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ABSTRACT: Chiral square-planar Rh(I) complexes based on new C_2-symmetric NHC ligands have been synthesized selectively in a few steps as single diastereoisomers. These chiral pre-catalysts were applied to the asymmetric transfer hydrogenation of 1-phenylpropanone and to the 1,2-addition of arylboronic acids to aldehydes. We demonstrated a proper functionalization of the aromatic rings connected to the nitrogen atoms of the NHC ligand improved significantly the asymmetric induction of the chiral Rh(I) NHC catalysts. Bulky substituents allowed a better control of the steric features of the catalyst quadrants because they behaved as conformational and chirality relays of the NHC chiral backbone.

INTRODUCTION

N-heterocyclic carbenes (NHCs) have been used as ligands in transition metal complexes for several decades.[1] Numerous studies on synthesis, coordination and reactivity of NHC ligands resulted in significant applications in homogeneous catalysis for various chemical transformations in racemic and asymmetric series.[2] During the past two decades, chiral monodentate C_2-symmetric *N*-heterocyclic carbene ligands were prepared according to three strategies: the use of chiral *N*-substituents (Figure 1, **A**), the synthesis of rigid tricyclic NHCs (Figure 1, **B**) and the use of chiral amine backbones (Figure 1, **C**).[2]

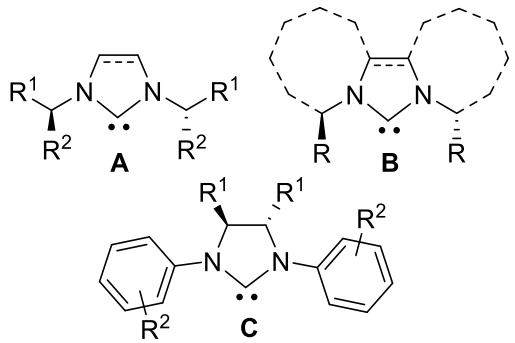


Figure 1. General structures of chiral monodentate C_2-symmetric *N*-heterocyclic carbene (NHC) ligands.

NHC ligands of type **C** draw a parallel with the stereochemical model of BINAP ligand. Because the point chirality is far from the NHC coordination center, it does not have a significant influence on a chemical reaction. However, the conformation of the aromatic *N*-substituents can be controlled provided the rotation around the C–N-bond is restricted by ortho substituents on the aryls (Figure 2).[3]

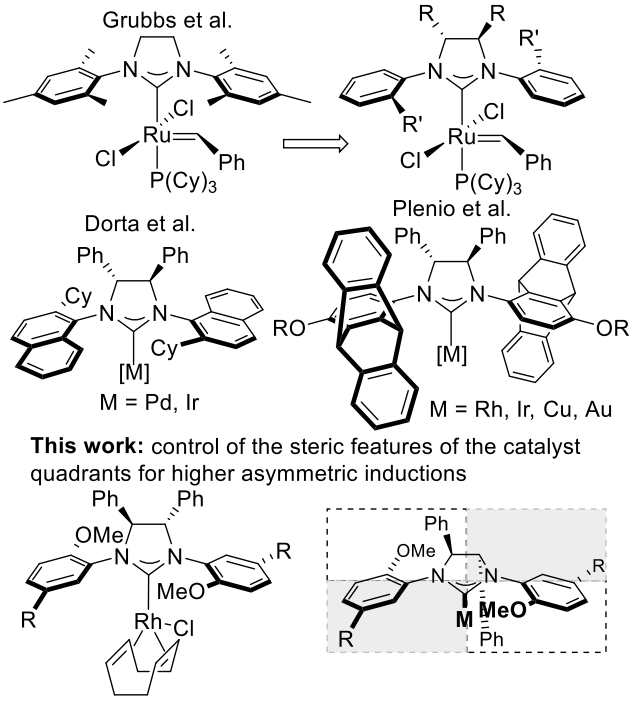


Figure 2. Examples of catalysts based on monodentate C_2-symmetric NHC ligands with chiral amine backbones.

Following the pioneering work of Grubbs et al. (Figure 2) for the first enantioselective ruthenium catalyzed olefin metathesis in the desymmetrization of achiral trienes,[3] chiral NHC based catalysts have been developed for various organic reactions using well-defined organometallic species[4] or one-pot procedures.[5] In recent reports, steric fine tuning of such chiral NHC ligands has been investigated through a modular strategy and proved to be determining. Indeed, Dorta et al. have developed chiral NHC ligands substituted by naphthyl wingtips for effective Pd catalyzed cross-couplings and Ir catalyzed hydroamination reactions (Figure 2).[4h-j,4m] At the meantime, Plenio et al. have reported chiral NHC ligands based on bulky triptycene are useful in the Cu catalyzed enantioselective borylation of α,β-unsaturated esters (Figure 2).[4k] Herein, we report on the design and development of new C_2-symmetric NHC ligands based on a chiral diphenylethylene diamine backbone (Figure 2). The resulting pure diastereomeric Rh(I) complexes were applied to the asymmetric transfer hydrogenation of ketones and to the 1,2-addition of arylboronic acids to aldehydes. Along our study, we demonstrated a proper functionalization of the aromatic rings connected to the nitrogen atoms improved the asymmetric induction of the enantiomerically pure NHC ligand. Because bulky substituents behaved as conformational and chirality relays of the NHC chiral backbone, the use of sterically demanding groups allowed a better control of the steric features of the catalyst quadrants.[6]

