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N-Heterocyclic Carbenes

Triptycene-Based Chiral and *meso*-N-Heterocyclic Carbene Ligands and Metal Complexes

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Abstract: Based on 1-amino-4-hydroxy-triptycene, new saturated and unsaturated triptycene-NHC (N-heterocyclic carbene) ligands were synthesized from glyoxal-derived diimines. The respective carbenes were converted into metal complexes [(NHC)MX] (M = Cu, Ag, Au; X = Cl, Br) and [(NHC)MCl(cod)] (M = Rh, Ir; cod = 1,5-cyclooctadiene) in good yields. The new azolium salts and metal complexes suffer from limited solubility in common organic solvents. Consequently, the introduction of solubilizing groups (such as 2-ethylhexyl or 1-hexyl by *O*-alkylation) is essential to render the complexes soluble. The triptycene unit infers special steric properties onto the metal complexes that enable the steric shielding of selected areas close to the metal center. Next, chiral and *meso*-triptycene based N-heterocyclic carbene ligands were prepared. The key step in the synthesis of the chiral ligand is the Buchwald–Hartwig amination of 1-bromo-4-butoxy-triptycene with (1*S*,2*S*)-1,2-diphenyl-1,2-diaminoethane, followed by cyclization to the azolinium salt with $HC(OEt)_3$. The analogous reaction with *meso*-1,2-diphenyl-1,2-diaminoethane provides the respective *meso*-azolinium salt. Both the chiral and *meso*-azolinium salts were converted into metal complexes including [(NHC)AuCl], [(NHC)RhCl(cod)], [(NHC)IrCl(cod)], and [(NHC)PdCl(allyl)]. An in situ prepared chiral copper complex was tested in the enantioselective borylation of α,β-unsaturated esters and found to give an excellent enantiomeric ratio (*er* close to 90:10).

Introduction

Triptycene, being the first representative of the iptycene family,[1] was first synthesized in the early 1940s[2] and is characterized by an unusual D_3h symmetry. In the 1980s, iptycene chemistry was rediscovered by Hart et al., and only then did the field evolve at a faster pace.[3] Recently, iptycenes have found numerous applications in polymer chemistry,[4] molecular machines,[5] material science, and in host–guest chemistry.[6] The special geometric properties of triptycene motivated their use as backbones for modified ligands in organometallic chemistry. The chemistry of triptycene-based phosphines was pioneered by Gelman et al., and a number of *trans*-chelating 1,8-phosphine-substituted triptycenes have been synthesized as well as the catalytic properties of the respective metal complexes studied.[7] The Bartlett synthesis of triptycene relies on the reaction of anthracene and benzoquinone and, based on this approach, the synthesis of 1-aminotriptycenes has been well established.[2] Anilines are very convenient precursors for N-heterocyclic carbenes (NHC).[8] The same should hold true for amino-triptycenes. Peris et al.[9] and Bielawski et al.[10] reported on triptycene-based NHC ligands. However, the respective metal complexes do not utilize the special steric properties of the triptycene backbone,[11] because the NHC unit is attached symmetrically through the respective 2,3-positions of triptycene. Consequently, the two remaining triptycene wings are far away from the metal center, and exert only little effect on the coordination sphere of the metal ion. Our strategy is to connect the heterocyclic carbene unit to the 1-position of the triptycene. The steric bulk on the two sides of each aryl unit in the triptycene-based *N*,*N*′-diaryl NHC ligand should be very different, thus offering the chance for stereoselective catalysis in the respective transition metal complexes.[12] Quadrant diagrams are simple but useful representations of the stereochemical properties of ligands in the coordination sphere of transition metals (Scheme 1).[13] Depending on the steric properties of the ligand, certain quadrants can be sterically inaccessible. Controlling the orientation of substrates undergoing catalytic transformations at the metal center may lead to a defined stereochemistry in the reaction product.[14] To benefit from the stereodirecting effect of a ligand, the coordination sphere of the metal center has to be modulated in a well-defined manner. Certain ligands seem to be highly capable in this respect, and are useful for a large number of different chemical transformations. This led Jacobsen to coin the term "privileged chiral ligands."[15] Several of those privileged ligands are phos-

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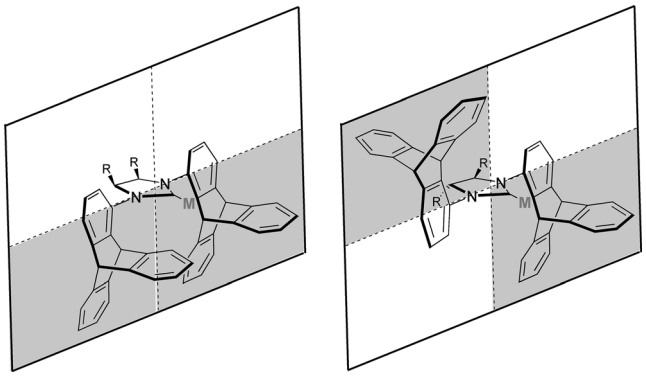
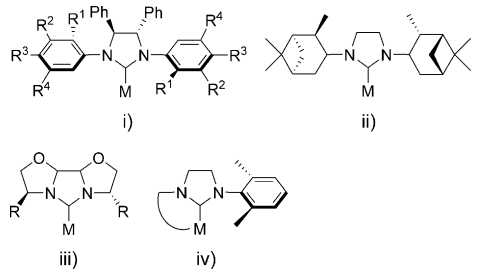
Supporting information, including general experimental, full sets of ^1H and ^{13}C NMR spectra, additional synthetic procedures, determination of enantiomeric ratios, cyclic voltammograms, and mass spectra, as well as the ORCID identification number for the corresponding author of this article can be found under http://dx.doi.org/10.1002/chem.201601474.



Scheme 1. Prototypical chiral bistriptycene-NHC metal complexes in quadrant diagrams; conformational control is possible once R is a sterically demanding group.

phines,[16] but the closely related NHC ligands are much less prominent in this context.[17]

One problem of NHC ligands[18] in stereoselective synthesis is that stereodirecting groups at the ligand tend to be remote from the catalytically active metal center. Several strategies have been employed to overcome such problems, and to obtain NHC ligands suitable for asymmetric catalysis[12a,19] (Scheme 2):[12b] i) to convey chiral information from the 4,5-position to the active site by increasing the steric bulk of the *N*-substituents through a gearing effect;[20] ii) the introduction of a rigid chiral framework;[21] iii) bicyclic or tricyclic NHC ligands with blocked N–R rotation[22] or iv) bidentate NHC ligands.[23]



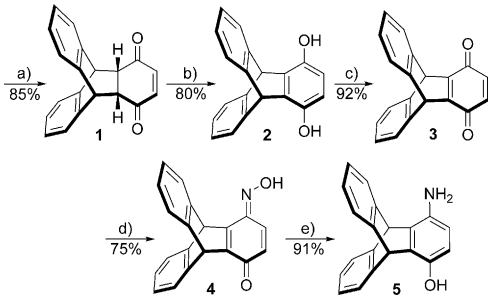
Scheme 2. Four types of chiral NHC-metal complexes.

The primary objective of the present study is to synthesize triptycene-based NHC ligands as well as stereochemically defined (chiral and *meso*) triptycene based NHC-metal complexes. The rigid geometry of the bulky triptycene unit[1] should enable the deep penetration of the space close to a catalytically active metal, prevent the M–C(NHC) rotation, and thus, may enable stereoselective catalysis (Scheme 2). For such ligands an efficient gearing mechanism based on the C_3-symmetric triptycene is likely.[6c] Steric bulk at the imidazole ring acts on one triptycene wing, orienting the second one, and shielding the space close to the metal to enable steric control at the metal center.

