EurJIC
European Journal of Inorganic Chemistry

Research Article
doi.org/10.1002/ejic.202300178

Chemistry Europe
European Chemical Societies Publishing

www.eurjic.org

Facile Synthesis of Triptycene-Azolium Salts and NHC-Metal Complexes

Alexander Kaps[a] and Herbert Plenio*[a]

The cycloaddition reactions of eleven substituted anthracenes with nosylated quinone imines provides a convenient route to the respective triptycenes. Following re-aromatization, selective O-butylation and cleavage of the nosyl-group the respective triptycene anilines are obtained, which are converted into the respective imidazolium salts according to established procedures. Deprotonation of the imidazolium salts provide new triptycene-NHC-metal complexes (M = AuCl, RhCl(cod), IrCl(cod), $RhCl(CO)_2$, $IrCl(CO)_2$, $PdI_2(py)$, $PtCl_2(py)$, Pd(allyl)Cl) with unusual ligand sterics.

Introduction

Triptycene- and pentiptycene-NHC ligands derived from amino-triptycenes and aminopentiptycenes impart unique steric properties on the respective NHC-metal complexes since one aryl flap of a triptycene or two flaps of a pentiptycene[1] shield distinct segments of the coordination sphere of the respective NHC-metal complex. The steric peculiarities of such NHC ligands are illustrated using the quadrant model (Scheme 1) for four different types of iptycene NHC metal complexes, which have been synthesized before by us. Obviously, the selective shielding of certain quadrants has a significant influence on the catalytic behavior of the respective metal complexes. Bis-Pentiptycene-NHC ligands (type A in Scheme 1) are sterically very demanding and metal ions coordinated by such ligands are located in a deep pocket shielded from the environment.[2] The corresponding NHC-gold complexes have been successfully employed in the efficient gold-catalyzed alkyne hydration[3] and in the gold-catalyzed hydrohydrazidation of alkynes.[4] A nickel complex of the closely related pentiptycene-diimines was shown to be a highly efficient catalyst for the homopolymerization of ethene as well as for the copolymerization of ethene with polar monomers,[5] which is mainly attributed to the steric shielding of the transition metal.

Hoveyda-Grubbs-type ruthenium-complexes with a type B pentiptycene-NHC ligand experience steric bulk on one side of the metal center, while the opposite N*i*Pr side group remains readily accessible. The oscillation of a ruthenium-carbene unit between the sterically demanding pentiptycene side and the open *i*Pr side in ROMP reactions leads to the preferential insertion of a sterically undemanding monomer (cyclooctene) into the growing polymer chain on the pentiptycene side and the insertion of a sterically demanding (but more reactive) monomer (norbornene) on the *i*Pr side of the complex. The corresponding metal complex is thus an efficient catalyst for the alternating copolymerization (aROMP) of these two monomers leading to an AB-type polymer with a very high degree of alternation.[6] In type C metal complexes, the metal are shielded from the "back-side" and while being accessible from the "front-side".[7] NHC-metal complexes of type D are chiral and provide an asymmetric environment for substrate conversion, which has been exploited in the enantioselective borylation of olefins.[7]

Motivated by the interesting properties of such metal complexes, we wish to present here a significantly improved synthetic route to the respective NHC ligands, which allows access to a large variety of different triptycene-NHC based on various substituted anthracenes.

Results and Discussion

Synthesis of Amino-triptycenes. Previously, we reported on the synthesis of triptycene-anilines with an ortho-methyl group, which were prepared in a five-step procedure starting from 2,3-dimethylbenzoquinone and anthracene.[8] An additional reaction step is the etherification of the –OH-group with a long alkyl chain, which is attached at a later stage of the synthesis to improve solubility.

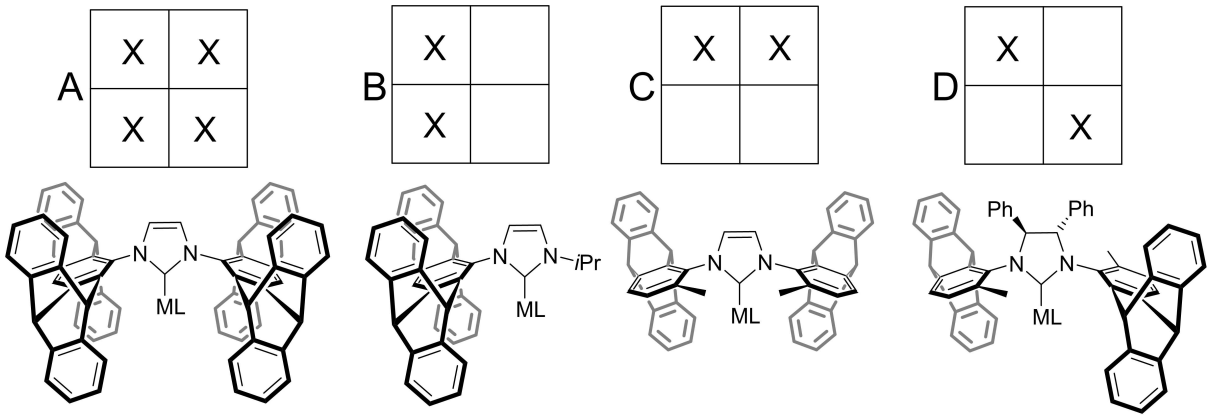
We wish to present here a simplified synthetic approach, which enables the synthesis of a variety of new NHC-metal complexes from substituted anthracenes. A critical step in the previous approach is the introduction of the nitrogen atom using hydroxylamine via oxime formation, which is slowed down by the presence of the two methyl groups. This step requires 60 d under reflux (step d) in Scheme 2) for triptycene quinones derived from plain anthracene and is even more sluggish for triptycene quinones derived from substituted anthracenes.[8] However, the ortho-methyl group next to the

[a] M. Sc. A. Kaps, Prof. Dr. H. Plenio
Organometallic Chemistry
Technical University of Darmstadt
Alarich-Weiss-Str. 12, 64287 Darmstadt (Germany)
E-mail: herbert.plenio@tu-darmstadt.de

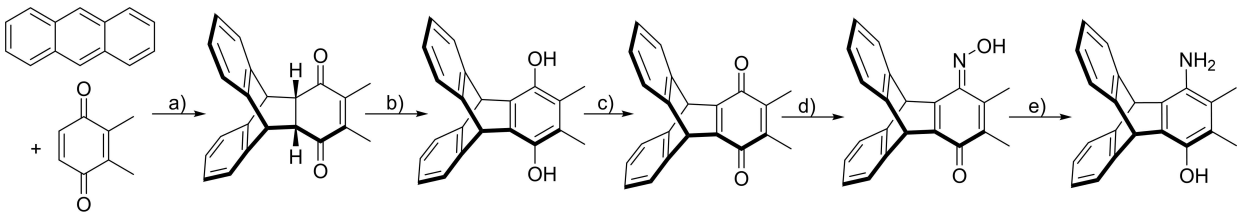
Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejic.202300178

Part of the "NHC-Ligands in Organometallic Chemistry and Catalysis" Special Collection.

Research Article
doi.org/10.1002/ejic.202300178



Scheme 1. Stereochemical properties of triptycene- and pentiptycene-NHC-metal complexes in the quadrant representation.

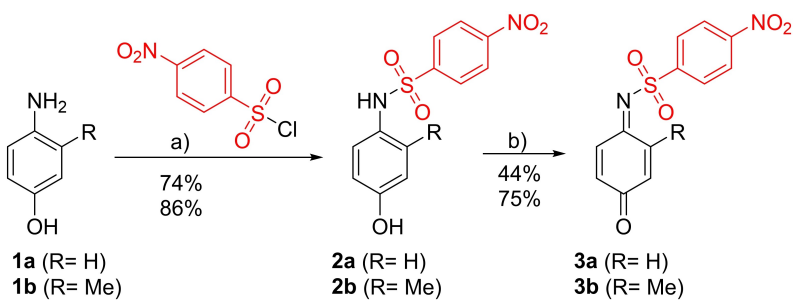


Scheme 2. Previous synthesis of aminotriptycene.

nitrogen is essential for the stability of the envisaged catalytically active NHC-metal complexes, which otherwise tend to decompose via ortho-metalation of the sp^2-CH group.[9]

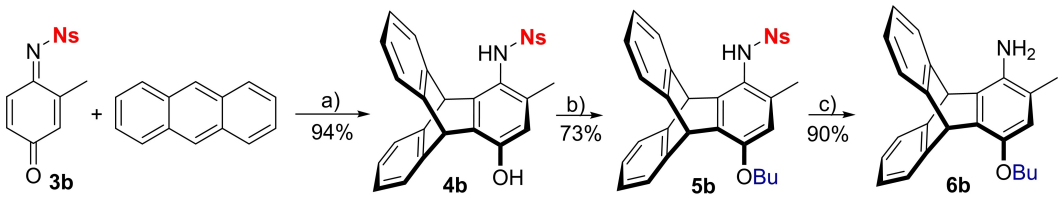
The new approach presented here relies on commercially available 2-methyl-*p*-aminophenol (or *p*-aminophenol), which is reacted with 4-nitrobenzenesulfonylchloride (nosylchloride) to provide the respective nosylated aminophenol, which is then oxidized with ammonium cerium(IV)-nitrate to obtain the respective nosylated quinone-imine (Scheme 3).[10] The quinone imine (R = Me) is readily available in large amounts and up to 85 g of **3b** were synthesized by us in a single batch. The nosyl group serves as an electron-withdrawing group that activates the quinone-imine for the cycloaddition reactions with anthracenes[11] and other dienes.[12] It also acts as a nitrogen protective group[13] to allow selective O-alkylation at a later stage of the synthesis. In addition, the orthogonal deprotection step (using thiophenol)[14] of the nosyl group is very mild, being compatible with most functional groups and provides the respective anilines in very good yields.[13]

An exemplary reaction sequence leading to a simple amino-triptycene is provided in Scheme 4. The nosylated quinone-imine **3b** is reacted with anthracene and the crude material used for the acid catalyzed tautomerization to afford the nosylated amino, hydroxy-triptycene **4b** in 94% yield. The –OH group serves an anchor for the *n*-butyl group, which is helpful in increasing the solubility of the triptycenes[7] and converting the oxidation-prone aminophenol to a stable ether. Selective O-butylation requires optimized reaction conditions. The use of NaH as a base and butylchloride as an alkylating agent are the key ingredients to provide amino, butoxy-triptycene **5b** (yield



Scheme 3. Synthesis of nosylated quinone-imines **3a** and **3b**. Reagents and conditions: a) pyridine, NsCl, CH_2Cl_2, $T = 0\,^{\circ}C$; b) ammonium cerium(IV)-nitrate, $CH_3CN/H_2O/CH_2Cl_2$, rt.