RESULTS AND DISCUSSIONS

The NHC ligand synthesis started by a double Buchwald-Hartwig amination reaction[7] using (*S*,*S*)-diphenylethylenediamine (DPEN) and one of the substituted 1-bromo-2-methoxy-benzene **1a-e** previously prepared[8] (Schemes 1, S1). The resulting secondary diamines **2a-e** were isolated in good to high yields (e.g. 66-98%) after purification by flash chromatography. The molecular structures of **2a-e** were consistent with their elemental analyses, mass and NMR spectra. The corresponding dihydroimidazolium salts **3a-e** were prepared as pure diastereoisomers in 69% to quantitative yields by reacting amines **2a-e** with excess of triethylorthoformate and tetrafluoroborate ammonium (Scheme 1). Salts **3a-e** were characterized by their elemental analyses, mass and NMR spectra. The identifications of the CH units between the N atoms are of particular significance in the cations **3a-e** as their ^{1}H and ^{13}C signals are observed respectively around δ8.9 ppm and 158 ppm which is typical of such dihydroimidazolium salts. Afterwards, Rh(I) complexes **4a-e** were prepared in two steps. At first, pure diastereomeric salts **3a-e** were allowed to react with Ag(I) oxide in acetonitrile at 60 °C for 24 hours (Scheme 1). Second, the resulting Ag(I) complexes reacted subsequently with $[Rh(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) without any purification, through transmetallation in dichloromethane for 64 hours (Scheme 1). The resulting Rh(I) complexes **4a-e** were isolated as pure diastereoisomers in average to high yields (56-90%) after purification by flash chromatography and recrystallization. They were characterized by their elemental analyses, mass and NMR spectra. The ^{13}C NMR resonances of the carbene carbon nuclei were observed at δ 212-213 ppm with coupling constants *J*(Rh,C) of 46-47 Hz and confirmed the formation of the carbene complexes. Because the rotation around the Rh-C axis was restricted by the steric hindrance, ^{13}C and ^{1}H NMR spectra indicated all the atoms were inequivalent. Single crystals of Rh(I) complex **4d** were obtained by slow evaporation of a chloroform/n-hexane mixture. According to an X-ray diffraction analysis, complex **4d** crystallized in an orthorhombic crystal system with a $P2_12_12_1$ space group and a Flack parameter of -0.045(12). The ORTEP of **4d** comprised two independent Rh complexes·and one molecule of n-pentane (Figure 3, Figure S1, Table S1). Each central Rh atom adopted a square planar coordination geometry, being coordinated to the chloride, the 1,5-cyclooctadiene and the carbene ligand without any crystallographic mirror plane bisecting the molecule in the Cl-Rh-C(NHC) plane (Figure 3). The measured distances of 1.991(6) Å (Figure 3) and 2.007(6) Å (Figure S1) between the Rh and carbon of the carbene proved to be similar to the 2.02-2.07 Å usually measured for unsaturated[10] and saturated[11] carbene ligands.

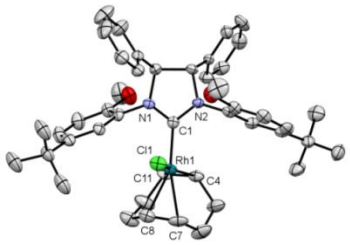


Figure 3. ORTEP of compound (S_a,S_a,*R*,*R*)-**4d·(0.5 n-pentane):** at the 50% probability level. One complex, one pentane molecule and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Rh1-Cl1 = 2.3767(15), Rh1-C1 = 1.991(6), Rh1-C7 = 2.226(7), Rh1-C8 = 2.205(7), Rh1-C4 = 2.091(6), Rh1-C11 = 2.3767(15), N1-C1 = 1.344(7), N2-C1 = 1.354(8), C7-C8 = 1.354(10), C4-C11 = 1.384(9), N1-C1-N2 = 106.4(5), N1-C1-Rh1 = 124.0(5), N2-C1-Rh1 = 129.6(4), C1-Rh1-Cl1 = 90.1(16). CCDC 1848614.[9]