Results and Discussion

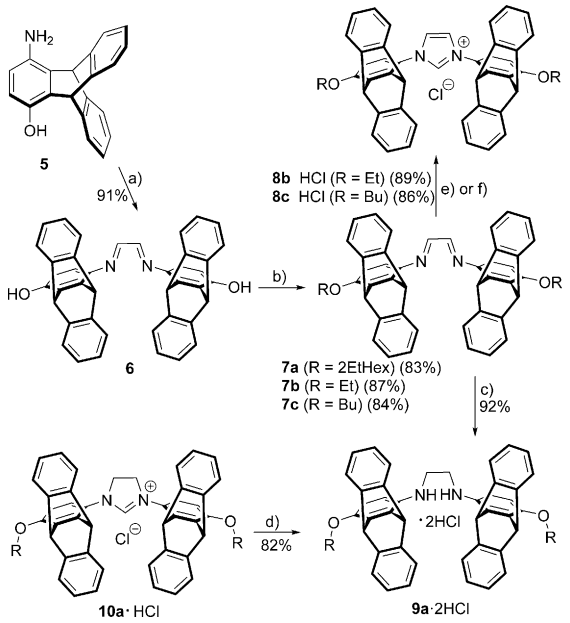
Synthesis of bistriptycene-N-heterocyclic carbene ligands and metal complexes

Triptycene quinone **3** was synthesized according to a modified literature procedure from Bartlett et al.,[2] and then converted into the known (9*s*,10*s*)-4-amino-9,10-dihydro-9,10-[1,2]benzenoanthracene-1-ol (Scheme 3, **5**) based on a modified procedure from Yang et al.[24] The synthesis of aminophenol **5** proved to conveniently work on a large scale, as it relies on inexpensive starting materials. Furthermore, the purification of the intermediates does not require chromatography. In our hands, the five-step synthesis provides an overall yield of 43%, with the lowest yielding step in the synthesis being the selective conversion of the quinone into the monooxime (yield 75%).

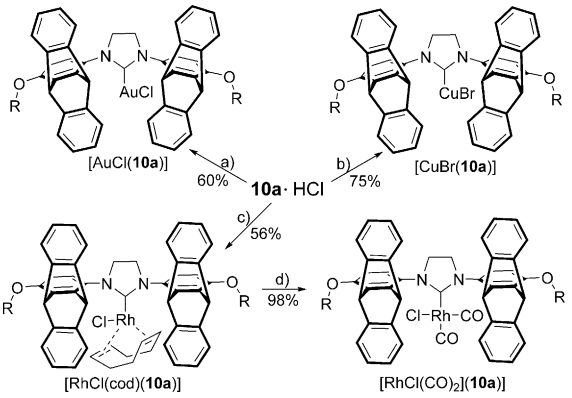


Scheme 3. Synthesis of (9*s*,10*s*)-4-amino-9,10-dihydro-9,10-[1,2]benzenoanthracene-1-ol. Reagents and conditions: a) anthracene, 1,4-benzoquinone, xylene, reflux; b) acetic acid (AcOH), HBr, reflux; c) $KBrO_3$, AcOH, H_2O, reflux; d) $NH_2OH{\cdot}HCl$, THF, H_2O, 50 °C; e) hydrazine hydrate, Pd/C, THF, reflux.

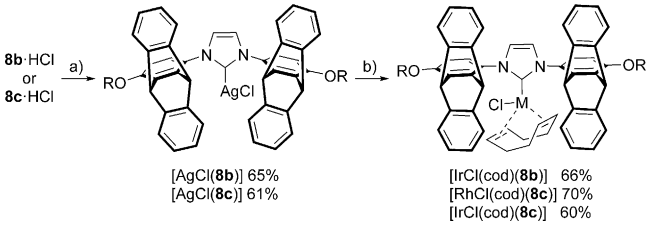
The amino group in **5** can be used to build an NHC ligand following the standard reaction sequence (Scheme 4).[25] The phenolic-OH in **5** is helpful, since it has two advantages: it is electron-donating, leading to a more electron-rich NHC ligand, and it provides a handle for the functionalization with long-chain alkyl groups. This alkylation step is very important to improve the otherwise poor solubility of the triptycene derivatives in common organic solvents.[26] However, the selective alkylation of the -OH group in **5** was not successful in the presence of the -NH_2 unit. Therefore, **5** was first converted into the diimine **6** with glyoxal (Scheme 4).[27] This diimine is poorly soluble in most solvents other than DMSO. Reactions of this diimine with various alkyl halides RX (R = 2-Et-hexyl, Et, *n*Bu) led to the respective O-alkylated diimines **7a**, **7b**, and **7c**. Diimine **7b** (R = Et) displays poor solubility (insufficient for recording decent ^{1}H NMR spectra), that of **7c** (R = Bu) is modest, but the solubility of **7a** (*R* = 2-Et-hexyl)[28] in common solvents is good. However, the 2-ethyl-hexyl group also has drawbacks because the chirality of the side chain will cause problems when attempting to obtain single crystals of the diastereomeric mixtures. **7b** and **7c** were converted into the respective imidazolium salts **8b**·HCl and **8c**·HCl employing the established Hintermann procedure.[29] Alternatively, diimine **7a** was



Scheme 4. Reagents and conditions: a) glyoxal (aq. 40% wt), HCOOH, MeCN, 60 °C; b) 2-ethylhexyl bromide, K_2CO_3, KI, DMF, 70 °C or alkyl iodide, K_2CO_3, DMF, 70 °C; c) $LiAlH_4$, THF, −10 °C to RT; d) $HC(OEt)_3$, HCOOH, 120 °C; e) $EtOCH_2Cl$, 100 °C; f) $(CH_2O)_n$, Me_3SiCl, EtOAc, 70 °C.



Scheme 5. Reagents and conditions: a) $[AuCl(SMe_2)]$, $NaOCMe_2Et$, THF, −78 °C to RT; b) $[CuBr(SMe_2)]$, $NaOCMe_2Et$, THF, RT; c) $[RhCl(cod)]_2$, $NaOCMe_2Et$, THF, RT; d) CO, CH_2Cl_2, RT.



Scheme 6. Reagents and conditions: a) Ag_2O, CH_2Cl_2, 40 °C; b) $[MCl(cod)]_2$ (M = Rh, Ir), CH_2Cl_2, 40 °C.

first reduced to the diamine **9a** and then cyclized to the imidazolinium salt **10a**·HCl (Scheme 4).[30]

Despite the limited solubility of the azolium chlorides **8** and **10**, several metal complexes could be synthesized. The respective carbene was generated from **10a**·HCl and sodium amylate, followed by reaction with suitable metal precursors $[AuCl(Me_2S)]$, $[CuBr(Me_2S)]$, and $[RhCl(cod)]_2$ (Scheme 5). The reaction of [RhCl(cod)(**10a**)] with CO led to the formation of $[RhCl(CO)_2$(**10a**)] in almost quantitative yield (Scheme 5). The unsaturated imidazolium salts **8b**·HCl and **8c**·HCl could be converted into the respective metal complexes [AgCl(**8b**)], [AgCl(**8c**)], [IrCl(cod)(**8b**)], [IrCl(cod)(**8c**)], and [RhCl(cod)(**8c**)] (Scheme 6). Complexes of the **b** and **c** series with ethoxy or butoxy groups are characterized by modest solubility, leading to ^{13}C NMR spectra with poor signal-to-noise ratios. This primarily concerns the carbene carbon atoms, which are characterized by long relaxation times.[31]

X-ray crystal structure analysis of [IrCl(cod)(8b)]

Single crystals of this complex were grown by recrystallization from isopropanol/CH_2Cl_2. The crystal structure is highly indicative concerning the role of the triptycene ligand (Figure 1). Iridium displays a typical square-planar coordination geometry with a crystallographic mirror plane bisecting the molecule in the Cl–Ir–C(NHC) plane; bond lengths within the coordination sphere of Ir are normal.[32] In the solid state, the two triptycene flaps are oriented in a *syn*-orientation. However, based on NMR data, the triptycene unit in the metal complex should be able to rotate rapidly around the (aryl)C–N single bond, as was shown for related NHC-metal complexes, in which rotation was only blocked in the presence of bulky substituents in the 4- and 5-positions of the heterocyclic carbene.[33] In the ^1H and the ^{13}C NMR spectra of [IrCl(cod)(**8b**)] there is no evidence for different isomers (*syn* and *anti*). The detailed analysis of NOESY (signals of the cod ligand) and HMBC spectra did not provide evidence for an exclusive *syn*-isomer at room temperature. Based on this, we conclude that the solution complex [IrCl(cod)(**8b**)] exists as a mixture of rapidly interconverting isomers. Furthermore, it is hard to see any stereodirecting effect, which could lead to the formation of a single (*syn*) isomer. Consequently, the exclusive formation of the *syn* isomer in the crystal appears to be a solid state phenomenon.

