rhodium complexes with chiral chelating NHC ligands, in these cases up to 99% *ee* was obtained [13d,20a–d,46].

Complexes **5c**–**5e** show up to four times higher yields compared to **5b** but with much lower enantiomeric excess. The *β-trans* positioned phenyl groups increase the sterical bulk of the complexes so much that a specific orientation of the relatively rigid acetophenone, and therefore a kinetic differentiation between the *Re*- and *Si*-sides, is rarely possible. These catalysts might be much more efficient for smaller and less rigid substrates, where the carbonyl function is not in conjugation with an aromatic system. Given this, pyruvic acid ester was used for the next experiments, which could be converted after hydrosilylation and hydrolysis of the silylether to the optically active 2-hydroxypropanoic acid esters (Scheme 5).

This reaction is known since the seventies with chiral phosphine ligands, like BMPP and DIOP, first mentioned by Ojima [47]. The different enantiomeric excess values obtained with the catalysts **5a**–**5d** are summarized in Table 3 for the ethyl ester and in Table 4 for the *n*-propyl ester of pyruvic acid. The *β-cis* positioned methyl group in complex **5a** shows nearly no enantiomeric excess for the catalytic hydrosilylation of ethylpyruvate. For the more sterically protected system **5c**–**5e** higher yields were obtained than for the less demanding complexes **5a** and **5b**.

The trend for the enantiomeric excess is opposite to the results obtained for the hydrosilylation of acetophenone: Complex **5b** still shows a reasonable enantiomeric excess (29%), but it is now much lower than the values obtained with complexes **5c**–**5e**, which increased dramatically. Although the optical induction tends to decrease with the introduction of larger substituents at the backbone of the dioxanyl ring, enantiomeric excesses of around 70% were obtained at −20 °C, and even at room temperature a decrease of only 10% was noted.

The small temperature dependence for the optical induction could be caused by steric and/or different electrostatic interaction in the current complex. Another point is the influence of the substitution pattern of the ligand on the absolute configuration of the product: the catalysts with a *β-cis* positioned allyl group (**5a**, **5b**) provide the opposite enantiomer compared to the *β-trans* positioned phenyl groups of complexes **5c**–**5e**.

The hydrosilylation of *n*-propylpyruvate yields in principle similar results (Table 4), with an unsurprising small increase of the enantiomeric excess. For example, an enantiomeric excess of 74% was obtained at a reaction temperature of −22 °C with complex **5c**. Similar results were found by Ojima with the catalytic systems of bis[μ-chloro(η^4-1,5-cyclooctadiene)rhodium(I)] and BMPP (60% *ee*) and DIOP (76% *ee*) [47]. The yields obtained with **5c** are higher than the results obtained with a monophosphine ligand, and in the same region as for the bidentate ligand DIOP.

3. Conclusions

These results show some of the highest enantiomeric excess values for non-chelating ligands for the catalytic hydrosilylation reaction. A monodentate ligand system is presented that does not necessitate a ligand excess in chiral catalysis, due to the strong metal–carbon (carbene) bond, and which can compete with chelating ligands in terms of *ee* values obtained. These results show the high potential for this C_2-symmetrical ligand system in the broader field of asymmetric catalysis, particularly if non-chelating ligands are necessary for steric or electronic (strong donors) reasons, e.g. for the use as a ligand in a Grubbs-catalyst system.

4. Experimental section

General Considerations. All reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques or in a MBraun glove box containing less than 1 ppm of oxygen and water. Compounds **2a** [35], **2b** [29], **4b** [29], **5b** [29], and bis[μ-ethoxy-(η^4-1,5-COD)rhodium] [48] were prepared according to the literature. Experimental details for the known compounds **1c** [32], **1f** [32], **1g** [32], can be found in the Supporting Information. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a JEOL-JMX-GX 270 or 400 MHz spectrometer at room temperature and referenced to the residual ^{1}H and ^{13}C signals of the solvents. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br. = broad signal. Coupling constants *J* are given in Hz. Elemental analyses were carried out by the Microanalytical Laboratory at the TU München. Enantiomeric excess was determined with a Chrompack CP9000 gas chromatograph using a Lipodex A and Lipodex D column from Macherey–Nagel and a FID detector. Starting at 40 °C for 20 min, ramp in 20 min from 40 to > 80 °C, and hold at 80 °C.