The isolated NHC Rh(I) complexes **4a-e** were then applied as pre-catalysts in two asymmetric organic reactions. At first, we studied the asymmetric transfer hydrogenation of propiophenone to 1-phenylpropanol **5** as such a reaction was often studied applying chiral NHC Rh(I) complexes as catalysts (Table 1).[10,12] While using 5 mol% of KO*t*Bu as a base in *i*PrOH at 80 °C, the pre-catalysts **4a-b** substituted respectively by H and Me at the meta position of each 2-MeO-aromatic unit led to average to good yields of secondary alcohol **5** along with low enantiomeric excess (Ee) (entries 1,2). If complex **4c** bearing cyclohexyl substituents led to poor results (entry 4), the use of complex **4d** holding bulky *t*Bu groups afforded product **5** in a high yield with a 49% Ee (entry 5). Complex **4e** bearing adamantyl substituents allowed a further increase of the steric hindrance and led to secondary alcohol **5** in high yield with an improved 60% Ee (entry 7). Hence, the results demonstrated the use of sterically demanding substituents allowed a better control of the Rh catalyst quadrants as they acted as conformational and chirality relays of the chiral DPEN backbone. Finally, a slight increase of Ee was observed through the use of 10 mol% of *t*BuOK. Indeed, it is well established the transfer hydrogenation of ketones depends on the nature and amount of the base co-catalyst (entries 8-10).[10c] In order to check if catalysts were decomposing along the reactions, Hg(0) trapping experiments were performed (entries 3, 6). While decreases of yield and Ee were observed for catalyst **4b**, the reaction was almost quenched using catalyst **4d**.

Scheme 1. Synthesis of the dihydroimidazolium salts **3a-e** and the Rh(I) complexes **4a-e**.

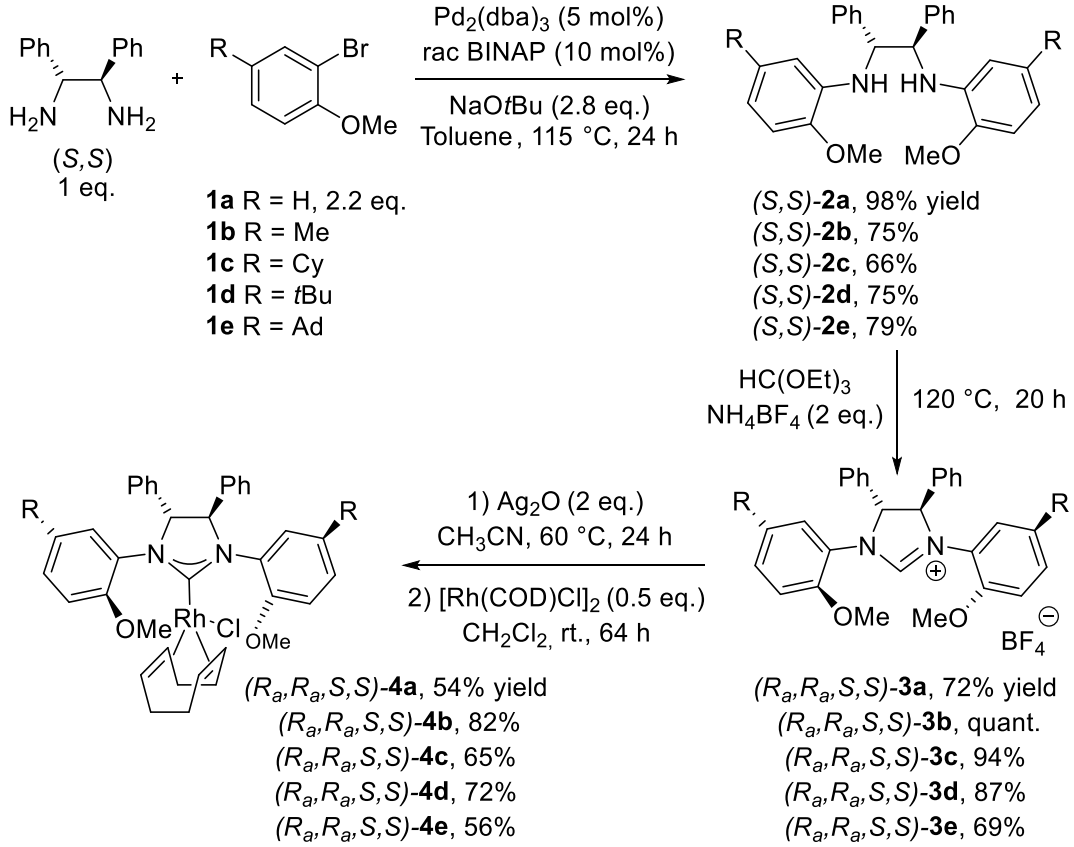
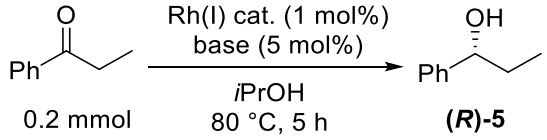


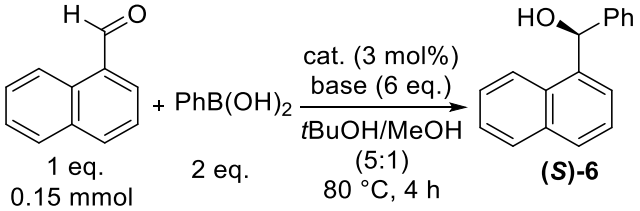
Table 1. Rh(I) catalyzed transfer hydrogenation of propiophenone to 1-phenylpropanol **5**.