Research Article
doi.org/10.1002/ejic.202300178



Scheme 4. Synthesis of amino-triptycene **6b**. Reagents and conditions: a) $CHCl_3$, reflux followed by AcOH, HBr, reflux; b) NaH, BuCl, DMF, $T = 50\,^{\circ}C$; c) PhSH, K_2CO_3, CH_3CN, $T = 50\,^{\circ}C$.

73%) – employing K_2CO_3 as the base instead leads to selective N-alkylation. Finally, the thiophenol induced cleavage of the nosyl group provides the amino-triptycene **6b** (yield 90%) after three simple steps in 62% overall yield from anthracene and the nosylated quinone-imine.

This reaction sequence has been applied for the synthesis of 15 different amino-triptycenes using various substituted anthracenes (Scheme 5). The alkyl substituted anthracenes undergo cycloaddition reactions followed by re-aromatization in very good yields typically exceeding 75% - regardless of the steric bulk of the anthracene substituents (**4e**, **4f**, **4g**, **4h**, **4i**). Among the heteroatom substituted anthracenes 1,4-dibromo-anthracene, 1-bromo-anthracene, 1-chloro-anthracene and 1-(COOMe)-anthracene provide good yields of the respective triptycene (**4l**, **4m**, **4n**, yields 63–92%) – except for the sterically hindered 9,10-dibromoanthracene, which fails to react. Cycloaddition is less efficient for oxygen-substituted anthracenes: 1,8-dimethoxyanthracene yield 48% and 34% (**4j**, **4k**, R = H, Me) of the respective triptycene. The cycloaddition reaction with 1,4-diacetoxy-anthracene requires $Mg(ClO_4)_2$ additive and the respective triptycene **4d** is obtained in 31% yield. The limited product formation with the methoxy-substituted anthracenes is unexpected, since the related cycloaddition reactions with benzoquinone provides the respective triptycenes in very good yields.[15]

Cycloaddition reactions with unsymmetrically substituted anthracenes produce isomeric triptycenes (Scheme 5). The triptycenes derived from 1,4-substituted, 2,6-substituted, 2,7-substituted and 1,8-substituted anthracenes form enantiomers (**4c**, **4d**, **4j**, **4k**, **4l**, **4m**, **4n**), but no attempt was made to separate those isomers. In addition, several cycloaddition reactions generate syn- and anti-isomers (**4h**, **4i**, **4j**, **4k**, **4l**, **4m**, **4n**) in the triptycenes (see discussion of NMR spectra and Scheme 11). For most triptycenes separation of the syn/anti-isomers is easily done at the stage of compounds **5** and **6** - either by chromatography or by recrystallization. Typically, syn- and anti-isomers are formed in equal amounts. There are, however, three exceptions: The syn-isomers of triptycenes **4n** (R = COOMe) and **4k** (R = OMe) are formed exclusively in the presence of $Mg(ClO_4)_2$. It is likely, that the joint coordination of Mg^{2+} by the two oxygen-containing functional groups (–COOMe, CO) preferentially arranges these two groups on the same side during the cycloaddition reaction. In the reactions of 2,7-(tBu)$_2$-anthracene with the quinone-imine the two **4h** isomers are formed in a 2:1 ratio. The preferred isomer has the two tert.-butyl groups on the oxygen-side of the N-nosylated quinone-imine (syn-isomer). This is probably due to the combined steric bulk of the two tert.-butyl groups on one side of the anthracene, which could interfere with the bulky nosyl-group on the nitrogen side of the quinone-imine.

In order to increase the solubility and the stability of the aminotriptycenes the hydroxyl-group in compounds **4** is reacted with butyl chloride to the corresponding butylether **5** (Scheme 6). The alkylating reagents can react with the oxygen or the nitrogen based functional groups and the selectivity of the alkylation reaction had to be optimized. The selective O-alkylation with NaH as the base provides the respective butyl ethers in good yields. The scope of the N/O-selective alkylation reactions was tested for 13 different triptycenes (Scheme 6).

The deprotection of the nosylated nitrogen in compounds **5** to provide the anilines **6** is the next step (Scheme 7). The scope of the deprotection reaction was initially tested for 11 different nosylated triptycenes and for all reactions the isolated yields are in the range from 71–92%. Cleavage of the protective group with thiophenol occurs under mild conditions and is orthogonal to most functional groups. The aminotriptycenes obtained are easily converted into the respective imidazolium or imidazolinium salts following standard procedures (Schemes 8, 9, 10), which in turn are precursors for NHC-metal complexes.

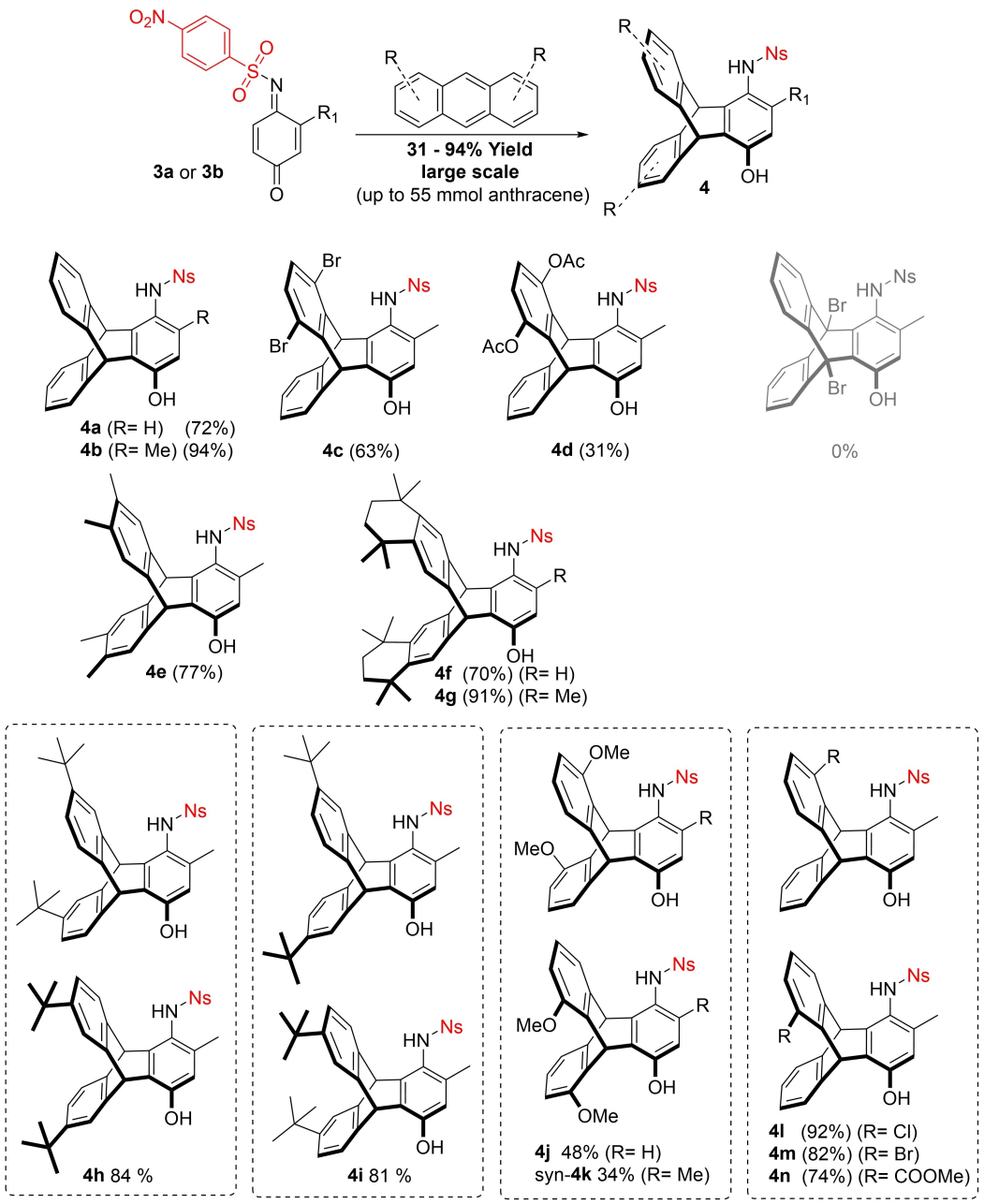
The syn- and anti-isomer of bromide **6m** can be separated via column chromatography on a 10 g-scale. This triptycene is important, since the bromo substituent on the other triptycene wing can be functionalized in numerous ways by employing different cross-coupling reactions. Substituents introduced in this way will be in close vicinity to a transition metal center and should influence its properties, which will be the subject of future studies.

Aminotriptycene **6b** can be converted directly into imidazole **7b** (Scheme 8), followed by alkylation with iPrI to provide imidazolium salt **8b**·HI, which serves as a convenient entry into the synthesis of NHC-metal complexes.