4.1. (2R,4S,5S)-5-Amino-2-(1-naphthyl)-4-phenyl-1,3-dioxacyclohexane (**1d**)

Analogous to the preparation procedure of **1c**, (1*S*,2*S*)-2-amino-1-phenyl-1,3-propandiol hydrobromide (**c**) (11.1 g, 44.7 mmol) was dissolved in 75 mL freshly distilled 1-naphthaldehyde and under stirring phosphorus(V) oxide (15 g, 105.7 mmol) was added in small portions. Because the aldehyde can not be removed under mild conditions directly a steam distillation was carried out at 180 °C. The mother liquor was extracted with diethyl ether, and the ether phase was treated with glacial acidic acid. The organic phase was washed ten times with 30 mL water and the water phases were combined and a mixture of KOH and K_2CO_3 was added until an alkaline pH-value was obtained. The water phase was extracted with $CHCl_3$. At this stage the side product (imine) precipitates as a white solid, which can be recycled to the corresponding amine by the addition of acidic or formic acid in a THF/water solution. The organic phases are combined and dried over $MgSO_4$, the solvent was removed in vacuum afterward. The yield was 5.3 g of a high viscous yellow oil, which precipitates slowly under air. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19–7.28 (12H, m), 6.31 (1H, s, *CH*(OR)$_2$), 5.29 (1H, d, J_{HH} = 1.1 Hz, *H*CPh), 4.45 and 4.41 (2H, ABX-system, J_{AB} = 11.4 Hz, J_{Ax} = 2.2 Hz, J_{Bx} = 1.5 Hz, C*H*$_2$), 3.03 (1H, m, *H*CNH$_2$), 1.54 (2H, br., N*H*$_2$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 139.0, 133.8, 133.4, 130.6 (CC_{Ar}), 129.6, 128.6, 128.6, 128.5, 127.6, 126.3, 125.6, 125.6, 125.5, 125.1, 124.1, 123.9 (CH_{Ar}), 100.5 (*O*CO), 81.7 (*C*H$_2$), 73.3 (*C*Ph), 50.0 (*C*NH$_2$).

4.2. (4S,5S)-5-Amino-2,2,4-triphenyl-1,3-dioxacyclohexane (**1e**)

Water-free aluminum chloride (25.5 g, 191.3 mmol) was dissolved under ice cooling in 100 mL of acetonitrile. The cold bath was removed and in small portions (1*S*,2*S*)-2-amino-1-phenyl-1,3-propandiol (**c**) (15.3 g, 91.6 mmol) was added. A solution of benzophenone (19.6 g, 107.7 mmol) in 50 mL of dry acetonitrile was

slowly added. The mixture was sealed and stirred for 11 days, added to a mixture of crushed ice (500 g) and 50 g of K_2CO_3. The mixture was stirred until the ice melted and filtered to remove the aluminum salts. The solid was washed with acetonitrile and the combined filtrates were extracted six times with 50 mL diethyl ether, and the organic phase was dried with $MgSO_4$. The solvent was removed in vacuum and the residue was redissolved with 100 mL diethyl ether. The organic phase was extracted six times with 40 mL of a 10% acidic acid solution, and to the water phase were added KOH and K_2CO_3 until an alkaline pH-value was obtained. The water phase was extracted four times with 50 mL of $CHCl_3$. To the organic phase was added $MgSO_4$, the solid was filtered off and the solvent was removed to obtain a high viscous yellow oil in 3% yield (950 mg, 2.87 mmol), which precipitates slowly under air. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.21 (15H, m), 5.09 (1H, d, J_{HH} = 1.8 Hz, *H*CPh), 4.31 and 4.12 (2H, ABX-system, J_{AB} = 11.4 Hz, J_{Ax} = 2.2 Hz, J_{Bx} = 1.8 Hz, C*H*$_2$), 2.79 (1H, m, *H*CNH$_2$), 1.66 (2H, br., NH$_2$).