Entry	Pre-catalyst	Base	Yield (%)[a]	Ee (%)[b]
1	(*Ra,Ra,S,S*)-**4a**	*t*BuOK (5)	47	8
2	(*Ra,Ra,S,S*)-**4b**	*t*BuOK (5)	80	13
3[c]	(*Ra,Ra,S,S*)-**4b**	*t*BuOK (5)	65	3
4	(*Ra,Ra,S,S*)-**4c**	*t*BuOK (5)	6	-
5	(*Ra,Ra,S,S*)-**4d**	*t*BuOK (5)	99	49
6[c]	(*Ra,Ra,S,S*)-**4d**	*t*BuOK (5)	7	-
7	(*Ra,Ra,S,S*)-**4e**	*t*BuOK (5)	95	60
8	(*Ra,Ra,S,S*)-**4d**	*t*BuOK (10)	99	53
9	(*Ra,Ra,S,S*)-**4d**	*t*BuONa (10)	8	-
10	(*Ra,Ra,S,S*)-**4d**	KOH (10)	85	21

[a] Typical experiments are provided. Yields measured by GC. [b] Ee values measured by HPLC. [c] in presence of one Hg(0) drop.

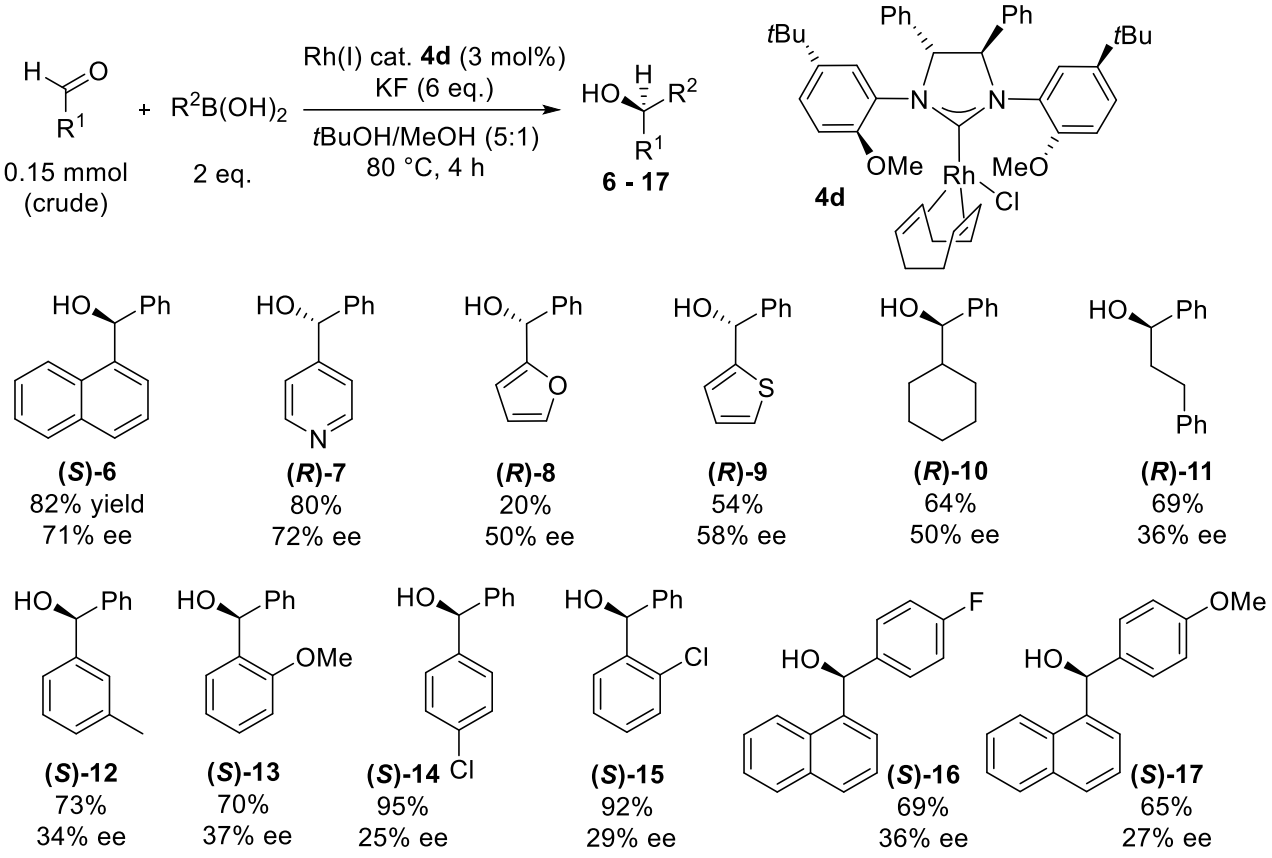
Table 2. Rh(I) catalyzed 1,2-addition of phenylboronic acid to 1-naphtaldehyde.



Entry	Pre-catalyst	Base (eq.)	Yield (%)[a]	Ee (%)[b]
1	(*Ra,Ra,S,S*)-**4a**	KF (6)	54	17
2[d]	(*Ra,Ra,S,S*)-**4b**	KF (6)	89	2
3	(*Ra,Ra,S,S*)-**4c**	KF (6)	77	21
4[c]	(*Ra,Ra,S,S*)-**4d**	KF (6)	82	71
5	(*Ra,Ra,S,S*)-**4e**	KF (6)	56	59
6	(*Ra,Ra,S,S*)-**4d**	*t*BuOK (2)	12	-
7	(*Ra,Ra,S,S*)-**4d**	AgF (2)	0	-
8	(*Ra,Ra,S,S*)-**4d**	KF (2)	84	45

[a] Typical experiments are provided. Isolated yields. [b] Ee values measured by HPLC. [c] 71% yield and 71% ee in presence of one Hg(0) drop.