The Rh(I/II) redox potentials in [RhCl(cod)(**8b**)] ($E = 0.873$ V) and the ν(CO) in [RhCl(CO)$_2$(**8b**)] ($\nu(CO)_{av} = 2041.5\ cm^{-1}$) were determined to evaluate the donor properties of NHC ligand **8b**. The IR and the CV data are comparable to those of the IXyl-type NHC ligand ((N,N′-bis(2,6-dimethylphenyl)imidazol)-2-ylidene) ($\nu(CO)_{av} = 2040.5\ cm^{-1}$, $E = 0.855$ V) in the analogous rhodium complexes.[16]

The synthesis of an N-mesityl substituted triptycene-imidazolinium salt utilizes the reaction of **5b** with N-(2-iodoethyl)-2,6-dimethyl-aniline, followed by ring closure with

Research Article
doi.org/10.1002/ejic.202300178



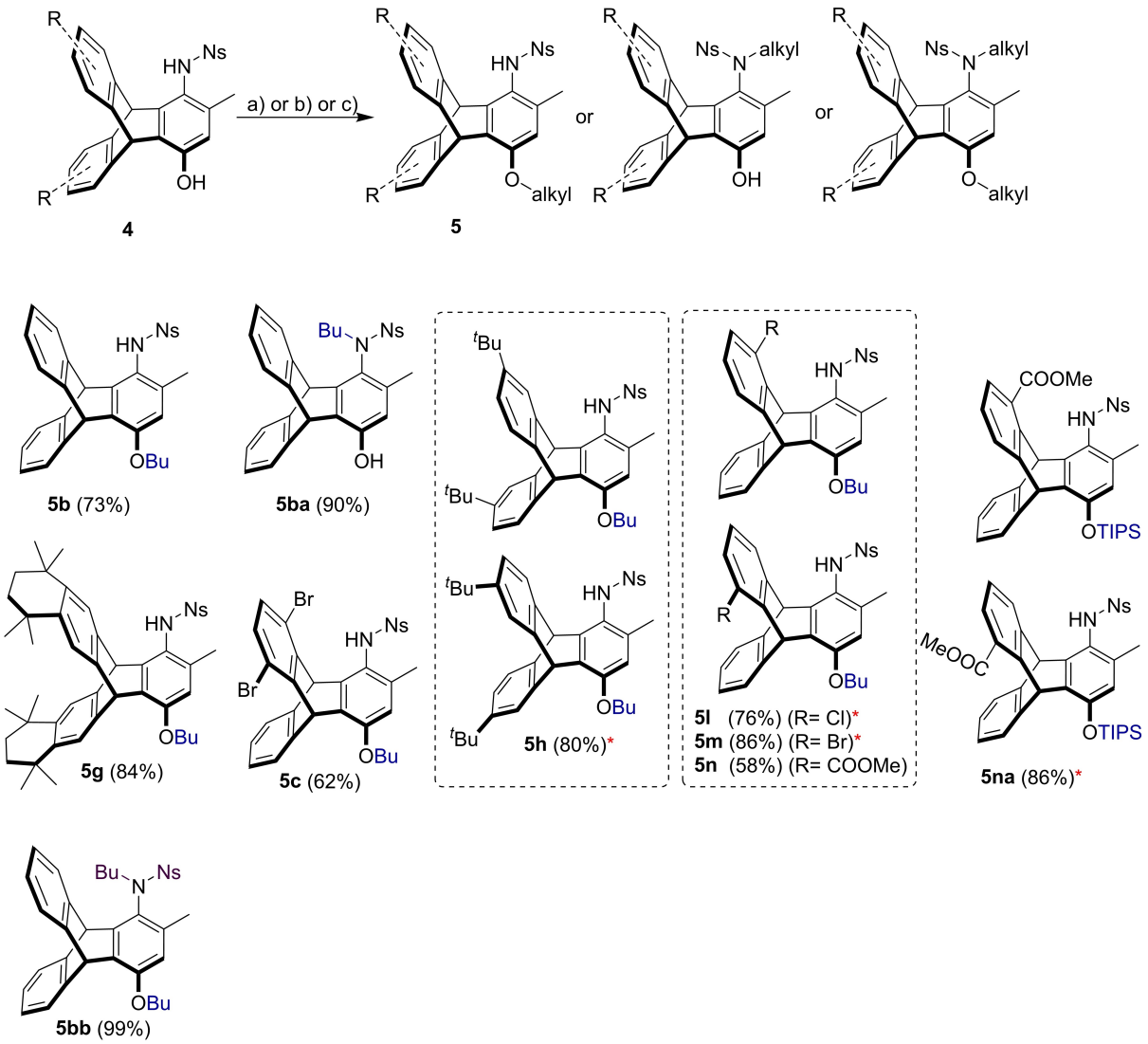
Scheme 5. Scope of anthracenes in the cycloaddition reactions with quinone-monoimines **3a** and **3b**. Reagents and conditions: solvent: $CHCl_3$ or 1,2-dichloroethane, reflux, 1–3 days; then AcOH, HBr (cat.) or ethanol/dioxane, HCl (cat), reflux.

$HC(OEt)_3$.[17] The respective NHC-gold complex was prepared to demonstrate the conversion into NHC-metal complexes.

Aniline **6g** with a sterically extremely demanding triptycene wings can also be converted into the respective imidazolium salt using established synthetic routes (Scheme 10).[17] This azolium salt and the respective (NHC)AuCl complex exist as two different (non-interconvertible) isomers [AuCl(syn-**12**)] and [AuCl(anti-**12**)]. The metal complexes were separated into the isomers by chromatography and characterized.

NMR-spectra. The NMR spectra of the various iptycenes can be complex, but the ^{1}H- and the ^{13}C NMR bridgehead resonances of the sp^3-CH groups of the central ring are located in a region devoid of most other resonances and are highly useful for the characterization of such compounds. Due to the central location of the bridgehead, the respective ^{13}C- and ^{1}H-resonances respond to chemical changes at the periphery of the triptycene. Depending on the nature and the orientation of the substituents, the bridgehead ^{1}H NMR resonances are found in the 5.73–7.22 ppm range and for ^{13}C NMR in the 33.0–51.1 ppm range (for more details see Tables 1, 2, 3 in Supporting Information). In the ^{1}H NMR the respective oxygen- or nitrogen bridgehead singlet resonances shift by up to 0.8 ppm depending on the nature of the substituents at the periphery of the triptycenes.

Research Article
doi.org/10.1002/ejic.202300178



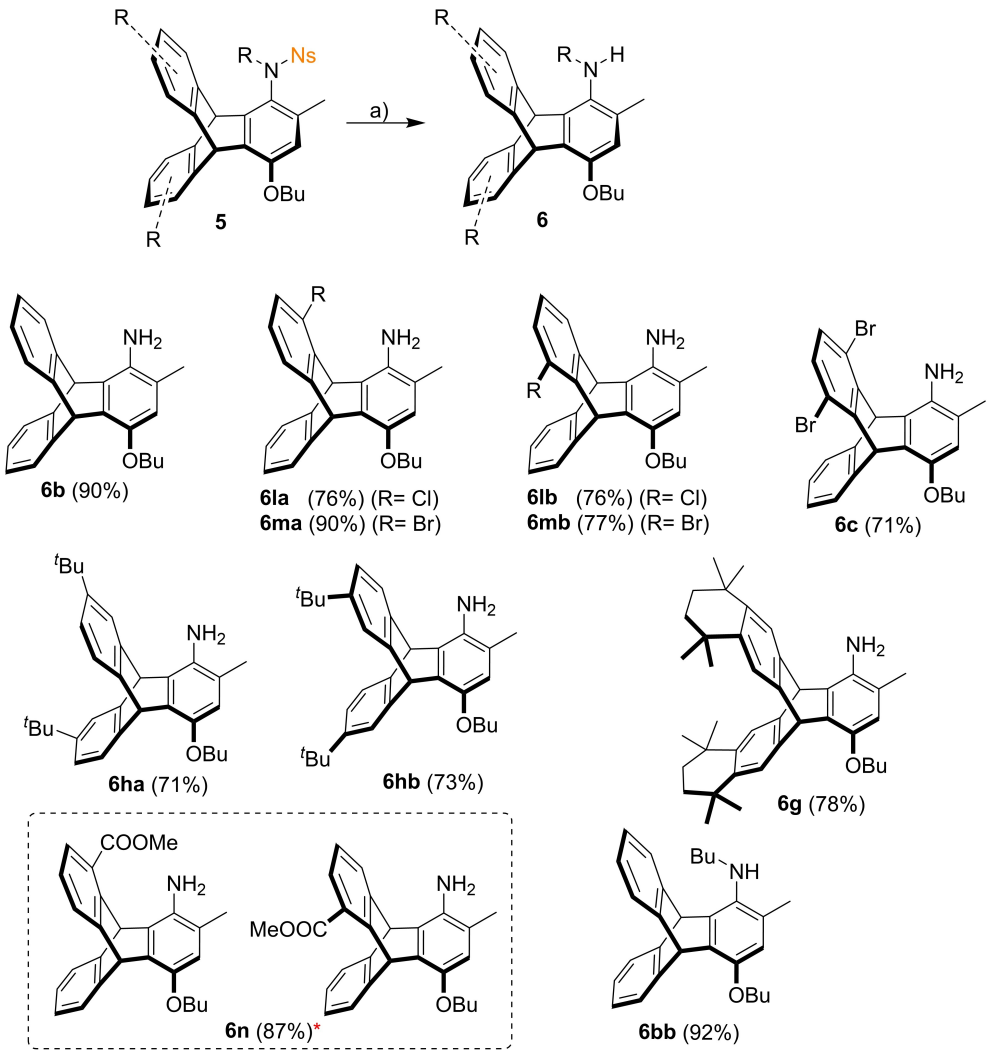
Scheme 6. Scope of N/O alkylation or O-silylation of amino, hydroxytriptycenes (nosyl protected). Reagents and conditions: a) NaH (2.5 eq, 60% dispersion in mineral oil), DMF (dry), $T = 0\,^{\circ}C$, 30 min, then BuCl, $T = 50\,^{\circ}C$, 24 h; b) DMF or MeCN, K_2CO_3, 30 min, rt. then alkyl-Br/alkyl-I, 50 °C, 24 h; c) DMF or MeCN, NaH or K_2CO_3, 30 min, rt. then alkyl-Cl/alkyl-Br/alkyl-I, $T = 50\,^{\circ}C$, 24 h; Silylation: TIPS-triflate, imidazole, DCM (dry), rt., 24 h. *Syn/anti can be separated by column chromatography.