The most important property of the bistriptycene NHC ligand is that the aryl flaps are reaching into the space above and below the plane of the *N*-aryl group bonded to the imida-

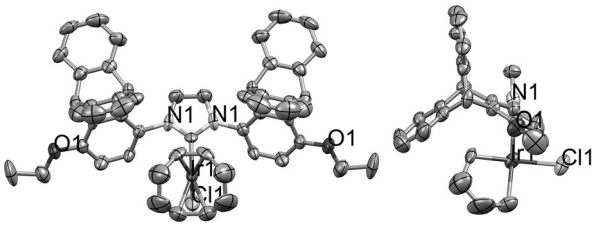


Figure 1. ORTEP-plots of the X-ray crystal structure[39,51] of complex [IrCl(cod)(**8b**)] (view onto the plane of the heterocycle and view perpendicular to the square-planar coordination sphere). Important bond lengths (pm) and angles (°): Ir–C(NHC) 206.1(15), Ir–Cl 237.7(4), Ir–C(cod) 207.3(9), 218.3(12), Cl-Ir-C(NHC) 93.1(4).

zolylidene. According to the quadrant model, two neighboring quadrants in the *syn*-complex are occupied by the bulky tripytcene units, whereas the two other quadrants lack sterically demanding groups. This offers the chance for stereoselective catalysis; however, this is restricted to the isomerically pure *syn*- or *anti* -complexes, both of which possess bulky groups to prevent isomer interconversion by rotation.

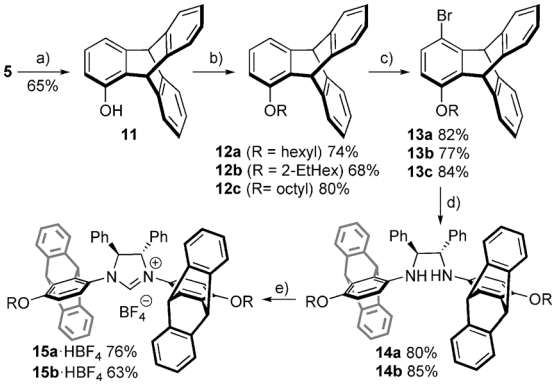
A typical feature of the *N*-aryl and the imidazolylidene rings in SIMes-type ligands is the orthogonality of the two ring planes.[32,34] However, in the crystal structure of [IrCl(cod)(**8b**)], those two planes are tilted with an angle of approximately 60°, which appears to result from the presence of the two bulky triptycene groups and the cod ligand. This tilting has two consequences. The obvious one being the partial removal of the triptycene flaps from the space surrounding the metal center, leading to an alleviation of the steric hindrance close to the metal center. This might be important concerning the potential stereoselective catalysis with related complexes. On the other hand, in the absence of a bulky cod ligand, the triptycene wing could rotate towards the metal. Furthermore, the presence of bulky groups in the 4- and 5-positions of the heterocycle (which are needed for the inhibition of rotation) will push the triptycene flaps back towards the metal center.

The other consequence of this tilting is the proximity of iridium to the *ortho*-carbon on the other side of the *N*-aryl group. This Ir–C distance is only 360 pm, whereas that of the other *ortho*-carbon is 440 pm. As a consequence, the respective C–H bond is oriented towards the metal center, possibly facilitating C–H-activation reactions. The packing of the rigid triptycene units in the crystal leads to the formation of extended pores, something which has been observed also for related iptycene structures.[35] As a consequence of this solid state property, it can be very difficult to completely remove solvent from solid iptycene derivatives. To better understand the steric bulk of NHC **8**, we have determined the buried-volume[36] (based on the crystal structure of [IrCl(cod)(**8b**)]) as 30.9%. This is slightly smaller than *N*-mesityl-substituted NHCs.[37,38]

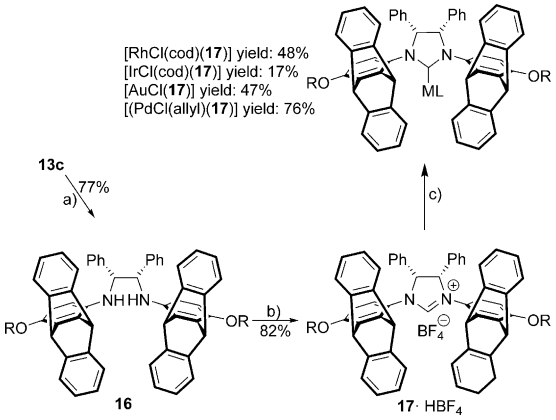
Synthesis of chiral and *meso*-NHC ligands

To enable stereocontrol in both the NHC ligands and derived metal complexes (and potentially in catalytic reactions with such metal complexes), substituents at the C_2-backbone of the azolinium unit are necessary. Based on (1*S*,2*S*)-1,2-diphenylethylenediamine and *meso*-1,2-diphenyl-1,2-diaminoethane, it is possible to establish the desired stereochemistry.

The synthesis of new chiral NHC·HBF_4 salts is summarized in Scheme 7. The known aminophenol **5**[2,24] was converted into the diazonium salt and reduced in situ to phenol **11**. Etherification of the hydroxyl group (leading to the **12** series) offers the chance to introduce solubilizing groups. The bromination of **12a**, **12b**, and **12c** produces the respective bromophenols **13a**, **13b**, and **13c**. The bromine substituent enables introduction of the chiral (1*S*,2*S*)-1,2-diphenylethylenediamine by Buchwald–Hartwig amination,[40] an established method involved in the synthesis of chiral NHC ligands.[20a,33b] In $CDCl_3$ solvent, the chiral diamines **14** exist as distinct rotamers. However, when recording the ^1H NMR spectra in [D_6]DMSO, the interconversion of the rotamers is fast on the NMR timescale and consequently, only a single set of isomers is observed, which considerably simplifies the NMR spectra. The cyclization of **14** provides good yields of the respective imidazolinium salts **15**, which are excellent precursors for the synthesis of chiral transition-metal complexes. The synthesis of the *meso*-azolinium salt was done in a similar manner utilizing **13c** and *meso*-1,2-diphenyl-1,2-diaminoethane (Scheme 8).



Scheme 7. Synthesis of chiral azolium salts as NHC precursors. Reagents and conditions: a) 50% aq. H_3PO_2, *t*BuONO, THF, 40 °C; b) *n*-hexyl iodide, K_2CO_3, DMF, 70 °C or 2-ethylhexyl bromide or octylbromide, K_2CO_3, KI, DMF, 70 °C; c) N-bromosuccinimide (NBS), DMF, 100 °C; d) (1*S*,2*S*)-1,2-diphenylethylenediamine, $Pd_2(dba)_3$ (dba = dibenzylideneacetone), *rac*-BINAP, sodium *tert*-pentoxide, toluene, 100 °C; e) $HC(OEt)_3$, NH_4BF_4, HCOOH, 120 °C.

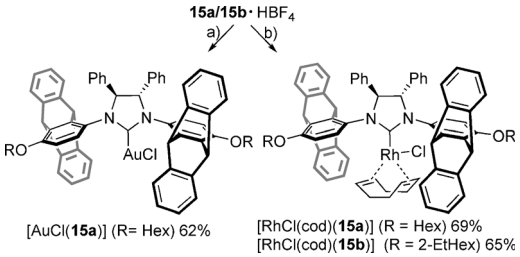


Scheme 8. Synthesis of *meso*-NHC ligands and metal complexes. Reagents and conditions: a) *meso*-1,2-diphenyl-1,2-diaminoethane, $Pd_2(dba)_3$, *rac*-BINAP, sodium *tert*-pentoxide, toluene, 100 °C, (R = C_6H_{17}); b) $HC(OEt)_3$, NH_4BF_4, HCOOH, 120 °C; c) [$AuCl(SMe_2)$] or [$RhCl(cod)]_2$ or [$IrCl(cod)]_2$ or [$PdCl(allyl)]_2$ with K_2CO_3, acetone, 60 °C.

Synthesis of chiral and *meso*-NHC-metal complexes

The reaction of **15a**·HBF_4 with [$AuCl(SMe_2)$] and K_2CO_3 in acetone[41] provides the respective gold complex in good yield (Scheme 9). The complexes with Rh were synthesized according to a related procedure.[42] The *meso*-NHC-metal complexes

were prepared in a similar manner (Scheme 8). In general, the *meso*-complexes are less well behaved than the chiral complexes, and the yields for the formation of the respective metal complexes are lower. All attempts to obtain single crystals suitable for X-ray crystal structure analysis of a chiral or a *meso* metal complex were unsuccessful.