4.3. 1,3-Di-[(2R,4S,5S)-2,4-diphenyl-1,3-dioxacyclohex-5-yl] imidazolium perchlorate (**2c**)

To a solution of (1.96 g, 7.7 mmol) (*2R,4S,5S*)-5-Amino-2,4-diphenyl-1,3-dioxacyclohexane **1c**, paraformaldehyde (117 mg, 3.9 mmol), 3.3 N perchloric acid (1.2 mL, 4.0 mmol) and a 40% aqueous glyoxal solution (1.2 mL, 10.5 mmol) was reacted in 10 mL of toluene. After the addition of the glyoxal solution an additional 2 mL of water were added to obtain a stirrable solution. To the aqueous phase were added 50 mL of diethyl ether and 25 mL of a concentrated Na_2CO_3 solution. The white slime was washed twice with diethyl ether (20 mL). The extract was dried over Na_2SO_4, and afterward the solvent was removed and the residue was recrystallized from CH_2Cl_2 with a methanol/diethyl ether solution. The yield was 947 mg (1.47 mmol, 38%) of a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (1H, s, NC*H*N), 7.55–7.01 (22H, m, C*H*$_{Ar}$ and NC*H*), 5.87 (2H, s, C*H*(OR)$_2$), 5.47 (2H, d, J_{HH} = 2.2 Hz, *H*CPh), 4.80 (2H, m, *H*CNR$_2$), 4.60 and 4.38 (4H, ABX-system, J_{AB} = 13.2 Hz, J_{Ax} = 2.6 Hz, J_{Bx} = <1 Hz, C*H*$_2$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 136.7, 135.3 (*C*C$_{Ar}$), 136.6 (*C*HCN), 129.3, 128.8, 128.5, 128.4, 125.9, 124.4 (*C*H$_{Ar}$), 122.0 ((*C*H)$_2$), 101.7 (*O*CO), 78.3 (*C*Ph), 69.4 (*C*H$_2$), 57.3 (*C*NR$_2$); anal. calcd. for $C_{35}H_{33}N_2O_8Cl$ (645.1 g mol^{-1}): C 65.16; H 5.16; N 4.34; found: C 64.92; H 5.16; N 4.29.

4.4. 1,3-Di-[(2R,4S,5S)-2-(1-naphthyl)-4-phenyl-1,3-dioxacyclohex-5-yl]imidazolium perchlorate (**2d**)

Analogous to the preparation procedure of **2c** were used 1.36 g (4.5 mmol) (*2R,4S,5S*)-5-amino-2-(1-naphthyl)-4-phenyl-1,3-dioxacyclohexane (**1d**), paraformaldehyde (68 mg, 2.3 mmol), 3.3 N perchloric acid (0.65 mL, 2.2 mmol) and a 40% aqueous glyoxal solution (0.4 mL, 3.5 mmol) were stirred in 5 mL of toluene. After the addition of the acid additional water and CH_2Cl_2 were added to obtain a stirrable solution. For the workup of the gummy light brown precipitate, which was formed after addition of 50 mL diethyl ether and 25 mL of a concentrated K_2CO_3 solution, it was dissolved in a mixture of CH_3Cl, CH_2Cl_2, methanol and water. The solvent was removed and a light colored precipitate was formed in the water phase, which was washed with diethyl ether and dried afterward under vacuum. The yield was 618 mg (0.83 mmol, 39%) of a light brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.83 (1H, s, NC*H*N), 7.93–7.02 (26H, m, C*H*$_{Ar}$ and NC*H*), 6.44 (2H, s, C*H*(OR)$_2$), 5.61 (2H, d, J_{HH} = 1.1 Hz, *H*CPh), 4.91 (2H, m, *H*CNR$_2$), 4.74 and 4.45 (4H, ABX-system, J_{AB} = 12.8 Hz, J_{Ax} = 1.8 Hz, J_{Bx} = <1 Hz, C*H*$_2$); ^{13}C{^{1}H} NMR (67 MHz, $CDCl_3$): δ = 136.6 (*C*HCN), 135.3, 133.6, 131.9, 130.3, 130.0, 128.8, 128.7, 128.3, 126.6, 125.9, 125.6, 125.6, 125.0, 124.6, 123.3, 123.1 (*C*$_{Ar}$), 122.0 ((*C*H)$_2$), 99.6 (*O*CO), 78.3 (*C*Ph), 69.5 (*C*H$_2$), 57.5 (*C*NH$_2$).