Scheme 2. Reaction scope of the Rh(I) catalyzed 1,2-addition of boronic acids to aldehydes (Typical experiments are provided).



At the end of the reactions, e.g. 5 hours, analyses of the catalytic reaction mixtures by dynamic light scattering (DLS) revealed the presence of particles in the 641 nm range with Hg(0) addition and around 769 nm without (Figure S2). Though all these results must be interpreted with caution,[13] they tend to suggest the molecular catalyst may gradually decompose throughout this catalyzed transfer hydrogenation to lead to inactive particles which apparently aggregate during the reaction to give larger particles (Figure S2).

Afterwards, chiral Rh(I) complexes **4a-e** were applied as precatalysts in another reference reaction, the asymmetric 1,2-addition of phenylboronic acid to 1-naphtaldehyde (Table 2). Indeed, the enantioselective addition of aryl nucleophiles to aromatic aldehydes is a well-established route to synthesize chiral diarylmethanols which are essential building blocks for the synthesis of various biologically active and pharmacy relevant compounds.[14] Many antihistamines, antiarrhythmic and therapeutic agents feature chiral diarylmethanol and diaryl carbinol derivatives as fundamental structural units. By comparison to the several chiral phosphine based Rh(I) complexes which were successfully applied to catalyze this reaction,[15] only few Rh species based on C_2 symmetric NHC have been used.[16] Indeed, the selected reaction was reported to be catalyzed by NHC Rh(I) complex bearing substituents with planar[16a-b] or central chirality[16c-d] on the NHC nitrogen atoms with modest to average Ee values. Therefore, after a brief optimization of the experimental conditions, our study was started at 80 °C using *t*BuOH/MeOH (5:1) solvent mixture and KF as a base (Scheme S2, Table 2). Rh(I) complexes **4a-c** bearing respectively H, Me and cyclohexyl substituents led to secondary alcohol **6** in average to good yields but low enantioselectivities (<21%) (entries 1-3). However, the use of Rh(I) complex **4d** carrying bulky *t*Bu groups afforded **6** in a high yield (82%) with a 71% Ee (entry 4). An increase of the steric hindrance through the use of complex **4e** bearing adamantyl substituents was here less effective as alcohol **6** was retrieved in lower yield (56%) and Ee (59%) (entry 5). The use of a reduced amount of KF or even of other bases led to significant decreases of reactivity and selectivity (entries 6-8). At that stage, the positive role of a large excess of KF[16] remains unclear as it might act concomitantly as a base and as a ligand through coordination of the fluoride anion to the Rh(I) complex. In order to check if any decomposition was occurring along the catalyzed 1,2-addition of phenylboronic acid to 1-naphtaldehyde, Hg(0) trapping experiment was performed using catalyst **4d** (Entry 4). The reaction yield was reduced by 10% but no change was noticed for the Ee. At the end of the reactions, analyses of the unfiltered catalytic reaction mixtures by dynamic light scattering (DLS) revealed the presence of particles in the 454 nm range with Hg(0) addition and in the 568 nm range without (Figure S3). Because the catalytic reaction was still running in the presence of Hg(0), the observed particles were, apparently, not related to any active Rh species and the molecular catalyst was rather stable throughout this catalytic process.[13]

The reaction scope of the enantioselective 1,2-addition of aryl nucleophiles to aldehydes was then investigated (Scheme 2). Similar to 1-naphtaldehyde, the reaction of heterocyclic aldehydes with phenylboronic acid led to secondary alcohols **7-9** in low to good yields, Ee values being average to good. Though the cyclohexanecarboxaldehyde reacted in a sim-

ilar way to offer alcohol **10**, the reaction of linear 3-phenylpropanal afforded **11** in lower yield and Ee. A similar trend was observed for the reaction of alkyl- or halide substituted benzaldehydes with phenylboronic acid as alcohols **12-15** were obtained in good yields but much lower enantioselectivities. Finally, the reaction of 1-naphtaldehyde with fluoro- or methoxy-substituted phenylboronic acid resulted in alcohols **16-17** with fair yields but low Ee values. On the whole, hindered substrates seemed to allow better asymmetric induction, probably due to more efficient ligand-substrate interactions. Hence, the enantioselectivity of such Rh(I) catalyzed 1,2-addition of aryl nucleophiles to aldehydes proved to be highly dependent of the reagent molecular structures.