Scheme 9. Synthesis of chiral NHC-metal complexes. Reagents and conditions: a) $[AuCl(SMe_2)]$, K_2CO_3, acetone, 60 °C; b) $[RhCl(cod)]_2$, K_2CO_3, acetone, 60 °C.

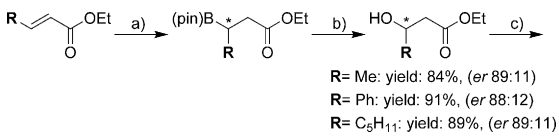
The NMR spectra of chiral NHCs **15a** and **15b** and of the *meso* NHC **17** reveal significant differences between the two isomers (i.e., chiral vs. *meso*). For example, the azolinium proton in the chiral **15a**·HBF_4 resonates at 9.19 ppm, the equivalent proton in **17**·HBF_4 at 9.69 ppm. The two bridgehead CH units of the triptycene (inside and outside) are observed at 5.82 and 6.48 ppm in [AuCl(**17**)], but at 5.38 and 5.91 ppm in [AuCl(**15a**)]. Most importantly, the respective metal complexes of both the *meso* and the chiral compounds each consist of a single isomer only. There is no evidence whatsoever for any representative of the two classes of compounds to be mixtures of isomers. This clearly shows that the orientation of the triptycene wings is controlled by the given orientation of the phenyl groups at the backbone of the heterocyclic unit. This was expected, since there are several examples in the literature for which this orientation control has been shown.[12b,20a,33d,43]

Donor properties of the bistriptycene-NHC

The redox potentials of [RhCl(cod)(**8a**)] ($E_{1/2} = +0.66$ V) and [IrCl(cod)(**8a**)] ($E_{1/2} = +0.71$ V) were determined. The Ir^{I}/Ir^{II} redox potential falls into the expected range, which is observed for related complexes with IMes ligands.[44] The $\tilde{\nu}$(CO) of NHC **10a** in $[IrCl(CO)_2$(**10a**)] was determined and found to be 3 cm^{-1} (Tolman electronic parameter 2055 cm^{-1}) higher than that of the reference complex $[IrCl(CO)_2(SIMes)]$. Both results are indicative of a slightly lower electron-donating capacity of ligand **10a**. The donor properties of the chiral and *meso*-NHC ligands were also evaluated by considering the Rh^{I}/Rh^{II} redox potential of [RhCl(cod)(**15a**)] ($E_{1/2} = 0.739$ V) and [RhCl(cod)(**17**)] ($E_{1/2} = 0.677$ V). This value is more cathodic than that of the related [(RhCl(cod)(SIMes)] species with 4-alkyoxy substituents ($E_{1/2} = 0.785$ V),[44] and suggests stronger electron-donating properties of NHC **15a** and **17** compared to the alkoxy-substituted SIMes.[25a]

Catalytic properties

Preliminary tests of the chiral NHC ligands in enantioselective catalysis were performed. The conjugate addition of heteroatom nucleophiles is a valuable tool for the introduction of a functional group into the β-position of α,β-unsaturated acceptors.[45] We therefore tested the asymmetric borylation of α,β-unsaturated esters as a preliminary probe of the enantiodirecting effect of the triptycene-NHC ligands. Several chiral NHC-copper complexes have been employed successfully for this reaction.[45,46] The in situ formed Cu complexes with chiral NHC **15a** induces the enantioselective borylation of three different α,β-unsaturated esters[21b,46e] (Scheme 10). The respective products are formed in virtually quantitative yields. The enantioselectivity of the borylation reaction was determined following the oxidative conversion of the borylated products into the respective chiral alcohols and the synthesis of the respective mandelic acid esters. The mandelic ester method is an established procedure for the determination of enantiomeric excess by NMR spectroscopy using the ^{1}H NMR integrals of the respective resonances in the diastereomeric esters.[47,48] For the three reactions studied, *er* values of close to 90:10 were observed.[49] These data show that enantioselective catalysis with triptycene-based NHC ligands is possible with excellent chiral induction comparable to that of other NHC-Cu complexes.[21b,46e] More (flexible) bulk at the periphery of the triptycene wings might be helpful to even better control the chiral space around the transition metal to improve chiral induction.



Scheme 10. Enantioselective borylation of a,ß-unsaturated esters. Reagents and conditions: a) **15a**·HBF_4 (5 mol%), CuCl (5 mol%), THF, sodium *tert*-pentoxide; $B_2(pin)_2$, 18 h, $T = -20$° C; b) THF, $NaBO_3 \cdot 4\,H_2O$, water, 3 h, RT; c) (*R*)-*O*-acetylmandelic acid, DMAP, CH_2Cl_2, DCC, 24 h, RT; (DMAP = 4-(dimethylamino)-pyridine, DCC = dicyclohexylcarbodimide). The ^{1}H NMR integrals of the protons in the diastereomeric esters were utilized for enantiomeric ratio (*er*) determination.

Conclusions

We have successfully up-scaled the synthesis of triptycene aminophenol **5** to provide large amounts of this compound from cheap starting materials. This triptycene aminophenol **5** was converted (via the glyoxal-derived diimines) into the respective azolium salts, which are convenient precursors for NHC-metal complexes. The inherently poor solubility of triptycene derivatives was overcome by installing solubilizing long alkyl groups on the phenolic OH group (leading to the **7** series). Based on this, several (soluble) metal complexes of the bistriptycene-NHC ligand with Cu, Ag, Au, Rh, and Ir were synthesized (complexes with **8b**, **8c**, or **10a**). The NMR spectra and the crystal structure of [IrCl(cod)(**8b**)] with a bistriptycene-NHC ligand revealed two limitations of this approach: i) despite the significant bulk of the triptycene group, the free rotation around the

N–C bond results in the formation of isomeric metal complexes, and ii) the lack of steric bulk in the 4- and 5-positions of the heterocycle allows a 60° tilt of the triptycene wings, thus relieving steric pressure from the space close to the metal center.

To obtain stereochemically defined NHC ligands, the Buchwald–Hartwig amination of bromotriptycene **13** with (1*S*,2*S*)-1,2-diphenylethylenediamine or *meso*-1,2-diphenyl-1,2-diaminoethane, followed by the cyclization of the diamine with $HC(OEt)_3$, were utilized. The respective reactions of the *meso*- and of the chiral azolium salt with suitable metal precursors provide the respective stereochemically defined chiral or *meso*-complexes [(NHC)ML] with **15a**, **15b**, or **17** for M = Rh, Ir, Au, Pd. Preliminary catalytic tests of the respective copper complexes with chiral NHC in the enantioselective borylation provide excellent yields and enantioselectivities.

Experimental Section

Synthesis of quinone 1:[2] Anthracene (51.18 g, 315.9 mmol) (recrystallized from xylene) and 1,4-benzoquinone (34.14 g, 315.9 mmol) (recrystallized from cyclohexane) were heated under reflux in xylene (300 mL) for 2 h. Next, the mixture was cooled to room temperature and the precipitated solid collected by filtration. The solid was first washed with a small amount of xylene, then thoroughly washed with hot water, and finally, with ethanol. After drying in vacuo, the product was obtained as pale yellow rhomboids (69.7 g, 85% yield). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.40$ (dd, $J = 5.4$, 3.2 Hz, 2H), 7.23–7.14 (m, 4H), 7.08 (dd, $J = 5.4$, 3.2 Hz, 2H), 6.31 (s, 2H), 4.87 (s, 2H), 3.14 ppm (s, 2H).

Synthesis of hydroquinone 2:[2] To a solution of **1** (50.0 g, 174.82 mmol) in glacial acetic acid (600 mL) at the boiling point, four drops of 40% aq. HBr were added. An exothermic reaction followed, and a fine cream-colored solid precipitated over a few minutes. After another 30 min at the boiling point, the reaction mixture was cooled to room temperature, and the solid collected by filtration. The solid was washed with acetic acid, then ethanol, and dried in vacuo (40.23 g, 80% yield). ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 8.81$ (s, 2H), 7.45–7.34 (m, 4H), 7.02–6.92 (m, 4H), 6.32 (s, 2H), 5.81 ppm (s, 2H).

Synthesis of quinone 3:[2] Hydroquinone **2** (12.0 g, 41.96 mmol) was dissolved in hot glacial acetic acid (900 mL), and then a solution of potassium bromate (2.69 g, 16.11 mmol) in 245 mL of hot water was added. A deep orange color developed immediately. The solution was heated under reflux for two minutes, hot water (250 mL) was added, and then boiling continued for a few minutes. The solution was cooled to room temperature and a yellow solid collected by filtration. The quinone was washed with acetic acid, water, and ethanol, and finally, dried in vacuo (10.93 g, 92% yield). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.47$–7.40 (m, 4H), 7.07–7.00 (m, 4H), 6.60 (s, 2H), 5.80 ppm (s, 2H).