Triptycenes derived from unsymmetrically substituted anthracenes occur as syn- and anti-isomers depending on whether the substituent R is located on the nitrogen- or the oxygen side of the triptycene (Scheme 11). The respective syn- and anti-isomers again are characterized by distinct bridgehead resonances in the ^{1}H- and ^{13}C NMR spectra. The syn/anti-assignment of the isomers by NMR spectroscopy is not straightforward, since from an NMR point of view the three triptycene wings are almost independent of each other. In the case of **4n** the functional group (–COOMe) contains protons and based on an NOE between the methyl group and the bridgehead CH-unit, the structure can be assigned. The halides **4l** and **4m** are easily separated by chromatography. Since the halide substituents are NMR-inactive NOESY is not helpful for isomer assignment. Fortunately, single crystals of **5m** were obtained (supporting) and the crystal structure analysis[18] shows this to be the anti-isomer. Based on the very similar NMR-spectra, of the bridgehead signals, the syn/anti-isomer of the chloro-substituted triptycene are also assigned based on this crystal structure analysis. Furthermore, the assignment of the oxygen- and the nitrogen-side orientation in the respective syn- and anti-isomers of the triptycenes can be reliably done utilizing C–H cross peaks of the ^{3}J or ^{4}J (^{1}H-^{13}C) coupling in the respective HMBC spectra (Scheme 11).

Conclusions

It has been shown that the newly established anthracene + quinone-imine cycloaddition route for the synthesis of triptycene-NHC ligands is much more convenient than the previously employed oxime route. The nosyl group fulfills a dual key role

Research Article
doi.org/10.1002/ejic.202300178



Scheme 7. Scope of deprotection for nosylated triptycenes. Reagents and conditions: a) PhSH, K_2CO_3, MeCN, $T = 50\,^{\circ}C$, 24 h. *Syn/anti can be separated by column chromatography.

since its electron-withdrawing nature activates the quinone-imine for cycloaddition reactions and since it serves as a convenient protecting group for nitrogen to allow selective O-/N-functionalization on the formed triptycene. The orthogonal cleavage of the nosyl group with thiols to generate the amino group is compatible with most other functional groups. The generality of this approach has been demonstrated for eleven anthracenes.

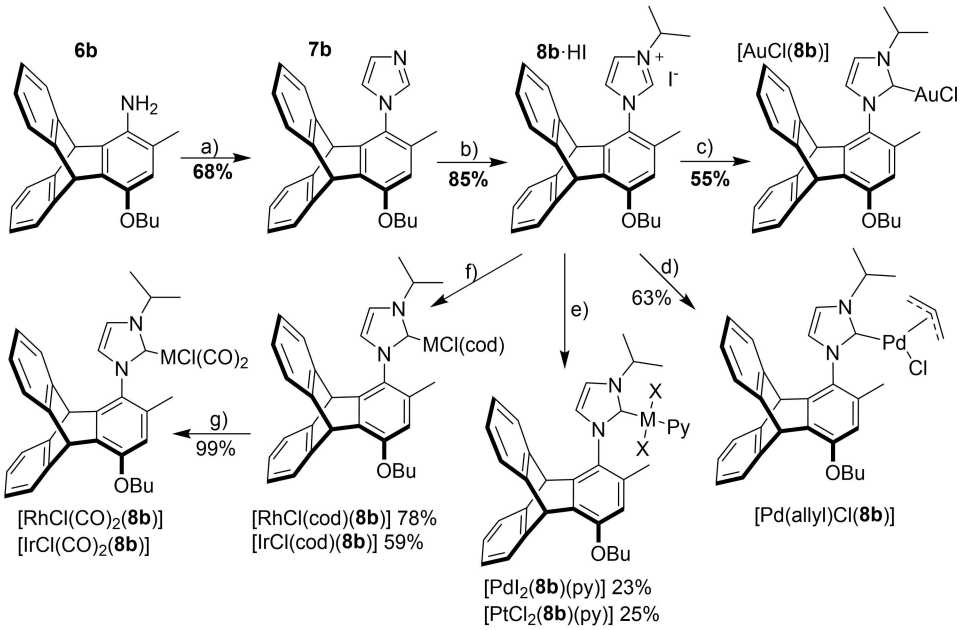
Triptycene-NHC metal complexes with versatile functional groups (such as -Br) near to the transition metal were synthesized, which should allow a variety of functionalization reactions based on cross-coupling reactions to introduce substituents which potentially interact with the transition metal and manipulate their catalytic properties, which will be the subject of future studies.

Experimental Section

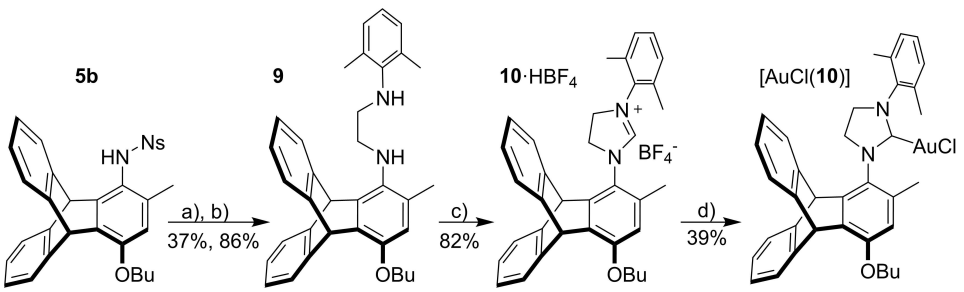
General procedure for aminophenol oxidation Nosylated aminophenol (1.0 eq) was suspended in MeCN, H_2O and DCM (ratio 2 : 1 : 2; per 1 mmol aminophenol 3.5 mL: 1.75 mL: 3.5 mL are used). Then cerium(IV) ammonium nitrate (2.0 eq) was added portion wise (within ca. 10 min). The reaction was stirred vigorously at r.t. for 1 h. Next the layers were separated and the MeCN/H_2O layer extracted with DCM. The combined DCM layer were washed with H_2O, separated, dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. Next, the crude product was dissolved in DCM and filtered over a silica plug. After the solvent was removed under reduced pressure, the quinone monoimine 3a or 3b was obtained as an orange solid.

General procedure for nosyl-protection: Ar-NH_2 (1.0 eq) was dissolved in DCM (4 mL per 1 mmol) and pyridine (3.0 eq). The reaction mixture was cooled to 0 °C and *p*-nitrobenzenesulfonyl chloride (1.0 eq) was added in portions. After completion of the reaction (TLC control), water was added to the reaction mixture, the layers were separated and the aqueous phase extracted with ethyl acetate. The combined organic solutions were washed with 2 M HCl

Research Article
doi.org/10.1002/ejic.202300178



Scheme 8. Synthesis of triptycene, isopropyl-imidazolium salt and NHC-metal complexes. Reagents and conditions: a) glyoxal, HCHO, AcOH, NH_4OAc, $T = 80\,^{\circ}C$, 12 h; b) *i*PrI (excess), $T = 80\,^{\circ}C$, MeCN, 24 h; c) K_2CO_3, acetone, [AuCl(SMe_2)], 6 h, $T = 50\,^{\circ}C$; d) Ag_2O 24 h, then $[Pd(allyl)Cl]_2$, CH_2Cl_2, 24 h; e) $Pd(OAc)_2 + KI$ (X = I) or $PtCl_2 + KCl$ (X = Cl), K_2CO_3, pyridine, $T = 80\,^{\circ}C$; 24 h; f) Ag_2O 24 h, [MCl(cod)] (M = Rh, Ir), 24 h; g) CO bubbling, 30 min, CH_2Cl_2.



Scheme 9. Synthesis of triptycene, 2,6-xylyl-imidazolinium salt **10**·HBF_4 and NHC-gold complex. Reagents and conditions: a) N-(2-iodoethyl)-2,6-dimethyl-aniline·HI, Na_2CO_3, DMF (dry), 60 h, $T = 50\,^{\circ}C$; b) PhSH, MeCN, $T = 50\,^{\circ}C$, 24 h; c) triethyl orthoformate, NH_4BF_4, 110 °C, 24 h; d) [AuCl(SMe_2)], K_2CO_3, acetone, $T = 50\,^{\circ}C$, 6 h.

(aq.) and H_2O. The organic phase was dried over $MgSO_4$, filtered and the solvent removed under reduced pressure.

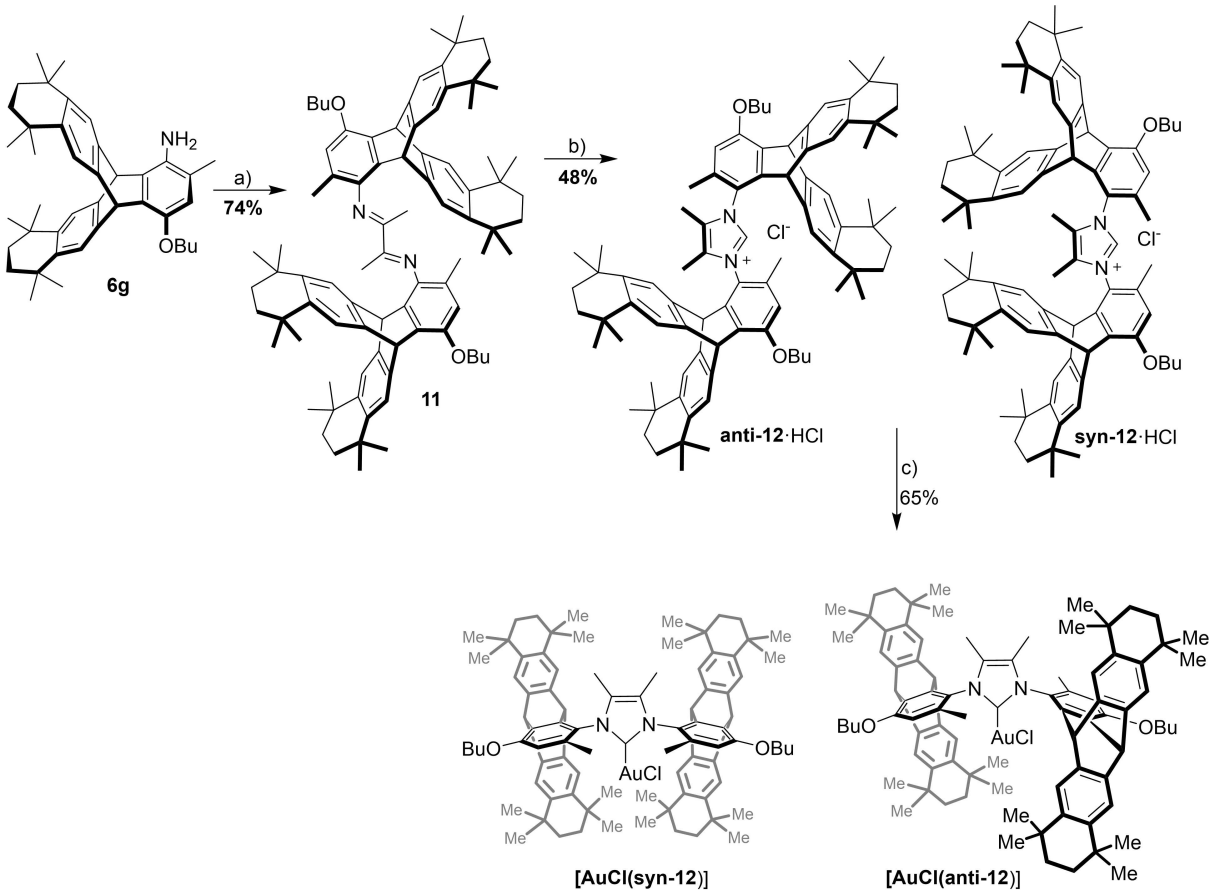
General procedure for quinone-imine/anthracene cycloaddition and aromatization to yield triptycenes 4: Anthracene 1.0 eq) and nosylated quinone-monoimine (1.0–1.3 eq **3a** or **3b**) were dissolved in $CHCl_3$ or DCE (approx. 5 mL per mmol). The reaction mixture was flushed with nitrogen and stirred under reflux for 1–3 days. The resulting precipitate was filtered off. If no precipitate had formed, the volatiles were evaporated under reduced pressure. Two methods were used to aromatize the Diels–Alder-adduct:

Method A: The crude Diels–Alder-adduct was suspended in AcOH, 4–5 drops of HBr (aq.) were added and refluxed until a clear yellow solution was obtained. After complete conversion (controlled by TLC). The reactions mixture was allowed to r.t. then water was added. The resulting precipitate was filtered off and washed several times with water, sat. aqueous $NaHCO_3$, dried and then triturated with pentane. The solid was purified by chromatography with Cy/EA through a silica gel column.

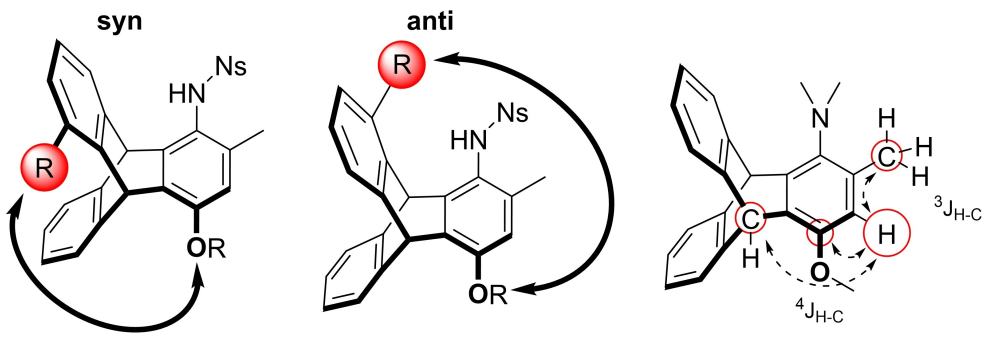
Method B: The crude Diels–Alder-adduct was suspended in EtOH/dioxane (approx. 10:1 v/v), 4–5 drops of HCl (37% aq.) were added and refluxed until a clear solution was obtained. After complete conversion (controlled by TLC) water is added to the reaction mixture. Either the resulting precipitate was filtered off, washed with water, dried and triturated with pentane or the mixture was extracted with EA dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The solid was purified by chromatography with Cy/EA through a silica gel column.

General procedure for O- or N-alkylation of 4 to triptycenes 5: O-alkylation: To a solution of the nosylated aminophenol (1.0 eq) in dry DMF, NaH (2.5 eq, 60% dispersion in mineral oil) is added at 0 °C The reaction mixture was warmed up to r.t. and stirred for another 30 min. Then alkylhalide (1.0 eq) is added and stirred for 24 h at 50 °C. N-alkylation: To a solution of the nosylated aminophenol (1.0 eq) in DMF or MeCN, K_2CO_3 (3.0 eq) is added at r.t. Then alkylhalide (1.0–4.0 eq) is added and stirred for 24 h at 50 °C. Work up: The reaction mixture is poured into water, sat. aqueous NH_4Cl is added and extracted with EA. The organic phase is dried over

Research Article
doi.org/10.1002/ejic.202300178



Scheme 10. Synthesis of very bulky bistriptycene azolium salts and the two isomeric NHC-gold complexes. Reagents and conditions: a) diacetyl, *p*-TsOH, EtOH, $T = 50\,^{\circ}C$, 24 h; b) $EtOCH_2Cl$, $T = 80\,^{\circ}C$, 24 h; c) Ag_2O then $[AuCl(SMe_2)]$, CH_2Cl_2.



Scheme 11. Triptycene syn- and anti-isomers and characteristic HMBC cross peaks useful for the assignment of the N- and O-side of the molecule.

$MgSO_4$, filtered and removed under reduced pressure. The crude product was purified by column chromatography.

General procedure for denosylation of 5 to triptycene 6: Alkylated aminotriptycene (1.0 eq), K_2CO_3 (6.0 eq) was charged in a Schlenk flask under N_2 in MeCN or THF. Then thiophenol (4.0 eq) was added and the reaction mixture was stirred at 50 °C until the triptycene is completely converted (controlled by TLC). The reaction mixture was allowed to r.t., H_2O was added and extracted with EA. The organic phase was dried and filtered over $MgSO_4$. The solvent was removed under reduced pressure and the resulting crude product was purified by column chromatography.

Synthesis of NHC metal complexes

[AuCl(8b)]. Starting materials used were azolium salt **8b**·HI (20 mg, 34.7 µmol, 1.0 eq), $[AuCl(SMe_2)]$ (14.4 mg, 34.7 µmol, 1.0 eq), K_2CO_3 (14.4 mg, 104 µmol, 3.0 equiv.) was added in acetone (2 mL), and the reaction mixture was stirred at 50 °C for 6 h. The volatiles were removed under reduced pressure, and the residue was purified by column chromatography (Cy/EA 5 : 1 v/v).

^1H NMR (500 MHz, CD_2Cl_2): δ 7.41 (d, $J = 6.9$ Hz, 2H), 7.38–7.31 (m, 2H), 7.18 (d, $J = 7.1$ Hz, 1H), 7.04–6.99 (m, 3H), 6.99–6.96 (m, 1H), 6.95–6.93 (m, 1H), 6.56 (s, 1H; ArC**H**), 5.92 (s, 1H; $\mathbf{CH}_{\text{-bridge}}$), 5.31–5.25

Research Article
doi.org/10.1002/ejic.202300178

(m, 1H), 4.87 (s, 1H; C**H**$_{\text{-bridge}}$), 4.10–4.02 (m, 2H; OC**H**$_2$CH$_2$), 2.01 (s, 3H; ArC**H**$_{3\text{-ortho}}$), 1.92–1.84 (m, 2H), 1.73 (d, J = 6.8 Hz, 3H; CH(C**H**$_3$)$_2$), 1.60 (d, J = 6.6 Hz, 3H; CH(C**H**$_3$)$_2$)), 1.60–1.56 (m, 2H), 1.11 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 182.2 (N**C**N), 154.8 (Ar**C**$_{\text{-OBu}}$), 146.3, 145.5, 145.3, 145.0, 144.5, 133.4, 132.9, 126.9, 126.2, 126.0, 125.9, 125.6, 125.5, 124.3, 124.1, 123.9, 123.7, 117.5, 111.6 (Ar**C**H), 69.0 (O**C**H$_2$CH$_2$), 50.3 (**C**H$_{\text{-bridge}}$), 47.4 (**C**H$_{\text{-bridge}}$), 32.0, 30.3, 23.9, 23.8, 20.0, 18.2, 14.3. *(Carbon signal of iPr – (**C**H(CH$_3$)$_2$) overlaps with the solvent signal).

HRMS (APCI): calcd. for $C_{33}H_{35}AuN_3O$ $[M-Cl+MeCN]^+$ 686.24403. Found 686.24395 (Δ = 0.09 mmu).

calcd. for $C_{31}H_{32}AuN_2O$ $[M-Cl]^+$ 645.21748. Found 645.21711 (Δ = 0.38 mmu). R_f = 0.14 (Cy/EA = 5:1 v/v). Yield: 55% (13 mg, 19.1 μmol).