CONCLUSIONS

Herein, we have reported the straightforward synthesis of enantiomerically pure Rh(I) complexes based on new C_2-symmetric NHC ligands bearing a chiral diphenylethylene diamine backbone. Applications to the asymmetric transfer hydrogenation of ketones and the 1,2-addition of arylboronic acids to aldehydes were subsequently investigated. Though the enantioselectivity of the developed Rh(I) NHC catalysts proved to depend on the substrate structure, we demonstrated a proper functionalization of the aromatic rings connected to the carbene nitrogen atoms improved drastically the asymmetric induction of the implied Rh(I) NHC catalysts. Indeed, the presence of sterically demanding substituents allowed a better control of the steric features of the catalyst quadrants because these bulky groups behaved as conformational and chirality relays of the NHC chiral backbone. Further applications of this concept will be reported in due course.

EXPERIMENTAL SECTION

General Methods and Instrumentation. All solvents were dried using standard methods and stored over molecular sieves (4 Å). All sensitive salts were weighted in a glovebox. All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques and were repeated two to four times. Analytical thin layer chromatography (TLC) was performed on Merck pre-coated 0.20 mm silica gel Alugram Sil 60 G/UV254 plates. Flash chromatography was carried out with Macherey silica gel (Kielselgel 60). ^{1}H (300 MHz), ^{13}C{^{1}H} (75 MHz) NMR spectra were acquired on Bruker Avance spectrometers. Chemical shifts (δ) are reported downfield of Me_4Si in ppm and coupling constants are expressed in Hz. Chloroform-*d* was purchased from Eurisotop and freshly filtered through basic alumina prior to use. 1,3,5-trimethoxybenzene and 1,2,4,5-tetrachlorobenzene were used as internal standards when needed. ^{1}H NMR shifts are given relative to the residual solvent resonance of $CDCl_3$ (at 7.26 ppm), and ^{13}C{^{1}H} NMR shifts are given relative to the residual solvent peak of $CDCl_3$ (at 77.16 ppm). HPLC analyses were performed on a Hitachi LaChromElite equipment with a Peltier oven and a DAD detector. Optical rotations were measured on a Perkin-Elmer 343 using a 10 cm cell. Gas chromatography analyses were done on GC Shimadzu 2010+with FID detectors using Supelco SPB-5 column (30 m, 0.25 mm,0.25 µm) and with nitrogen as gas carrier. GC-MS analyses were performed on a Shimadzu QP2010+ (EI mode) using Supelco column SLBTM-5ms (30m, 0.25mm, 0.25µm). HRMS-ESI analyses were performed at CUMA-Pharm. Dept.-University Lille Nord de-France. Elemental analyses were performed on an Elementar Vario Micro Cube apparatus at UCCS, University Lille Nord de France. X-ray diffraction analyses were performed at UCCS, University Lille Nord de France, on a Bruker APEX DUO. DLS measurements were performed on a Malvern Zetasizer Nano Series at 25 °C after decantation of the crude reaction solutions (20 minutes) and without any filtration. Aldehyde substrates were used as received. Purchased boronic acids were purified by flash chromatography on silica gel prior to use.

- General procedure for the synthesis of diamine precursors.

Rac-BINAP (10 mol%) was introduced in a large Schlenk tube along with a magnetic stirring bar. In a glovebox, $Pd_2(dba)_3$ (5 mol%) and NaO*t*Bu (2.8 equivalents) were subsequently added. Under a nitrogen flow, toluene (4 mL) was transferred to the Schlenk and the resulting mixture was stirred at room temperature for 30 minutes. In a separate Schlenk flask, (*S,S*)-DPEN (x mmol from glovebox) was dissolved in 4 mL toluene and transferred to the reaction mixture via cannula. The temperature was set at 30 °C and the reaction was stirred for further 60 minutes. Afterwards, the substituted 2-bromoanisole (2*x mmol) was dissolved in 4 mL toluene in a third Schlenk tube and the resulting solution was transferred to the reaction medium via cannula. The reaction was then stirred for 24 hours at 115 °C under a nitrogen flow. At the end, the resulting mixture was cooled and the remaining solvents were evaporated under vacuum. The residue was then dissolved in ethyl acetate and filtered over Celite. Purification was performed by flash chromatography on silica gel with a solid deposit and using petroleum ether and ethyl acetate solvent mixtures with a 5% elution gradient.

- General procedure for the synthesis of imidazolium salts.

The diamine precursor (1 equivalent) and NH_4BF_4 (2 equivalents) were introduced in a Schlenk tube containing a magnetic stirring bar. After a drying under vacuum of 30 minutes, $CH(OEt)_3$ (3 mL) was transferred to the Schlenk under a nitrogen flow and the remaining mixture was stirred overnight at 120 °C. After 12 hours, the reaction was stopped and the remaining solvent evaporated under vacuum. Purification of the product was carried out through flash chromatography on silica gel with a solid deposit and using petroleum ether and acetone solvent mixtures with a 20% elution gradient. Due to the hygroscopic nature of the resulting imidazolium salt, the latter was repeatedly dissolved in dry toluene and then evaporated under vacuum. Such an azeotrope treatment needed to be repeated 3 times in order to obtain a dry product which required to be stored under nitrogen.

- General procedure for the synthesis of Rh(I) complexes.