Synthesis of monooxime 4:[24] To a stirred solution of quinone **3** (12.1 g, 42.5 mmol) was added $NH_2OH{\cdot}HCl$ solution (15.3 g, 220.1 mmol dissolved in 35 mL water) in THF (350 mL). The reaction mixture was heated for 12 h at 50 °C and then cooled to room temperature. The volatiles were removed under reduced pressure, then the residue dissolved in CH_2Cl_2 and was washed with water. The organic layer was dried over anhydrous $MgSO_4$, and the filtrate was evaporated under reduced pressure. The residue was recrystallized from ethanol/water, and the product obtained as a yellow crystalline solid (9.5 g, 75% yield). Spectroscopic data are in accordance with literature data.[24]

Synthesis of aminophenol 5:[24] To a stirred solution of **4** (9.5 g, 31.7 mmol) were added Pd/C (0.95 g, 10 wt%) and hydrazine hydrate (65% aq., 168.5 mmol) in THF (250 mL), followed by refluxing for 2 h, and then filtered. Both flask and filter were washed with DCM. The filtrate was concentrated under reduced pressure, and the residue washed with pentane. The precipitate was collected by filtration and dried in vacuo (8.2 g, 91% yield). Spectroscopic data are in accordance with literature data.[24]

Synthesis of 11: To a solution of **1** (5.00 g, 17.52 mmol) in distilled THF (280 mL) under nitrogen was added 50% aq. H_3PO_2 (5.75 mL, 52.56 mmol). The solution was heated to 40 °C, and then a solution of *tert*-butyl nitrite (3.47 mL, 90%, 26.28 mmol) in THF (20 mL) was added dropwise. The mixture was kept at 40 °C for 24 h. The THF was then removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and washed with brine. The organic layer was separated, dried over $MgSO_4$, and the filtrate concentrated under reduced pressure. Silica gel column chromatography, with ethyl acetate/cyclohexane (1:10) as eluent, afforded **2** as a yellowish solid (3.05 g, 65% yield). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.46$–7.35 (m, 4H, H_{Ar}), 7.04–6.96 (m, 5H, H_{Ar}), 6.84 (dd, $J = 8.0$, 7.4 Hz, 1H, H_{Ar}), 6.45 (dd, $J = 8.1$, 0.9 Hz, 1H, H_{Ar}), 5.84 (s, 1H, $CHAr_3$), 5.42 (s, 1H, $CHAr_3$), 4.77 ppm (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 150.3$, 148.1, 145.7, 145.2, 131.2, 126.1, 125.3, 123.8, 123.8, 116.8, 113.1, 54.4, 47.1 ppm. HRMS (EI): *m/z*: calcd for $C_{20}H_{14}O$: 270.10345 $[M+H]^+$; found 270.1044.

Synthesis of 12a: To a solution of **11** (1.5 g, 5.5 mmol) in DMF (10 mL) was added K_2CO_3 (2.3 g, 16.6 mmol). The mixture was stirred for 5 min at room temperature, and then butyl iodide (1.06 mL, 7.2 mmol) was added in one portion. The reaction mixture was stirred at 70 °C for 24 h. The mixture was then cooled to room temperature, and water (150 mL) was added. The product was extracted a few times with diethyl ether, the extract was washed three times with water, followed by three times with brine, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure, and the obtained solid washed with cold methanol to give alkylated phenol **12a** (1.45 g, 74% yield). ^{1}H NMR (300 MHz, $CDcl_3$): $\delta = 7.48$–7.39 (m, 4H, H_{Ar}), 7.08–7.05 (m, 1H, H_{Ar}), 7.04–7.00 (m, 4H, H_{Ar}), 6.96 (dd, $J = 8.2$, 7.3 Hz, 1H, H_{Ar}), 5.96 (s, 1H, $CHAr_3$), 5.45 (s, 1H, $CHAr_3$), 4.03 (t, $J = 6.4$ Hz, 2H, OCH_2, hexyl), 1.95–1.85 (m, 2H, CH_2, hexyl), 1.66–1.54 (m, 2H, CH_2, hexyl), 1.50–1.42 (m, 4H, CH_2, hexyl), 1.05–0.98 ppm (m, 3H, CH_3, hexyl); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 154.1$, 147.6, 146.0, 145.6, 133.5, 126.0, 125.2, 125.1, 123.8, 123.7, 116.4, 109.9, 68.8, 54.5, 47.1, 31.8, 29.5, 26.0, 22.9, 14.2 ppm; HRMS (EI): *m/z*: calcd for $C_{26}H_{26}O$: 354.1978 $[M]^+$; found: 354.1977.

Synthesis of 13a and 13b: The respective alkylated phenol **12a** or **12b** (4.18 mmol) was dissolved in DMF (25 mL). Next, NBS (1.48 g, 8.36 mmol) was added in few portions, and the solution stirred for 24 h at 100 °C. After that, the reaction mixture was cooled to room temperature, and water (250 mL) was added. The product was extracted a few times with diethyl ether, the extract was washed three times with water, and then three times with brine, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure, and solid residue washed with cold methanol to give bromophenol **13a** (1.49 g, 82% yield), **13b** (1.48 g, 77% yield), or **13c** (1.63 g, 84%) as an off-white solid.

13a: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.47$–7.43 (m, 2H, H_{Ar}), 7.43–7.39 (m, 2H, H_{Ar}), 7.09 (d, $J = 8.7$ Hz, 1H, H_{Ar}), 7.04–7.00 (m, 4H, H_{Ar}), 6.46 (d, $J = 8.8$ Hz, 2H, H_{Ar}), 5.92 (s, 1H, $CHAr_3$), 5.87 (s, 1H, $CHAr_3$), 3.96 (t, $J = 6.4$ Hz, 2H, OCH_2, hexyl), 1.89–1.82 (m, 2H, CH_2, hexyl), 1.58–1.51 (m, 2H, CH_2, hexyl), 1.44–1.39 (m, 4H, CH_2, hexyl), 0.99–

0.95 (m, 3H, CH_3, hexyl); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.4, 146.4, 145.4, 145.0, 136.2, 129.0, 125.5, 125.3, 124.2, 123.9, 111.6, 110.1, 69.1, 53.6, 47.6, 31.7, 29.4, 26.0, 22.8, 14.2 ppm; HRMS (EI): *m/z*: calcd for $C_{26}H_{25}OBr$: 432.1083 $[M]^+$; found: 432.1078.

13b: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.46–7.42 (m, 2H, H_{Ar}), 7.41–7.37 (m, 2H, H_{Ar}), 7.08 (d, *J* = 8.7 Hz, 1H, H_{Ar}), 7.03–6.99 (m, 4H, H_{Ar}), 6.46 (d, *J* = 8.7 Hz, 1H, H_{Ar}), 5.89 (s, 1H, $CHAr_3$), 5.86 (s, 1H, $CHAr_3$), 3.85 (dd, *J* = 5.6, 1.2 Hz, 2H, OCH_2, 2-EtHex), 1.81 (hept, *J* = 6.1 Hz, 1H, CH, 2-EtHex), 1.63–1.45 (m, 4H, CH_2, 2-EtHex), 1.43–1.36 (m, 4H, CH_2, 2-EtHex), 1.00 (t, *J* = 7.5 Hz, 3H, CH_3, 2-EtHex), 0.98–0.94 ppm (m, 3H, CH_3, 2-EtHex); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 153.5, 146.39, 145.36, 145.0, 136.2, 129.0, 125.4, 124.2, 123.9, 110.0, 71.4, 53.6, 47.7, 39.6, 31.0, 29.3, 24.4, 23.3, 14.3, 11.5 ppm; HRMS (EI): *m/z*: calcd for $C_{28}H_{29}OBr$: 460.1396 $[M]^+$; found: 460.1399.