[IrCl(cod)(8b)]. A Schlenk-tube was charged azolium salt **8b**·HI (20 mg, 34.7 μmol, 1.0 eq), Ag_2O (4.0 mg, 17.4 μmol, 0.5 eq) and dissolved in DCM (2 mL). The mixture was stirred for 24 h at room temperature then $[IrCl(cod)]_2$ (11.7 mg, 17.4 μmol, 0.5 eq) was added. After completion of the reaction (checked by TLC) the mixture was filtered through celite and the solvent was removed under reduced pressure. The crude product was purified by short column chromatography (Cy/EA 10:1 v/v) to obtain the desired complex as yellow solid. (Isomer 2:1 ratio).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.38–8.30 (m, 0.58H$_{\text{minor}}$), 7.44–7.37 (m, 2H$_{\text{major}}$ + 0.49H$_{\text{minor}}$), 7.36 (d, J = 6.9 Hz, 0.54H$_{\text{minor}}$), 7.30–7.26 (m, 1H$_{\text{major}}$), 7.25 (d, J = 1.9 Hz, 1H$_{\text{major}}$), 7.22 (d, J = 6.9 Hz, 0.52H$_{\text{minor}}$), 7.19 (d, J = 2.1 Hz, 0.48H$_{\text{minor}}$), 7.09 (d, J = 7.3 Hz, 1H$_{\text{major}}$), 7.07–7.00 (m, 1H), 7.03–6.96 (m, 3H), 6.98–6.86 (m, 2H), 6.87–6.82 (m, 1H), 6.68 (d, J = 1.9 Hz, 0.50H$_{\text{minor}}$), 6.61 (s, 1H; ArC**H**$_{\text{major}}$), 6.50 (s, 0.55H; ArC**H**$_{\text{minor}}$), 5.93 (s, 1H C**H**$_{\text{-bridge major}}$ + 0.85H C**H**(CH$_3$)$_{2\text{ minor}}$), 5.91–5.81 (m, 1H; C**H**(CH$_3$)$_{2\text{ major}}$), 5.87 (s, 0.48H; C**H**$_{\text{-bridge minor}}$); 4.91 (s, 1H; C**H**$_{\text{-bridge major}}$), 4.38–4.31 (m, 0.63H; cod$_{\text{-minor}}$), 4.33–4.25 (m, 1H; cod$_{\text{-major}}$ + 0.5H cod$_{\text{-minor}}$), 4.17–3.98 (m, 4H; major + minor), 3.25–3.18 (m, 0.51H; cod$_{\text{-minor}}$), 3.17–3.10 (m, 1H; cod$_{\text{-major}}$), 2.46–2.39 (m, 0.56H; cod$_{\text{-minor}}$), 2.24 (s, 4H), 2.23–2.11 (m, 3H), 2.04–1.91 (m, 2H), 1.94–1.80 (m, 3H), 1.70 (s, 2H), 1.68 (d, J = 6.8 Hz, 4H), 1.65 (d, J = 6.9 Hz, 5H), 1.58 (d, J = 6.7 Hz, 5H), 1.53–1.47 (m, 4H), 1.40–1.28 (m, 4H), 1.05 (t, J = 7.4 Hz, 5H), 0.91–0.82 (m, 2H), 0.80–0.68 (m, 2H), 0.59–0.48 (m, 1H), 0.43–0.33 (m, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 181.1 (N**C**N$_{\text{major}}$), 179.7 (N**C**N$_{\text{minor}}$), 153.9 (Ar**C**$_{\text{-Obu minor}}$), 153.9 (Ar**C**$_{\text{-Obu major}}$), 147.2, 147.0, 146.6, 145.7, 145.5, 145.5, 144.6, 143.7, 135.4, 134.1, 133.6, 132.1, 128.8, 128.3, 125.8, 125.7, 125.6, 125.5, 125.4, 125.3, 125.3, 125.1, 125.1, 124.5, 124.3, 124.3, 124.3, 124.0, 123.7, 123.6, 123.2, 117.5, 117.1, 112.2 (Ar**C**H$_{\text{major}}$), 111.5 (Ar**C**H$_{\text{minor}}$), 84.5 (cod$_{\text{minor}}$), 84.2 (cod$_{\text{major}}$), 82.6 (cod$_{\text{minor}}$), 82.1(cod$_{\text{major}}$), 69.3 (O**C**H$_2$CH$_{2\text{ minor}}$), 69.3 (O**C**H$_2$CH$_{2\text{ major}}$), 53.6 (**C**H(CH$_3$)$_2$), 52.9 (cod), 52.4 (cod), 52.2 (cod), 50.5 (**C**H$_{\text{-bridge major}}$ + cod), 49.7(**C**H$_{\text{-bridge minor}}$), 47.5 (**C**H$_{\text{-bridge minor}}$), 47.4 (**C**H$_{\text{-bridge major}}$), 35.9, 35.3, 31.9, 31.9, 31.8, 31.5, 30.3, 29.8, 28.8, 28.5, 25.1, 24.4, 23.6, 22.8, 20.1, 20.0, 17.9, 14.3.

HRMS (APCI): calcd. for $C_{39}H_{44}IrN_2O$ $[M-Cl]^+$ 749.30774. Found 749.30792 (Δ = 0.04 mmu). R_f = 0.12 (Cy/EA = 10:1 v/v). Yield: 59% (16 mg, 20.4 μmol).

[IrCl(CO)$_2$(8b)]. The respective [IrCl(cod)(**8b**)] (15 mg, 19.1 μmol, 1.0 eq), complex was dissolved in CH_2Cl_2 and cooled to 0 °C. Then CO was bubbled through this solution for 30 min. The solvent was evaporated and the residue washed with pentane to obtain the product as a yellow solid.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.75 (s, 1H), 7.42 (d, J = 6.9 Hz, 1H), 7.38 (d, J = 6.8 Hz, 1H), 7.36 (d, J = 1.8 Hz, 1H), 7.22 (d, J = 6.8 Hz, 1H), 7.07–6.91 (m, 4H), 6.89 (d, J = 1.7 Hz, 1H), 6.56 (s, 1H; Ar**C**H), 5.92 (s, 1H; C**H**$_{\text{-bridge}}$), 5.61–5.51 (m, 1H; C**H**(CH$_3$)$_2$), 5.29 (s, 1H; C**H**$_{\text{-bridge}}$), 4.10–3.97 (m, 2H; OC**H**$_2$CH$_2$), 1.96 (s, 3H; ArC**H**$_{3\text{-ortho}}$), 1.93–1.85 (m, 2H), 1.70 (d, J = 6.8 Hz, 3H; CH(C**H**$_3$)$_2$), 1.67–1.58 (m, 2H), 1.54 (d, J = 7.5 Hz, 3H; CH(C**H**$_3$)$_2$), 1.07 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 181.8 (Ir**C**O), 175.5 (N**C**N), 168.6 (Ir**C**O), 154.8 (Ar**C**$_{\text{-OBu}}$), 147.0, 146.1, 145.2, 144.8, 133.0, 127.6, 125.7, 125.7, 125.6, 125.4, 125.3, 124.2, 123.9, 123.8, 118.6, 111.6 (Ar**C**H), 69.0, 53.8 (**C**H(CH$_3$)$_2$ assigned via DEPT)*, 50.1 (**C**H$_{\text{-bridge}}$), 47.4 (**C**H$_{\text{-bridge}}$), 32.0, 30.3, 24.3, 23.2, 20.0, 14.3. *(Carbon signal of iPr - **C**H(CH$_3$)$_2$ overlaps with the solvent signal).

HRMS (ESI): calcd. for $C_{33}H_{32}IrN_2O_3$ $[M-Cl]^+$ 697.20367. Found 697.20390 (Δ = 0.06 mmu). Yield: 99% (14 mg, 18.8 μmol).

[RhCl(cod)(8b)]. A Schlenk-tube was charged azolium salt **8b**·HI (20 mg, 34.7 μmol, 1.0 eq), Ag_2O (4.0 mg, 17.4 μmol, 0.5 eq) and dissolved in DCM (2 mL). The mixture was stirred for 24 h at room temperature then $RhCl(cod)]_2$ (8.6 mg, 17.4 μmol, 0.5 eq) was added. After completion of the reaction (checked by TLC) the mixture was filtered through celite and the solvent was removed under reduced pressure. The crude product was purified by short column chromatography (Cy/EA 10:1 v/v) to obtain the desired complex as yellow solid. (Isomer 2:1 ratio).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.54 (d, J = 6.6 Hz, 0.59 H; minor), 7.45 (dd, J = 6.0, 1.9 Hz, 0.65 H; minor), 7.41 (d, J = 7.1 Hz, 2H; major), 7.37 (d, J = 6.9 Hz, 0.60 H; minor), 7.29–7.23 (m, 1H; major), 7.23 (d, J = 4.4 Hz, 1.69H; major + minor), 7.16 (d, J = 1.9 Hz, 1H; minor), 7.10–6.84 (m, 9H), 6.69 (s, 1.59H; ArC**H**$_{\text{major}}$ + Ar**H**$_{\text{-minor}}$), 6.51 (s, 0.55 H; ArC**H**$_{\text{minor}}$), 6.32–6.23 (m, 0.55H; C**H**(CH$_3$)$_{2\text{ minor}}$), 6.20–6.10 (m, 1 H; C**H**(CH$_3$)$_{2\text{ major}}$), 5.97 (s, 0.61 H; C**H**$_{\text{-bridge minor}}$), 5.95 (s, 1H; C**H**$_{\text{-bridge major}}$), 5.89 (s, 0.52 H; C**H**$_{\text{-bridge minor}}$), 4.83 (s, 1H; C**H**$_{\text{-bridge major}}$), 4.82–4.78 (m, 0.50H; cod minor), 4.71–4.59 (m, 2.67H; cod$_{\text{-major + minor}}$), 4.20–4.04 (m, 2.70H; OC**H**$_2$CH$_{2\text{-major + minor}}$), 4.06–3.98 (m, 0.55H; OC**H**$_2$CH$_{2\text{-minor}}$), 3.55–3.50 (m, 0.45H; cod$_{\text{-minor}}$), 3.50–3.43 (m, 1H, cod$_{\text{-major}}$), 2.81–2.71 (m, 0.53H, cod minor$_{\text{-minor}}$), 2.54–2.46 (m, 1H, cod$_{\text{-major}}$), 2.48–2.35 (m, 1.73H), 2.34 (s, 3H), 2.17–2.06 (m, 1.64H), 1.96–1.80 (m, 4.84H), 1.77–1.68 (m, 6H), 1.67–1.58 (m, 9H), 1.60–1.50 (m, 6H), 1.48–1.37 (m, 1H), 1.34–1.20 (m, 1H), 1.20–1.09 (m, 0.85H), 1.07 (t, J = 7.4 Hz, 4.67H, CH$_2$C**H**$_{3\text{-major + minor}}$), 1.02–0.92 (m, 1H), 0.93–0.80 (m, 2.51H), 0.62–0.49 (m, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 183.6 (d, J = 51.9 Hz; N**C**N$_{\text{major}}$), 181.9 (d, J = 50.7 Hz; N**C**N$_{\text{minor}}$), 153.9 (Ar**C**$_{\text{-OBu}}$), 147.1, 146.8, 146.7, 145.7, 145.7, 145.7, 145.5, 144.6, 143.9, 135.6, 134.0, 133.8, 132.2, 129.0, 128.4, 125.8, 125.7, 125.6, 125.5, 125.4, 125.4, 125.2, 125.0, 124.8, 124.3, 124.3, 124.0, 124.0, 123.7, 123.7, 123.2, 117.7, 117.2, 112.4 (Ar**C**H$_{\text{major}}$), 111.6 (Ar**C**H$_{\text{minor}}$), 98.0 (d, J = 7.0 Hz; cod$_{\text{-major + minor}}$), 97.0 (d, J = 7.3 Hz; cod$_{\text{-minor}}$), 96.6 (d, J = 7.1 Hz; cod$_{\text{-major}}$), 69.3, 69.1 (d, J = 14.1 Hz; cod$_{\text{-major}}$), 68.6 (d, J = 14.5 Hz; cod$_{\text{-major}}$), 68.2 (d, J = 14.3 Hz; cod$_{\text{-minor}}$), 67.4 (d, J = 14.5 Hz; cod$_{\text{-minor}}$), 53.9 (**C**H(CH$_3$)$_2$), 50.4 (**C**H$_{\text{-bridge major}}$), 49.6 (**C**H$_{\text{-bridge minor}}$), 47.6 (**C**H$_{\text{-bridge minor}}$), 47.4 (**C**H$_{\text{-bridge major}}$), 34.9, 34.8, 31.9, 31.9, 31.2, 30.7, 30.7, 29.8, 29.8, 29.1, 28.1, 28.1, 25.3, 24.5, 23.6, 22.9, 20.3, 20.0, 17.8, 14.3.