Ag_2O (2 equivalents) was introduced to a Schlenk tube containing the dry imidazolium compound and a magnetic stirring bar. After a drying under vacuum of 30 minutes, CH_3CN (7 mL, degassed using the freeze-pump-thaw method) was transferred to the Schlenk under a nitrogen flow and the resulting mixture was stirred at 60 °C for 24 hours in the darkness. Afterwards, $[Rh(COD)Cl]_2$ (0.5 equivalents) was dissolved in CH_2Cl_2 (3 mL, degassed using the freeze-pump-thaw method) in a second Schlenk tube and transferred to the reaction mixture previously cooled at room temperature. The reaction was then pursued in the darkness under stirring and a nitrogen flow for 64 hours. At the end, the reaction mixture was filtered over Celite with an ethyl acetate wash. The resulting yellow solution was concentrated under vacuum and purified by flash chromatography on neutral alumina with a liquid deposit and using petroleum ether and acetone solvent mixtures with a 15% elution gradient. After the corresponding fractions were gathered and evaporated under vacuum, the resulting yellow solid was recrystallized twice from dichloromethane and pentane.

- General procedure for the Rh(I) catalyzed transfer hydrogenation of ketones.

Prior to the reaction, dry isopropanol was degassed under a nitrogen flow for 2 hours. Catalyst (1 mol%) and potassium tert-butoxide (10 mol%) were introduced in a Schlenk tube containing a magnetic stirring bar and dried under vacuum for 10 minutes. Under nitrogen, distilled propiophenone (0.2 mmol, 0.030 mL) and dry isopropanol (2 mL) were transferred to the Schlenk tube via syringe. The reaction mixture was then heated to 80^{0}C under stirring for 5 hours. After this time, a 0.1 mL aliquot of the reaction mixture was taken for GC analysis to ensure the reaction had gone to completion. At the end, the isopropanol was evaporated under vacuum and the product was purified by flash chromatography on silica gel with a (9:1) petroleum ether and ethyl acetate solvent mixture. Typical experiments are provided in Table 1.

- General procedure for the Rh(I) catalyzed additions of boronic acids to aldehydes.

Catalyst **7d** (3 mol%), purified boronic acid (2 equivalents, 0.3 mmol) and potassium fluoride (6 equivalents, 0.9 mmol, 0.052 g) were introduced in a Schlenk tube containing a magnetic stirring bar and

dried under vacuum for 10 minutes. Under nitrogen, distilled t-butanol (2.5 mL) and methanol (0.5 mL), as well as the aldehyde (0.15 mmol) were transferred to the Schlenk tube via syringe. The reaction mixture was then left under stirring at 80^{0}C for 4 hours. At the end, the reaction was cooled and subsequently quenched with brine. The aqueous solution was extracted thrice with ethyl acetate (3 x 10 mL) and the organic phases were dried over anhydrous magnesium sulfate and concentrated under vacuum. Purification of the product was performed via preparative thin layer chromatography on glass silica plates. Typical experiments are provided in Scheme 2.

(1*S*,2*S*)-*N*^{1},*N*^{2}-bis(5-(tert-butyl)-2-methoxyphenyl)-1,2-diphenylethane-1,2-diamine (2d)

To synthesize compound **2d**, reagents were used as follows: (*S*,*S*)-DPEN (0.376 g, 1.8 mmol), (+/-)BINAP (0.110 g, 10 mol%), $Pd_2(dba)_3$ (0.081 g, 5 mol%), NaOtBu (0.476 g, 5.0 mmol) and 4-tBu-2-bromoanisole **(1d)** (0.862 g, 3.6 mmol). The product was obtained as a white solid (0.714 g, 75% yield), Rf = 0.6, petroleum ether and ethyl acetate solvent mixture (95:5).

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.98 (s, 18 H, *t*Bu), 3.74 (s, 6 H, OMe), 4.51 (s, 2 H, CH), 5.22 (bs, 2 H, NH), 6.30 (s, 2 H_{Ar}) 6.51 (dd, J = 8.3, J = 2.2, 2 H_{Ar}), 6.59 (d, J = 8.3, 2 H_{Ar}), 7.04 (m, 10 H_{Ar}). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 31.5 (3 CH_3, Me), 34.2 (C), 55.7 (CH_3, OMe), 64.6 (CH), 109.1 (CH), 110.1 (CH), 113.3 (CH), 127.3 (CH), 127.8 (2 CH), 128.2 (2 CH), 136.7 (C), 140.9 (C), 143.9 (C), 145.4 (C). HRMS (ESI+): m/z calcd for $C_{36}H_{45}N_2O_2$ [MH$^+$] 537.34756, found 537.34604. Elemental analysis: calcd (%) for ($C_{36}H_{44}N_2O_2$): C, 80.56; H, 8.26; N, 5.22; found C, 80.77; H, 8.32; N, 5.08. $[\alpha]_D^{20}$ = -103 *(CH_2Cl_2, 9 mM).*

(*R*$_a$,*R*$_a$,4*S*,5*S*)-1,3-bis(5-(tert-butyl)-2-methoxyphenyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-3-ium tetrafluoroborate (3d)

To synthesize compound **3d**, diamine **2d** (0.714 g, 1.3 mmol) was combined with NH_4BF_4 (0.279 g, 2.7 mmol) in 3 mL $CH(OEt)_3$. The product was obtained as a beige solid (0.738 g, 87% yield). R_f = 0.6, petroleum ether and acetone solvent mixture (2:8).