13c: ^1H NMR (300 MHz, $CDCl_3$): δ = 7.56–7.32 (m, 4H), 7.16–6.92 (m, 5H), 6.45 (d, *J* = 8.8 Hz, 1H), 5.91 (s, 1H), 5.86 (s, 1H), 3.95 (t, *J* = 6.4 Hz, 2H), 1.97–1.75 (m, 2H), 1.59–1.50 (m, 2H), 1.47–1.28 (m, 8H), 1.02–0.82 ppm (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.4, 146.4, 145.3, 145.0, 136.2, 129.0, 125.5, 125.3, 124.2, 123.9, 111.6, 110.1, 69.0, 53.6, 47.5, 32.0, 29.5, 29.4, 26.3, 22.9, 14.3 ppm; HRMS: *m/z*: calcd for $C_{28}H_{29}OBr$: 460.1401; found: 460.14093.

Synthesis of 14a and 14b: Under nitrogen atmosphere, to a solution of $Pd_2(dba)_3$ (55.4 mg, 0.06 mmol) and BINAP (90.4 mg, 0.145 mmol) in toluene (15 mL) was added sodium *tert*-pentoxide (2.5 M in THF, 1.16 mL 2.9 mmol), and the resulting mixture stirred for 30 min at room temperature. After this time, 2.42 mmol of **13a** or **13b** (respectively) and (1*S*, 2*S*)-1,2-diphenylethylenediamine (256 mg, 1.2 mmol) were added, and the reaction mixture was heated to 100 °C for 24 h. After cooling to room temperature, the reaction mixture was filtered through a plug of silica, and the plug washed with CH_2Cl_2. The filtrate was evaporated under reduced pressure, and the residue purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 10:1, *v/v*) affording chiral diamine **14a** (888 mg, 80% yield) or **14b** (1.0 g, 85% yield) as a white solid.

14a: $[\alpha]_D^{20} = -34.7$ (*c* = 0.614 in $CHCl_3$); ^1H NMR (500 MHz, $[D_6]$DMSO): δ = 7.45 (d, *J* = 7.1 Hz, 2H, H_{Ar}), 7.41 (d, *J* = 7.1 Hz, 2H, H_{Ar}), 7.36 (d, *J* = 7.0 Hz, 4H, H_{Ar}), 7.21 (d, *J* = 7.4 Hz, 4H, H_{Ar}), 7.13–7.02 (m, 10H, H_{Ar}), 7.02–6.94 (m, 4H, H_{Ar}), 6.43 (d, *J* = 8.7 Hz, 2H, H_{Ar}), 6.31 (d, *J* = 8.7 Hz, 2H, H_{Ar}), 6.01 (s, 2H, $CHAr_3$), 5.92–5.88 (m, 2H), 5.81 (s, 2H, $CHAr_3$), 4.70–4.65 (m, 2H), 3.89–3.81 (m, 4H, OCH_2, hexyl), 1.71 (quint, *J* = 6.5 Hz, 4H, CH_2, hexyl), 1.48 (quint, *J* = 6.9 Hz, 4H, CH_2, hexyl), 1.38–1.31 (m, 8H, CH_2, hexyl), 0.92 ppm (t, *J* = 6.5 Hz, 6H, CH_3, hexyl); ^{13}C NMR (126 MHz, $[D_6]$DMSO): δ = 146.5, 145.7, 145.6, 145.4, 141.7, 137.2, 134.2, 133.6, 127.7, 126.7, 124.9, 124.7, 124.5, 123.5, 123.4, 123.3, 112.6, 111.2, 69.2, 65.3, 46.8, 46.7, 31.0, 28.8, 25.3, 22.1, 13.9 ppm; HRMS (EI): *m/z*: calcd for $C_{33}H_{31}ON$: 457.2400 $[M-C_{33}H_{33}NO]^+$; found: 457.2399; calcd for $C_{33}H_{32}ON$: 458.2478 $[M-C_{33}H_{32}NO]^+$; found: 458.2454.

14b: $[\alpha]_D^{20} = -34.8$ (*c* = 0.035 in $CHCl_3$); ^1H NMR (500 MHz, $[D_6]$DMSO): δ = 7.44 (d, *J* = 6.9 Hz, 2H, H_{Ar}), 7.38 (d, *J* = 7.1 Hz, 2H, H_{Ar}), 7.35 (d, *J* = 7.0 Hz, 2H, H_{Ar}), 7.32 (d, *J* = 7.0 Hz, 2H, H_{Ar}), 7.21–7.18 (m, 4H, H_{Ar}), 7.12–7.02 (m, 10H, H_{Ar}), 7.02–6.94 (m, 4H, H_{Ar}), 6.43 (d, *J* = 8.7 Hz, 2H, H_{Ar}), 6.29 (d, *J* = 8.8 Hz, 2H, H_{Ar}), 5.99 (s, 2H, $CHAr_3$), 5.89–5.84 (m, 2H), 5.78 (s, 2H, $CHAr_3$), 4.68–4.64 (m, 2H), 3.78–3.70 (m, 4H, OCH_2, 2-EtHex), 1.69 (hept, *J* = 12.1, 6.1 Hz, 2H, CH, 2-EtHex), 1.57–1.39 (m, 8H, CH_2, 2-EtHex), 1.37–1.31 (m, 8H, CH_2, 2-EtHex), 0.96–0.89 ppm (m, 12H, CH_3, 2-EtHex); ^{13}C NMR (126 MHz, $[D_6]$DMSO): δ = 146.7, 145.7, 145.6, 145.4, 141.7, 137.1, 133.9, 133.6, 127.7, 126.7, 124.9, 124.2, 124.5, 123.5, 123.4, 123.3, 112.6, 110.6, 71.3, 65.3, 46.8, 46.7, 38.8, 38.8, 30.2, 30.1, 28.5, 23.6, 22.6, 13.9, 11.0 ppm; HRMS (EI): *m/z*: calcd for $C_{42}H_{41}ON$: 575.3183 $[M-C_{28}H_{31}NO]^+$; found: 575.3180; calcd for $C_{35}H_{35}ON$: 485.2713 $[M-C_{35}H_{37}NO]^+$; found: 485.2712.

Synthesis of 15a·HBF$_4$ and 15b·HBF$_4$: The respective diamine **14a** or **14b** (0.981 mmol), NH_4BF_4 (103 mg, 0.982 mmol), $CH(OEt)_3$ (9 mL), and a catalytic amount of formic acid (2 drops) were stirred at 120 °C overnight. Next, the resulting suspension was cooled to room temperature, and diethyl ether (20 mL) was added. The precipitate was collected by filtration and washed a few times with diethyl ether. The corresponding azolium salts **15a**·HBF_4 (757 mg, 76% yield) and **15b**·HBF_4 (662 mg, 63% yield) were obtained as off-white solids.

15a·HBF$_4$: $[\alpha]_D^{20} = -188.0$ (*c* = 0.505 in DMSO); ^1H NMR (500 MHz, $[D_6]$DMSO): δ = 9.18 (s, 1H, NCHN), 7.66–7.62 (m, 6H, H_{Ar}), 7.49–7.43 (m, 6H, H_{Ar}), 7.39 (d, *J* = 7.2 Hz, 2H, H_{Ar}), 7.38–7.33 (m, 4H, H_{Ar}), 7.32–7.28 (m, 2H, H_{Ar}), 7.12–7.05 (m, 6H, H_{Ar}), 7.01 (td, *J* = 7.5, 1.2 Hz, 2H, H_{Ar}), 6.88 (d, *J* = 8.9 Hz, 2H, H_{Ar}), 6.38 (s, 2H), 6.24 (s, 2H), 5.92 (s, 2H), 4.05 (t, *J* = 6.4 Hz, 4H, OCH_2, hexyl), 1.82–1.75 (m, 4H, CH_2, hexyl), 1.54–1.46 (m, 4H, CH_2, hexyl), 1.39–1.33 (m, 8H, CH_2, hexyl), 0.94–0.90 ppm (m, 6H, CH_3, hexyl); ^{13}C NMR (126 MHz, $[D_6]$DMSO): δ = 157.8, 153.4, 144.8, 144.6, 144.4, 144.2, 142.3, 134.6, 129.6, 129.3, 128.0, 125.4, 125.3, 125.0, 124.4, 124.0, 123.8, 123.6, 123.4, 110.6, 74.6, 68.4, 47.1, 46.1, 30.9, 28.5, 25.2, 22.1, 13.8 ppm; HRMS (EI): *m/z*: calcd for $C_{53}H_{50}O_2N_2$: 746.3867 $[M-C_{14}H_{13}-BF_4]^+$; found: 746.3872.