HRMS (APCI): calcd. for $C_{39}H_{44}RhN_2O$ $[M-Cl]^+$ 659.25032. Found 659.25076 (Δ = 0.44 mmu). R_f = 0.04 (Cy/EA = 10:1 v/v). Yield: 78% (19 mg, 26.9 μmol).

[RhCl(CO)$_2$(8b)]. The respective [RhCl(cod)(**8b**)] (15 mg, 21.6 μmol, 1.0 eq), complex was dissolved in CH_2Cl_2 and cooled to 0 °C. Then CO was bubbled through this solution for 30 min. The solvent was evaporated and the residue washed with pentane to obtain the product as a yellow solid.

^{1}H NMR (500 MHz, CD_2Cl_2): 7.79 (s, 1H), 7.39 (d, J = 7.2 Hz, 2H), 7.34 (d, J = 6.8 Hz, 2H), 7.31–7.29 (m, 1H), 7.19 (d, J = 6.8 Hz, 1H), 7.02–6.87 (m, 5H), 6.87 (s, 1H), 6.52 (s, 1H; Ar**C**H), 5.89 (s, 1H; C**H**$_{\text{-bridge}}$), 5.58–5.50 (m, 1H; C**H**(CH$_3$)$_2$), 5.28 (s, 1H; C**H**$_{\text{-bridge}}$), 4.06–3.97 (m, 2H; OC**H**$_2$CH$_2$), 1.91 (s, 3H; ArCH$_{3\text{-ortho}}$), 1.89–1.81 (m, 2H), 1.66 (d, J = 6.6 Hz, 3H; CH(C**H**$_3$)$_2$), 1.63–1.54 (m, 2H), 1.50 (d, J = 6.9 Hz, 3H; CH(C**H**$_3$)$_2$), 1.03 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 186.3 (d, J = 54.0 Hz; Rh**C**O), 183.0 (d, J = 74.2 Hz; N**C**N), 176.2 (d, J =

43.5 Hz; Rh**C**O), 154.7 (Ar**C**$_{\text{-OBu}}$), 146.9, 146.1, 145.3, 145.2, 144.9, 134.1, 133.1, 129.1, 128.0, 127.3, 125.8, 125.8, 125.6, 125.4, 125.3, 124.2, 124.0, 123.7, 118.7, 111.6 (Ar**C**H), 69.0, 54.5 (**C**H(CH_3)$_2$), 50.0 (**C**H$_{\text{-bridge}}$), 47.4 (**C**H$_{\text{-bridge}}$), 32.0, 24.4, 23.4, 20.0, 18.7, 14.3.

HRMS (ESI): calcd. for $C_{32}H_{32}RhN_2O_3$ $[M-Cl-CO]^+$ 579.15133. Found 570.15173 ($\Delta = 0.40$ mmu). Yield: 99% (14 mg, 21.3 μmol).

[PdCl(allyl)(8b)]. A Schlenk-tube was charged azolium salt **8b**·HI, (20 mg, 34.7 μmol, 1.0 eq), Ag_2O (4.0 mg, 17.4 μmol, 0.5 eq) and dissolved in DCM (2 mL). The mixture was stirred for 24 h at room temperature then $[PdCl(allyl)]_2$ (6.4 mg, 17.4 μmol, 0.5 eq) was added. After completion of the reaction (checked by TLC) the mixture was filtered through celite and the solvent was removed under reduced pressure. The crude product was purified by short column chromatography (Cy/EA 3:1 v/v) to obtain the desired complex as yellow solid. (Isomer 1:1 ratio).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.94–7.82 (m, 1H), 7.57 (d, $J = 7.1$ Hz, 1H), 7.43–7.35 (m, 4H), 7.34–7.30 (m, 2H), 7.30–7.24 (m, 2H), 7.06–6.92 (m, 10H), 6.55 (s, 1H; Ar**C**H), 6.52 (s, 1H; Ar**C**H), 5.90 (s, 2H; C**H**$_{\text{-bridge}}$), 5.69–5.60 (m, 1H; C**H**(CH_3)$_2$), 5.60–5.53 (m, 1H; C**H**(CH_3)$_2$), 5.36 (s, 1H; C**H**$_{\text{-bridge}}$), 5.17 (s, 1H; C**H**$_{\text{-bridge}}$), 4.83–4.68 (m, 1H), 4.37–4.26 (m, 1H), 4.10–3.99 (m, 4H; O**C**H_2**C**H_2), 3.85 (d, $J = 7.4$ Hz, 1H), 3.79 (d, $J = 7.5$ Hz, 1H), 2.76 (d, $J = 13.3$ Hz, 1H), 2.62 (d, $J = 6.6$ Hz, 1H), 2.55–2.47 (m, 2H), 2.15 (s, 3H; Ar**C**$\mathbf{H}_{\text{3-ortho}}$), 1.97 (s, 3H; Ar**C**$\mathbf{H}_{\text{3-ortho}}$), 1.91–1.82 (m, 4H), 1.68 (d, $J = 6.8$ Hz, 3H), 1.64–1.59 (m, 6H), 1.59–1.54 (m, 6H), 1.51 (d, $J = 6.5$ Hz, 3H), 1.32–1.16 (m, 4H), 1.05 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 182.0 (N**C**N), 181.5 (N**C**N), 154.1 (Ar**C**$_{\text{-OBu}}$), 146.6, 146.0, 145.9, 145.7, 145.0, 145.0, 144.6, 134.6, 134.2, 132.9, 132.6, 129.3, 129.2, 126.7, 126.0, 125.9, 125.8, 125.7, 125.5, 125.4, 124.2, 124.2, 124.1, 124.0, 123.9, 123.8, 123.7, 118.0, 117.9, 115.0, 114.5, 111.8 (Ar**C**H), 111.5 (Ar**C**H), 72.7, 71.8, 69.2 (O**C**H_2**C**H_2), 65.0, 53.1 (**C**H(CH_3)$_2$), 50.1 (**C**H$_{\text{-bridge}}$), 50.0 (**C**H$_{\text{-bridge}}$), 49.4, 49.0, 47.4 (**C**H$_{\text{-bridge}}$), 47.4 (**C**H$_{\text{-bridge}}$), 31.9, 24.5, 24.1, 24.1, 23.8, 20.0, 19.0, 18.6, 15.3, 14.3.

HRMS (ESI): calcd. for $C_{34}H_{37}N_2OPd$ $[M-Cl]^+$ 595.19353. Found 595.19462 ($\Delta = 0.19$ mmu). Yield: 63% (13.9 mg, 22.0 mmol).

[PdI$_2$(py)(8b)]. A Schlenk-tube was charged azolium salt **8b**·HI (25.0 mg, 43.4 μmol, 1.0 eq), $Pd(OAc)_2$ (1.0 eq), KI, K_2CO_3 (59.9 mg, 434 μmol, 10.0 eq) were dissolved in dry pyridine (3 mL) and stirred at 80 °C for 24 h. After this time the mixture was filtered through celite and the solvent was removed under reduced pressure. The crude product was purified by short column chromatography (DCM/Cy 5:1 v/v -> 2:1 v/v) to obtain the desired complex as yellowish solid.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.58 (d, $J = 5.5$ Hz, 2H), 8.18 (d, $J = 7.5$ Hz, 1H), 7.66 (t, $J = 7.8$ Hz, 1H), 7.45 (d, $J = 7.4$ Hz, 1H), 7.37 (d, $J = 6.8$ Hz, 1H), 7.30–7.24 (m, 1H), 7.22–7.14 (m, 2H), 7.06–7.01 (m, 1H), 6.98–6.92 (m, 3H), 6.88–6.81 (m, 2H), 6.58 (s, 1H; Ar**C**H), 6.07–6.00 (m, 1H; C**H**(CH_3)$_2$), 6.00 (s, 1H, C**H**$_{\text{-bridge}}$), 5.95 (s, 1H, C**H**$_{\text{-bridge}}$), 4.12–4.02 (m, 2H), 2.16 (s, 3H), 1.95–1.88 (m, 2H), 1.75 (d, $J = 6.7$ Hz, 3H), 1.68–1.61 (m, 5H), 1.08 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 154.6 (Ar**C**$_{\text{-OBu}}$), 154.1 (**C**H$_{\text{Py}}$), 149.0, 147.5, 146.5, 145.8, 145.4, 144.9, 138.0, 135.5, 133.0, 128.5, 128.0 (**C**H$_{\text{Py}}$), 127.9 (**C**H$_{\text{Py}}$), 125.6, 125.5 (**C**H$_{\text{-backbone}}$), 124.9, 124.6, 124.2, 123.9, 123.7, 117.9 (**C**H$_{\text{-backbone}}$), 112.1 (Ar**C**H), 68.9 (O**C**H_2**C**H_2), 55.2 (**C**H$_{\text{-}i\text{Pr}}$), 50.0 (**C**H$_{\text{-bridge}}$), 47.5 (**C**H$_{\text{-bridge}}$), 32.0 (OCH$_2$**C**H$_{\text{2-Bu}}$), 23.5 (**C**H$_{\text{3-}i\text{Pr}}$), 22.6 (**C**H$_{\text{3-}i\text{Pr}}$), 22.5 (Ar**C**H$_{\text{3-ortho}}$), 20.1 (**C**H$_2$CH$_{\text{3-Bu}}$), 14.4 (CH$_2$**C**H$_{\text{3-Bu}}$).