4.5. 1,3-Di-[(4S,5S)-2,2,4-triphenyl-1,3-dioxacyclohex-5-yl] imidazolium perchlorate (**2e**)

Analogous to the preparation procedure of **2c** were used 950 mg (2.9 mmol) (*4S,5S*)-5-amino-2,2,4-triphenyl-1,3-dioxacyclohexane (**1e**), paraformaldehyde (41 mg, 1.4 mmol), 3.3 N perchloric acid (0.39 mL, 1.29 mmol) and a 40% aqueous glyoxal solution (0.25 mL, 2.2 mmol) were stirred in 5 mL of toluene. To the aqueous phase were added 25 mL diethyl ether and 25 mL of a concentrated K_2CO_3 solution. The white precipitate was washed twice with diethyl ether (15 mL) and dried in vacuum. The yield was 252 mg (0.32 mmol, 26%) of a light brown solid. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.70 (1H, s, NC*H*N), 7.66–7.05 (32H, m, C*H*$_{Ar}$ and NC*H*), 5.38 (2H, m, *H*CPh), 4.56 (2H, m, *H*CNR$_2$), 4.51 and 4.22 (4H, ABX-system, J_{AB} = 12.9 Hz, J_{Ax} = 2.2 Hz, J_{Bx} = n/a, C*H*$_2$).

4.6. 1,3-Di-[(2R,4S,5S)-2,4-diphenyl-1,3-dioxacyclohex-5-yl] imidazolin-2-ylidene (**4c**)

In a mixture of 80 mL of liquid ammonia and 20 mL of THF 1.87 g (2.9 mmol) 1,3-di-[(*2R,4S,5S*)-2,4-diphenyl-1,3-dioxacyclohex-5-yl] imidazolium perchlorate (**2c**) and 285 mg (11.9 mmol) of NaH was added. The solvent was removed in vacuo and the residue was extracted with 20 mL *n*-hexane and 20 mL THF. The solvent was removed in vacuo to obtain a pale yellow solid in 95% yield (1.50 g, 2.75 mmol). ^{13}C{^{1}H} NMR (100 MHz, THF-d$_8$): δ = 212.3 (NCN), 139.4, 138.8 (*C*C$_{Ar}$), 129.6, 129.0, 127.2, 127.0, 126.2, 124.9 (*C*H$_{Ar}$), 121.0 ((*C*H)$_2$), 101.6 (*O*CO), 79.8 (*C*Ph), 69.7 (*C*H$_2$), 57.4 (*C*NR$_2$).

4.7. Chloro (η^4-1,5-cyclooctadiene)(1,3-di-[(1R,2R,3R,5S)-2,6,6-trimethylbicyclo[3.1.1]hept-3-yl] imidazolin-2-ylidene) rhodium(I) (**5a**)