15b·HBF$_4$: $[\alpha]_D^{20} = -175.2$ (*c* = 0.448 in $(CH_3)_2CO$); ^1H NMR (300 MHz, $[D_6]$DMSO): δ = 9.19 (s, 1H, NCHN), 7.66 (d, *J* = 7.4 Hz, 6H, H_{Ar}), 7.53–7.42 (m, 6H, H_{Ar}), 7.41–7.26 (m, 8H, H_{Ar}), 7.16–6.99 (m, 8H, H_{Ar}), 6.90 (d, *J* = 8.9 Hz, 2H, H_{Ar}), 6.40 (s, 2H), 6.26 (s, 2H), 5.91 (s, 2H), 3.95 (d, *J* = 5.4 Hz, 4H, OCH_2, 2-EtHex), 1.78 (hept, *J* = 6.2 Hz, 2H, CH, 2-EtHex), 1.63–1.44 (m, 8H, CH_2, 2-EtHex), 1.43–1.30 (m, 8H, CH_2, 2-EtHex), 1.02–0.88 ppm (m, 12H, CH_3, 2-EtHex); ^{13}C NMR (75 MHz, $[D_6]$DMSO): δ = 157.8, 153.6, 144.8, 144.6, 144.4, 144.3, 142.3, 134.6, 134.6, 129.6, 129.3, 128.0, 125.5, 125.4, 125.0, 124.4, 124.1, 123.7, 123.6, 123.6, 110.4, 74.7, 70.8, 47.1, 46.3, 30.2, 28.5, 23.6, 23.6, 22.6, 13.9, 11.1 ppm; HRMS (EI): *m/z*: calcd for $C_{57}H_{58}O_2N_2$: 802.4493 $[M-C_{14}H_{13}-BF_4]^+$; found: 802.4488.

Synthesis of [AuCl(15a)]: Azolium salt **15a**·HBF_4 (110 mg, 0.108 mmol) was dissolved in a mixture of acetone (6 mL) and methanol (2 mL). To the resulting solution was added Amberlite IRA-410 (chloride form) ion-exchange resin (600 mg, washed with methanol prior to use). The mixture was vigorously stirred at room temperature for 24 h and then filtered. The solvent was removed in vacuo. To the obtained white solid was first added $[AuCl(SMe_2)]$ (31.9 mg, 0.108 mmol) and acetone (3 mL), followed 10 min later by powdered K_2CO_3 (44 mg, 0.318 mmol). The resulting suspension was stirred at 60 °C overnight in the dark. After this time, the solvent was removed in vacuo, and dichloromethane was added. The mixture was filtered through a pad of Celite, and the pad was then washed with dichloromethane. The solvent was concentrated and the solid residue purified by column chromatography (silica gel, pentane/diethyl ether, 10:1, v/v) to provide the desired gold complex as a white solid (78 mg, 62% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.60–7.42 (br, 12H, H_{Ar}), 7.40 (d, *J* = 6.8 Hz, 2H, H_{Ar}), 7.37 (d, *J* = 7.2 Hz, 2H, H_{Ar}), 7.24–7.13 (br, 2H, H_{Ar}), 7.09–7.02 (m, 4H, H_{Ar}), 7.00–6.72 (m, {t, 2H, *J* = 7.7 Hz + t, 2H, *J* = 7.2 Hz + br, 2H}, H_{Ar}), 6.48 (d, *J* = 8.8 Hz, 2H, H_{Ar}), 5.88 (s, 2H, $CHAr_3$), 5.72–5.49 (br, 2H, CH, backbone), 5.39 (s, 2H, $CHAr_3$), 3.99–3.89 (m, 2H, OCH_2, hexyl), 1.85 (quint, *J* = 6.5 Hz, 4H, CH_2, hexyl), 1.58–1.50 (m, 4H, CH_2, hexyl), 1.46–1.38 (m, 8H, CH_2, hexyl), 0.97 ppm (t, *J* = 7.0 Hz, 6H, CH_3, hexyl); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 194.81 (C-Au), 154.0, 145.6, 145.2, 144.5, 144.2, 143.8, 137.5, 135.1, 129.9, 129.8, 126.9, 125.9, 125.6, 125.5, 125.3, 124.3, 124.2, 124.1, 110.0, 78.5, 68.7, 49.9,

47.2, 31.7, 29.4, 26.0, 22.8, 14.2 ppm; HRMS (EI): *m/z*: calcd for $C_{53}H_{50}O_2N_2$: 746.3867 $[M-C_{14}H_{12}-AuCl]^+$; found: 746.3863.

General procedure for the synthesis of [RhCl(cod)(15 a)] and [RhCl(cod)(15 b)]: A vial was charged with the corresponding NHC·HBF_4 (1 equiv), $[RhCl(cod)]_2$ (0.5 equiv), and K_2CO_3 (3 equiv). The resulting mixture was suspended in acetone (2.0 mL), and stirred for 20 h at 60 °C. After this time the solvent was removed in vacuo and dichloromethane was added (3 mL). The mixture was filtered through a pad of silica. The pad of silica was then washed with dichloromethane until the filtrate became colorless, and the solvent was removed in vacuo. The solid residue was washed with cold methanol. The respective rhodium complexes [RhCl(cod)(**15 a**)] (74 mg, 69% yield) and [RhCl(cod)(**15 b**)] (60 mg, 65% yield) were obtained as yellow solids.

[RhCl(cod)(**15 a**)]: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.54 (d, J = 7.0 Hz, 1H, H_{Ar}), 7.91 (d, J = 7.5 Hz, 2H, H_{Ar}), 7.60–7.52 (m, 5H, H_{Ar}), 7.48–7.43 (m, 2H, H_{Ar}), 7.42–7.39 (m, 1H, H_{Ar}), 7.38–7.33 (m, 5H, H_{Ar}), 7.32–7.29 (m, 2H, H_{Ar}), 7.04–7.00 (m, 2H, H_{Ar}), 6.99 (d, J = 7.3 Hz, 1H, H_{Ar}), 6.97–6.92 (m, 2H, H_{Ar}), 6.89 (t, J = 7.3 Hz, 2H, H_{Ar}), 6.81 (t, J = 7.4 Hz, 1H, H_{Ar}), 6.67 (d, J = 8.8 Hz, 1H, H_{Ar}), 6.65–6.59 (br, 1H), 6.54 (d, J = 8.7 Hz, 1H, H_{Ar}), 6.33 (d, J = 7.2 Hz, 1H, H_{Ar}), 5.91 (s, 1H), 5.83 (s, 1H), 5.65 (s, 1H), 5.38 (s, 1H), 5.24–5.21 (m, 1H), 5.13–5.10 (m, 1H), 4.92–4.85 (m, 1H, H_{cod}), 4.46 (q, J = 7.2 Hz, 1H, H_{cod}), 4.08–4.02 (m, 1H), 4.02–3.92 (m, 3H), 3.85–3.79 (m, 1H, H_{cod}), 2.74–2.68 (m, 1H, H_{cod}), 2.19–2.10 (m, 1H), 1.96–1.80 (m, 5H), 1.79–1.70 (m, 1H, H_{cod}), 1.60–1.49 (m, 7H), 1.46–1.36 (m, 9H), 1.01–0.93 (m, 6H, CH_3, hexyl), 0.93–0.86 (m, 1H, H_{cod}), 0.49–0.39 ppm (m, 1H, H_{cod}); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 217.8 (d, $J_{(C\text{-}Rh)}$ = 47 Hz, $C_{carbene}$), 153.4, 153.1, 146.6, 146.0, 145.5, 145.4, 144.8, 144.6, 144.5, 144.5, 144.3, 142.9, 140.1, 138.8, 134.8, 134.0, 130.8, 129.7, 129.6, 129.2, 129.2, 128.8, 128.7, 127.5, 127.3, 126.3, 126.2, 125.5, 125.2, 125.1, 124.9, 124.88, 124.86, 124.8, 124.2, 123.9, 123.8, 123.6, 123.0, 122.8, 122.6, 109.5, 109.0, 99.9, 97.5, 97.5, 78.5, 78.2, 69.8 (d, J = 13.6 Hz), 68.9, 68.6, 67.8 (d, J = 13.5 Hz), 49.7, 49.5, 47.3, 47.3, 33.0, 31.80, 31.75, 30.9, 29.6, 29.4, 28.4, 27.8, 26.1, 26.0, 22.8, 14.2 ppm; HRMS (EI): *m/z*: calcd for $C_{67}H_{61}O_2N_2Rh$: 1028.3783 $[M-HCl\text{-}C_8H_{12}]^+$; found: 1028.3802.