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.14 (s, 18 H, *t*Bu), 3.96 (s, 6 H, OMe), 5.76 (s, 2 H, CH), 6.87 (m, 2 H_{Ar}), 7.24 (m, 2 H_{Ar}), 7.27 (m, 2 H_{Ar}), 7.40 (m, 10 H_{Ar}), 8.93 (s, 1 H, imid). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 31.1 (3 CH_3, Me), 34.2 (C), 56.4 (CH_3, OMe), 75.5 (CH), 111.8 (CH), 122.4 (C), 124.0 (CH), 127.3 (CH), 128.0 (2 CH), 129.6 (2 CH), 130.1 (CH), 135.2 (C), 144.7 (C), 151.0 (C), 158.0 (CH, imid). HRMS (ESI+): m/z calcd for $C_{37}H_{43}N_2O_2$ [M$^+$] 547.33191, found 547.32965. Elemental analysis: calcd (%) for ($C_{37}H_{43}BF_4N_2O_2$ + 1 H_2O) C, 68.10; H, 6.95; N, 4.29; found C, 67.84; H, 7.02; N, 4.09. $[\alpha]_D^{20}$ = -304 *(CH_2Cl_2, 1 mM)*

(*R*$_a$,*R*$_a$)-chloro-(1,5)-cyclooctadiene-((4*S*,5*S*)-1,3-bis(5-tertiobutyl-2-methoxy-phenyl)-4-5-diphenylimidazolidin-2-ylidene)rhodium (4d)

To synthesize complex **4d**, Ag_2O (0.269 g, 1.2 mmol) and $[Rh(COD)Cl]_2$ (0.143 g, 0.3 mmol) reacted with imidazolium salt **3d** (0.369 g, 0.6 mmol). The complex was obtained as a yellow solid (0.329 g, 72% yield). R_f = 0.7, petroleum ether and acetone solvent mixture (85:15). Recrystallisation by using CH_2Cl_2 and n-hexane followed by drying under vacuum (0.329 g, 72% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.15 (s, 9 H, *t*Bu), 1.28 (s, 9 H, *t*Bu), 1.35 (m, 3 H, CH_2, COD), 1.58 (m, 3 H, CH_2, COD), 1.91 (m, 2 H, CH_2, COD), 3.13 (m, 1 H, CH, COD), 3.49 (m, 1 H, CH, COD), 3.80 (s, 3 H, OMe), 3.90 (s, 3 H, OMe), 4.52 (m, 1 H, CH, COD), 4.64 (m, 1 H, CH, COD), 4.92 (d, J = 6.0, 1 H, CH), 5.50 (d, J = 6.0, 1 H, CH), 6.82 (dd, J = 9.0, 4 H_{Ar}), 7.00 (d, J = 3.0, 2 H_{Ar}), 7.30 (m, 9 H_{Ar}), 7.57 (d, J = 8.5, 2 H_{Ar}), 8.51 (d, J = 1.3, 1 H_{Ar}).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 27.3 (CH_2), 29.6 (CH_2), 31.2 (CH_2), 31.4 (3 CH_3, CMe), 31.6 (3 CH_3, CMe), 33.3 (CH_2), 33.9 (C), 34.6 (C), 55.5 (CH_3, OMe), 55.6 (CH_3, OMe), 66.7 (d, $J_{CH\text{-}Rh}$ = 14.8, CH), 69.2 (d, $J_{CH\text{-}Rh}$ = 14.6, CH), 74.2 (CH), 76.5 (CH), 97.4 (d, $J_{CH\text{-}Rh}$ = 7.0, CH), 98.0 (d, $J_{CH\text{-}Rh}$ = 6.4, CH), 109.7 (CH), 111.5 (CH), 124.4 (CH), 126.1 (CH), 127.6 (C), 127.8 (2 CH), 127.9 (2 CH), 128.2 (CH), 128.3 (CH), 128.5 (C), 128.6 (4 CH), 128.8 (CH), 132.4 (CH), 140.2 (C), 141.2 (C), 142.2 (C) 143.8 (C), 152.3 (C), 154.3 (C), 212.6 (d, $J_{C\text{-}Rh}$ = 46.4, C).

HRMS (ESI+): m/z calcd for $C_{45}H_{54}N_2O_2Rh$ [M-Cl] 757.32348, found 757.32159.

Elemental analysis: calcd (%) for ($C_{45}H_{54}N_2O_2Rh$ + 1 H_2O) C, 66.62; H, 6.96; N, 3.45; found C, 66.75; H, 7.13; N, 3.06.

$[\alpha]_D^{20}$ = -108 *(CH_2Cl_2, 4 mM).*

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the web.

Additional data, experimental procedures and characterizations for other compounds, copies of ^{1}H and ^{13}C NMR spectra of all final products (new or reported), copies of HRMS spectra of new compounds, copies of HPLC analyses. (PDF)

Cif file of compound **4d**. (CIF)

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Notes

The authors declare no competing financial interest.

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