A solution of 399 mg (0.81 mmol) bis[μ-chloro(η^4-1,5-cyclooctadiene)rhodium(I)] in 20 mL THF was cooled to −78 °C and 179 mg (2.24 mmol) lithium *tert*-butanolate was added and stirred for 30 min. Afterward 860 mg (1.95 mmol) 1,3-di-[(1*R*,2*R*,3*R*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]hept-3-yl]imidazolium perchlorate (**2a**) was added. The mixture was stirred for 3 days at room temperature, the solvent was removed in vacuo, and the precipitate was purified by column chromatography ($R_f \approx 0.8$) and dried in vacuo. Yield: 773 mg (1.32 mmol, 81%) of a light yellow powder. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.01 (1H, d, J_{HH} = 9.3 Hz, NC*H*CHN), 7.00 (1H, d, J_{HH} = 9.3 Hz, NC*H*CHN), 5.86 (2H, m, *H*CNR$_2$), 5.03 (2H, m, C*H*), 3.51 (1H, m, C*H*), 3.40 (1H, m, C*H*), 3.19, 2.68, 2.54–1.83, 1.58, 1.04 (22H, m, C*H*, C*H*$_2$), 1.39 (3H, d, J_{HH} = 6.9 Hz, C*H*$_3$), 1.30 (6H, s, C(C*H*$_3$)$_2$), 1.28 (6H, s, C(C*H*$_3$)$_2$), 1.24 (3H, d, J_{HH} = 7.2 Hz, C*H*$_3$); ^{13}C{^{1}H} NMR (68 MHz, $CDCl_3$): δ = 182.2 (d, J = 51.3 Hz, N*C*N), 118.3, 118.1 ((*C*H)$_2$), 98.2 (d, J = 6.7 Hz, *C*H), 97.5 (d, J = 7.3 Hz, *C*H), 67.8 (d, J = 14.5 Hz, *C*H), 67.0 (d, J = 14.5 Hz, *C*H), 60.3, 60.0 (*C-3*), 48.5, 48.0 (*C-2*), 45.9, 43.8 (*C-4*), 41.8, 41.7 (*C-6*), 39.1, 39.0 (*C-7*), 38.3, 38.2 (*C-1*), 35.7, 34.9 (*C-5*), 33.0, 28.8, 28.7 (*C*H$_2$), 28.2, 27.9, 23.5, 23.2, 21.1, 21.0 (*C*H$_3$); anal. calcd. for $C_{31}H_{48}N_2ClRh$ (587.08 g mol^{-1}): C 63.42, H 8.24, N 4.77; found: C 63.41, H 8.20, N 4.59.

4.8. Chloro (η^4-1,5-cyclooctadiene)(1,3-di-[(2R,4S,5S)-2,4-diphenyl-1,3-dioxacyclohex-5-yl]imidazolin-2-ylidene) rhodium(I) (**5c**)

A solution of 457 mg (0.93 mmol) bis[μ-chloro(η^4-1,5-cyclooctadiene)rhodium(I)] in 20 mL THF was cooled to −78 °C and a solution of 1.02 g (1.87 mmol) 1,3-di-[(*2R,4S,5S*)-2,4-diphenyl-1,3-dioxacyclohex-5-yl]imidazolin-2-ylidene (**4c**) in 10 mL of THF was added. The solution was stirred for 45 min and at the beginning

a visible color change occurred. Afterward the solvent was removed in vacuo. The precipitate was purified by column chromatography ($R_f \approx 0.15$), and crystallized from a CH_2Cl_2/diethyl ether solution. Yield: 555 mg (0.70 mmol, 38%) of light yellow rectangular crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.18 (22H, m, C*H*$_{Ar}$ and NC*H*), 5.97 (1H, s, C*H*(OR)$_2$), 5.95 (1H, m, *H*CNR$_2$), 5.86 (1H, s, C*H*(OR)$_2$), 5.78 (1H, m, *H*CNR$_2$), 5.55 (1H, d, J_{HH} = 2.6 Hz, *H*CPh), 5.39 (1H, d, J_{HH} = 2.6 Hz, *H*CPh), 5.07 (1H, m, C*H*), 4.75 (1H, m, C*H*), 4.65 and 4.29 (2H, ABX-system, J_{AB} = 12.1 Hz, J_{Ax} = 2.6 Hz, J_{Bx} = 2.2 Hz, C*H*$_2$), 4.43 and 4.28 (2H, ABX-system, J_{AB} = 12.4 Hz, J_{Ax} = 2.6 Hz, J_{Bx} = n/a, C*H*$_2$), 2.52 (1H, m, C*H*), 2.43 (1H, m, C*H*), 2.20–1.59 (8H, m, C*H*$_2$); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ = 183.0 (d, J = 52.9 Hz, NCN), 137.7, 137.6, 137.6, 135.3 (C*C*$_{Ar}$), 129.3, 129.0, 128.5, 128.5, 128.5, 128.3, 127.9, 126.8, 126.1, 126.0, 126.0, 126.0 (*C*H$_{Ar}$), 122.5, 121.6 ((NCH)$_2$), 102.2, 102.0 (OCO), 98.6 (d, J = 7.3 Hz, *C*H), 98.1 (d, J = 6.7 Hz, *C*H), 81.9, 80.1 (*C*Ph), 73.0, 72.4 (*C*H$_2$), 69.3 (d, J = 14.5 Hz, *C*H), 66.0 (d, J = 14.5 Hz, *C*H), 58.2, 55.9 (*C*NR$_2$), 34.6, 31.5, 30.2, 27.4 (*C*H$_2$); anal. calcd. for $C_{43}H_{44}N_2O_4ClRh \bullet 0.33\ CH_2Cl_2$ (819.49 g mol^{-1}): C 63.51, H 5.49, N 3.42; found: C 63.40, H 5.51, N 3.43.