[RhCl(cod)(**15 b**)]: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.54 (d, J = 7.3 Hz, 1H, H_{Ar}), 7.92 (d, J = 7.6 Hz, 2H, H_{Ar}), 7.60–7.52 (m, 5H, H_{Ar}), 7.48–7.44 (m, 2H, H_{Ar}), 7.40–7.32 (m, 6H, H_{Ar}), 7.28 (d, J = 7.4 Hz, 2H, H_{Ar}), 7.03–7.00 (m, 2H, H_{Ar}), 6.99 (d, J = 7.4 Hz, 1H, H_{Ar}), 6.97–6.92 (m, 2H, H_{Ar}), 6.88 (t, J = 7.3 Hz, 2H, H_{Ar}), 6.80 (t, J = 7.4 Hz, 2H, H_{Ar}), 6.67 (d, J = 8.8 Hz, 1H), 6.64–6.59 (br, 1H), 6.55 (d, J = 8.6 Hz, 1H), 6.32 (d, J = 7.2 Hz, 1H), 5.89 (s, 1H), 5.81 (s, 1H), 5.64 (s, 1H), 5.36 (s, 1H), 5.21 (s, 1H), 5.13–5.11 (m, 1H), 4.92–4.86 (m, 1H, H_{cod}), 4.45 (q, J = 7.2 Hz, 1H, H_{cod}), 3.98–3.92 (m, 1H, H_{cod}), 3.91–3.80 (m, 4H), 2.72–2.66 (m, 1H, H_{cod}), 2.20–2.11 (m, 1H, H_{cod}), 1.96–1.87 (m, 1H, H_{cod}), 1.86–1.79 (m, 2H, CH, 2-EtHex), 1.78–1.71 (m, 1H, H_{cod}), 1.65–1.46 (m, 11H), 1.46–1.34 (m, 9H), 1.05–0.92 (m, 12H, CH_3, 2-EtHex), 0.92–0.83 (m, 2H, H_{cod}), 0.46–0.36 ppm (m, 1H, H_{cod}); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 217.82 (d, $J_{(C\text{-}Rh)}$ = 47 Hz, $C_{carbene}$), 153.5, 153.2, 153.2, 146.6, 146.0, 145.5, 145.3, 144.8, 144.6, 144.5, 144.4, 144.3, 143.0, 140.2, 138.8, 134.9, 133.99, 133.95, 130.8, 129.7, 129.6, 129.22, 129.18, 128.73, 128.68, 127.4, 127.3, 126.3, 126.2, 125.5, 125.2, 125.1, 125.0, 124.9, 124.8, 124.2, 123.9, 123.6, 123.0, 122.8, 122.6, 109.4, 109.3, 108.8, 99.9, 97.4, 78.5, 78.2, 71.3, 71.0, 69.8 (d, J = 14.1 Hz), 67.8 (d, J = 15.3 Hz), 49.6, 49.5, 47.6, 47.4, 39.8, 39.6, 39.5, 33.06, 31.13, 31.09, 31.03, 30.95, 30.8, 29.9, 29.42, 29.37, 29.34, 29.29, 28.4, 27.7, 24.52, 24.48, 24.44, 24.35, 23.31, 14.27, 11.62, 11.60, 11.5, 11.4 ppm; HRMS (EI): *m/z*: calcd for $C_{71}H_{70}O_2N_2ClRh$: 1120.4175 $[M-C_8H_{12}]^+$; found: 1120.4135; calcd for $C_{71}H_{69}O_2N_2Rh$: 1084.4409 $[M-HCl-C_8H_{12}]^+$; found: 1084.4440.

General procedure for the asymmetric β-borylation of α,β-unsaturated esters (according to a modified literature procedure):[46c] Imidazolinium salt **6 a**·HBF_4 (30.36 mg, 5 mol%) and CuCl (2.82 mg, 5 mol%) were placed into a flame-dried Schlenk tube under nitrogen. Next, THF (2 mL) and sodium *tert*-pentoxide (2.5 M in THF, 29.5 μL, 13 mol%) were added. The mixture was stirred for 15 min at room temperature and then cooled to −20 °C. After this, bis(pinacolato)diboron (158.4 mg, 0.623 mmol), the respective α,β-unsaturated ester (0.567 mmol), and MeOH (49.5 μL, 1.13 mmol) were added. The mixture was stirred for 18 h (time is not optimized) at −20 °C and subsequently, filtered through a silica pad. The silica pad was washed with Et_2O, and the resulting filtrate was concentrated under reduced pressure. In all cases, complete conversion of α,β-unsaturated ester was observed by ^{1}H NMR analysis of the crude mixture.

Oxidation procedure (according to a modified protocol):[21a] The resulting crude mixture was dissolved in THF (5 mL). Next, $NaBO_3{\cdot}4H_2O$ (436.2 mg, 2.84 mmol) and water (5 mL) were added, and the obtained suspension stirred for 3 h at room temperature After this, the mixture was diluted with water (20 mL), and the product was extracted with Et_2O. The combined extracts were washed with brine and dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the residue purified by column chromatography (silica, cyclohexane/ethyl acetate, 7:1, *v/v*).

Ethyl 3-hydroxybutanoate: 63 mg, 84% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.18 (q, J = 7.2 Hz, 2H), 2.98 (br, 1H), 2.54–2.36 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H), 1.23 ppm (d, J = 6.3 Hz, 3H).

Ethyl 3-hydroxy-3-phenylpropanoate: 100 mg, 91% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.34 (m, 4H), 7.31–7.27 (m, 1H), 5.14 (dt, J = 8.8, 3.5 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 3.22 (d, J = 3.5 Hz, 1H), 2.79–2.69 (m, 2H), 1.27 ppm (t, J = 7.2 Hz, 3H).

Ethyl 3-hydroxyoctanoate: 95 mg, 89% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.17 (q, J = 7.2 Hz, 2H), 4.03–3.96 (m, 1H), 2.89 (br, 1H), 2.50 (dd, J = 16.4, 3.1 Hz, 1H), 2.40 (dd, J = 16.4, 9.0 Hz, 1H), 1.56–1.49 (m, 1H), 1.48–1.38 (m, 2H), 1.38–1.25 (m, 8H), 0.89 ppm (t, J = 6.9 Hz, 3H). All spectral data match those reported in ref. [50].

Synthesis of *O*-acetylmandelates for the determination of enantiomeric ratio: β-Alcohol product (0.0818 mmol), (*R*)-*O*-acetylmandelic acid (20.6 mg, 0.106 mmol), and a catalytic amount of DMAP were placed into a flame-dried Schlenk tube under nitrogen. Then CH_2Cl_2 (2 mL) was added, and the obtained solution cooled to 0 °C. Next, DCC (21.9 mg, 0.106 mmol) was added and the mixture stirred at room temperature for 24 h. The obtained white suspension was filtered to remove dicyclohexylurea. The filtrate was diluted with CH_2Cl_2 (10 mL), washed with sodium bicarbonate solution, brine, and dried over $MgSO_4$. The solvent was evaporated under reduced pressure, and the obtained crude mixture was analyzed by ^{1}H NMR spectroscopy (500 MHz, $CDCl_3$, no internal integration standard was used) to determine the enantiomeric ratio.

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Keywords: chiral · copper · homogeneous catalysis · iridium · N-heterocyclic carbene

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FULL PAPER

N-Heterocyclic Carbenes

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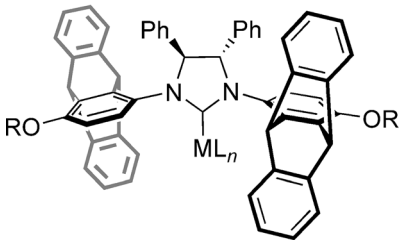
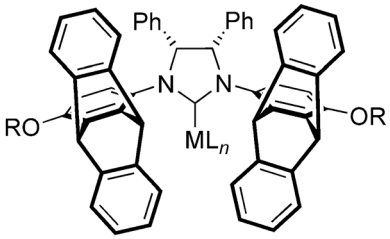
Triptycene-Based Chiral and *meso*-N-Heterocyclic Carbene Ligands and Metal Complexes





From triptycene to enantioselective catalysis: New triptycene-based chiral and *meso*-N-heterocyclic carbenes were synthesized. The triptycene unit infers favorable steric properties onto the respective NHC-metal complexes, enabling the shielding of selected areas close to the metal center.