4.9. Chloro (η^4-1,5-cyclooctadiene)(1,3-di-[(2*R*,4*S*,5*S*)-2-(1-naphthyl)-4-phenyl-1,3-dioxacyclohex-5-yl]imidazolin-2-ylidene) rhodium(I) (**5d**)

A solution of 160 mg (0.32 mmol) bis[μ-chloro(η^4-1,5-cyclooctadiene)rhodium(I)] in 12 mL of THF was cooled to −78 °C and 83 mg (1.04 mmol) lithium-*tert*-butanolate was added and stirred for 30 min. Afterward 550 mg (0.74 mmol) 1,3-di-[(2*R*,4*S*,5*S*)-2-(1-naphthyl)-4-phenyl-1,3-dioxacyclohex-5-yl]imidazolium perchlorate (**2d**) was added and a color change from orange to yellow occurred. The mixture was stirred for 3 days at room temperature, the solvent was removed in vacuo and the precipitate was purified by column chromatography ($R_f \approx 0.2$) and dried in vacuo. Yield: 294 mg (0.33 mmol, 51%) of a light yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12–7.22 (26H, m, C*H*$_{Ar}$ and NC*H*), 6.53 (1H, s, C*H*(OR)$_2$), 6.47 (1H, s, C*H*(OR)$_2$), 6.05 (1H, m, *H*CNR$_2$), 5.94 (1H, m, *H*CNR$_2$), 5.66 (1H, m, *H*CPh), 5.56 (1H, m, *H*CPh), 5.22 (1H, m, *C*H), 4.93 (1H, m, *C*H), 4.75 and 4.48 (2H, ABX-system, J_{AB} = 12.4 Hz, C*H*$_2$), 4.63 and 4.35 (2H, ABX-system, J_{AB} = 12.1 Hz, C*H*$_2$), 2.63 (1H, m, C*H*), 2.54 (1H, m, C*H*), 2.37–1.75 (8H, m, C*H*$_2$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 182.7 (d, J = 53.0 Hz, NCN), 137.5, 137.4, 135.2, 133.5, 133.4, 132.7, 132.6, 130.2, 130.2, 129.7, 129.7, 129.5, 128.7, 128.6, 128.4, 128.3, 128.1, 127.9, 127.7, 126.5, 126.3, 126.2, 125.8, 125.8, 125.6, 125.5, 125.0, 124.9, 123.3, 123.2, 123.0, 122.9 (C$_{Ar}$), 122.3, 121.5 ((NCH)$_2$), 99.6, 99.2 (OCO), 98.4 (d, J = 6.1 Hz, *C*H), 97.9 (d, J = 6.1 Hz, *C*H), 81.7, 79.7 (*C*Ph), 72.8, 72.2 (*C*H$_2$), 69.2 (d, J = 13.8 Hz, *C*H), 65.9 (d, J = 14.6 Hz, *C*H), 58.1, 55.6 (*C*NH$_2$), 34.5, 31.3, 30.1, 25.4 (*C*H$_2$); anal. calcd. for $C_{51}H_{48}N_2O_4ClRh \cdot 0.15\ CH_2Cl_2$ (904.05 g mol^{-1}): C 67.96, H 5.38, N 3.10; found: C 67.93, H 5.70, N 2.92.

4.10. Chloro (η^4-1,5-cyclooctadiene)(1,3-di-[(4*S*,5*S*)-2,2,4-triphenyl-1,3-dioxacyclohex-5-yl] imidazolin-2-ylidene) rhodium(I) (**5e**)

A solution of 68 mg (0.14 mmol) bis[μ-chloro(η^4-1,5-cyclooctadiene)rhodium(I)] in 7 mL of THF was cooled to −78 °C and 34 mg (0.43 mmol) lithium *tert*-butanolate was added and stirred for 30 min. Afterward 243 mg (0.31 mmol) of 1,3-di-[(4*S*,5*S*)-2,2,4-triphenyl-1,3-dioxacyclohex-5-yl]imidazolium perchlorate (**2e**) was added and a color change from orange to yellow occurred. The mixture was stirred for 3 days at room temperature, the solvent was removed in vacuo, and the precipitate was purified by column chromatography ($R_f \approx 0.5$) and dried in vacuo. Yield: 138 mg (0.15 mmol, 48%) of a light yellow powder. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.79–7.21 (32H, m, C*H*$_{Ar}$ and NC*H*), 5.85 (1H, m, *H*CNR$_2$), 5.68 (1H, m, *H*CNR$_2$), 5.54 (1H, m, *H*CPh), 5.43 (1H, m, *H*CPh), 4.99 (1H, m, *C*H), 4.71 (1H, m, *C*H), 4.65 and 4.17 (2H, ABX-system, J_{AB} = 12.1 Hz, C*H*$_2$), 4.49 and 4.12 (2H, ABX-system, J_{AB} = 12.2 Hz, C*H*$_2$), 2.52 (1H, m, C*H*), 2.34 (1H, m, C*H*), 2.17–1.55 (8H, m, C*H*$_2$); ^{13}C {^{1}H} NMR (68 MHz, $CDCl_3$): δ = 182.5 (d, J = 52.9 Hz, NCN), 143.8, 143.6, 139.1, 139.0, 137.8, 135.6 (C*C*$_{Ar}$), 129.2, 129.0, 129.0, 128.5, 128.3, 128.3, 128.3, 128.2, 128.1, 127.9, 127.8, 127.6, 126.8, 126.6, 126.1, 125.2, 124.9, 124.9 (*C*H$_{Ar}$), 122.5, 121.4 ((NCH)$_2$), 102.1 (OCO), 98.4 (d, J = 7.3 Hz, *C*H), 98.0 (d, J = 6.7 Hz, *C*H), 75.0, 73.5 (*C*Ph), 69.0 (d, J = 14.0 Hz, *C*H), 67.5, 66.7 (*C*H$_2$), 65.9 (d, J = 14.5 Hz, *C*H), 58.0, 56.1 (*C*NH$_2$), 34.4, 31.4, 30.0, 27.3 (*C*H$_2$); anal. calcd. for $C_{55}H_{52}N_2O_4ClRh \cdot 0.66\ CH_2Cl_2$ (999.99 g mol^{-1}): C 66.86, H 5.38, N 2.80; found: C 66.94, H 5.80, N 2.63.

5. Theoretical section

All calculations were performed with the Turbomole-6.0 [49] set of program systems. Throughout density functional theory was employed. The geometries of the molecules were optimized with the PBE (Perdew, Burke, Ernzerhof) functional [50]. As a basis set the triple-ζ-quality basis set of Ahlrichs et al. was used exclusively [51]. Further corrections for the dispersion energies were added, in order to account properly for the different *van der Waals* interactions among the phenyl groups and with the chlorine at the transition metal center. The dispersion corrections were performed according to the approach of Grimme et al. [52] Overall this computational level is denoted as PBE-D/TZVP. The vibrational calculations were carried out with numerical derivatives. All energy minima are derived without symmetry constraints and are characterized according to their vibrational frequencies. The chosen grid-size is m = 4 and the scf accuracy is scfconv = 7.

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Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.04.001.

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