HRMS (ESI): calcd. for $C_{36}H_{38}I_2N_3OPd$ $[M+H]^+$ 888.0134 Found 888.0138 ($\Delta = 1.0$ mmu). $R_f = 0.12$ (DCM/Cy = 1:1 v/v). Yield: 22% (9 mg, 10.1 μmol).

[PtCl$_2$(py)(8b)]. A Schlenk-tube was charged with azolium salt **8b**·HI (25.0 mg, 43.4 μmol, 1.0 eq), $PtCl_2$ (43.4 μmol, 1.0 eq), K_2CO_3 (59.9 mg, 433.6 μmol, 10.0 eq) were dissolved in dry pyridine (3 mL) and stirred at 80 °C for 24 h. After this time the mixture was filtered through celite and the solvent was removed under reduced pressure. The crude product was purified by short column chromatography (DCM/Cy 2:1 v/v) to obtain the desired complex as yellowish solid.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.60 (d, $J = 5.7$ Hz, 2H), 8.13 (d, $J = 7.4$ Hz, 1H), 7.64 (t, $J = 7.7$ Hz, 1H), 7.45 (d, $J = 7.3$ Hz, 1H), 7.36 (d, $J = 6.6$ Hz, 1H), 7.27 (d, $J = 6.6$ Hz, 1H), 7.21–7.14 (m, 3H), 7.02 (t, $J = 7.4$ Hz, 1H), 6.98–6.91 (m, 2H), 6.85 (t, $J = 7.5$ Hz, 1H), 6.73 (s, 1H), 6.56 (s, 1H; Ar**C**H), 6.21–6.10 (m, 1H; C**H**(CH_3)$_2$), 5.94 (s, 1H; C**H**$_{\text{-bridge}}$), 5.33 (s, 1H; C**H**$_{\text{-bridge}}$), 4.11–4.01 (m, 2H; O**C**H_2**C**H_2), 2.17 (s, 3H), 1.94–1.87 (m, 2H), 1.73 (d, $J = 6.8$ Hz, 3H), 1.68–1.61 (m, 2H), 1.61 (d, $J = 6.9$ Hz, 3H), 1.08 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ 154.4 (Ar**C**$_{\text{-OBu}}$), 154.2 (**C**H$_{\text{Py}}$), 147.6, 146.6, 145.8, 145.5, 144.7, 137.9, 135.3, 132.7, 128.9, 127.9, 126.5, 125.5, 125.4, 125.1, 124.8, 124.1, 123.9, 123.7, 116.9, 111.9 (Ar**C**H), 68.9, 53.3 (**C**H(CH_3)$_2$), 50.0 (**C**H$_{\text{-bridge}}$), 47.5 (**C**H$_{\text{-bridge}}$), 32.1, 30.3, 23.5, 22.6, 22.3, 20.1, 14.4.

HRMS (ESI): calcd. for $C_{36}H_{37}N_3OPt$ $[M-2Cl]^{2+}$ 361.12868 Found 361.12886 ($\Delta = 0.03$ mmu). $R_f = 0.18$ (DCM/Cy = 1:1 v/v). Yield: 25% (9 mg, 10.7 μmol).

[AuCl(10)]. Starting materials used were azolium-salt **10**·HBF_4 (16 mg, 26 μmol, 1.0 eq), $[AuCl(SMe_2)]$ (8.1 mg, 27 μmol, 1.0 eq), K_2CO_3 (10.8 mg, 78 μmol, 3.0 equiv.) was added in acetone (2 mL), and the reaction mixture was stirred at 50 °C for 6 h. The volatiles were removed under reduced pressure, and the residue was purified by column chromatography (Cy/EA 5:1 v/v).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.47–7.37 (m, 4H), 7.39–7.29 (m, 2H), 7.25 (d, $J = 7.2$ Hz, 1H), 7.09–6.95 (m, 4H), 6.57 (s, 1H; Ar**C**H), 5.92 (s, 1H; C**H**$_{\text{-bridge}}$), 5.44 (s, 1H; C**H**$_{\text{-bridge}}$), 4.26–3.97 (m, 6H), 2.71 (s, 3H), 2.40 (s, 3H), 2.30 (s, 3H), 1.93–1.84 (m, 2H), 1.67–1.58 (m, 2H), 1.07 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 196.1 (N**C**N), 154.5 (Ar**C**$_{\text{-OBu}}$), 146.5, 145.7, 145.6, 145.4, 144.4, 137.9, 136.9, 136.6, 134.1, 133.2, 129.8, 129.7, 129.6, 126.9, 126.1, 126.0, 125.9, 125.7, 125.2, 124.4, 124.3, 123.7, 112.1 (Ar**C**H), 69.0 (O**C**H_2**C**H_2), 53.4, 51.3, 50.9 (**C**H$_{\text{-bridge}}$), 47.5(**C**H$_{\text{-bridge}}$), 32.0, 20.0, 18.9, 18.4, 18.3, 14.3.

HRMS (APCI): calcd. for $C_{38}H_{39}AuN_3O$ $[M-Cl+MeCN]^+$ 750.27533. Found 750.27552 ($\Delta = 0.19$ mmu). $R_f = 0.07$ (Cy/EA = 5:1 v/v). Yield: 39% (8 mg, 10.0 μmol).

[AuCl(syn-12)] and **[AuCl(anti-12)]**. A Schlenk-tube was charged with azolium salt **12**·HCl, (60 mg, 48 μmol, 1.0 eq), Ag_2O (5.6 mg, 0.5 eq) and dissolved in DCM (4 mL). The mixture was stirred for 24 h at room temperature then $[AuCl(SMe_2)]$ (15.7 mg, 48 μmol, 1.0 eq) was added. After completion of the reaction (checked by TLC) the mixture was filtered through celite and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (Cy/EA 10:1 -> 3:1 v/v) to obtain the desired complex as white solid. Yield: 65% (45 mg, 31 μmol; both isomers).

anti-Isomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (s, 2H), 7.26 (s, 2H), 7.10 (s, 2H), 7.01 (s, 2H), 6.61 (s, 2H; Ar**C**H), 5.77 (s, 2H; C**H**$_{\text{-bridge}}$), 4.63 (s, 2H; C**H**$_{\text{-bridge}}$), 4.23–4.01 (m, 4H; O**C**H_2**C**H_2), 2.42 (s, 6H; Ar**C**$\mathbf{H}_3$), 2.01–1.93 (m, 10H;), 1.71–1.65 (m, 4H; C$\mathbf{H}_2$CH$_3$), 1.62–1.50 (m, 16H), 1.31–1.09 (m, 54H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.6 (N**C**N), 154.2 (Ar**C**$_{\text{-OBu}}$), 145.7, 142.8, 141.7, 141.6, 141.6, 141.5, 141.5, 141.0, 140.9, 133.7, 132.1, 126.3, 124.6, 122.0, 121.9, 121.8, 121.6, 111.7 (Ar**C**H), 68.5 (O**C**H_2**C**H_2), 49.9 (**C**H$_{\text{-bridge}}$), 46.6 (**C**H$_{\text{-bridge}}$), 35.4, 35.3, 35.2, 34.4, 34.4, 34.3, 34.3, 32.5, 32.4, 32.1, 32.1, 32.0, 31.9, 31.8, 31.7, 29.9, 22.8, 19.7, 18.6 (Ar**C**H$_{\text{3-ortho}}$), 14.2 (CH$_2$**C**H$_{\text{3-Bu}}$), 9.9.

$R_f = 0.36$ (Cy/EA = 10:1 v/v). Yield: 18 mg.

Research Article
doi.org/10.1002/ejic.202300178

syn-Isomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (s, 2H), 7.38 (s, 2H), 7.36 (s, 2H), 7.28 (s, 2H), 6.51 (s, 2H; ArC**H**), 5.82 (s, 2H; C**H**$_{\text{-bridge}}$), 5.22 (s, 2H; C**H**$_{\text{-bridge}}$), 4.17–4.04 (m, 4H; OC**H**$_2$CH$_2$), 2.02–1.89 (m, 10H), 1.73–1.53 (m, 20H), 1.49 (s, 6H), 1.35–1.20 (m, 48H), 1.12 (t, J= 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.2 (N**C**N), 154.0 (Ar**C**$_{\text{-OBu}}$), 145.3, 143.0, 141.9, 141.8, 141.7, 141.5, 141.4, 140.9, 134.2, 132.9, 127.1, 125.1, 122.3, 122.1, 121.9, 121.6, 112.3 (Ar**C**H), 68.9 (OCH$_2$**C**H$_2$), 50.1 (**C**H$_{\text{-bridge}}$), 46.7 (**C**H$_{\text{-bridge}}$), 35.4, 35.4, 35.3, 35.2, 34.5, 34.5, 34.4, 34.3, 33.1, 32.5, 32.4, 32.2, 32.1, 32.0, 31.9, 31.8, 31.6, 19.6, 18.5 (Ar**C**H$_{\text{3-ortho}}$), 14.2 (CH$_2$**C**H$_{\text{3-Bu}}$), 9.7.

R_f = 0.08 (Cy/EA = 7 : 1 v/v). Yield: 27 mg. HRMS (ESI): calcd. for $C_{89}H_{111}N_3O_2Au$ $[M-Cl+MeCN]^+$ 1450.83399. Found 1450.83420 (Δ = 0.34 mmu). calcd. for $C_{87}H_{108}N_2O_2Au$ $[M-Cl]^+$ 1409.80710. Found 1409. 80703 (Δ = 0.08 mmu).

Supporting Information

Additional synthetic procedures, NMR-spectra (^{1}H, ^{13}C), hi-res mass spectra, IR spectroscopy, cyclic voltammetry, crystal data. Additional references cited within the Supporting Information.[19]

Acknowledgements.

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) via grant PI 178/20-2. We thank the Heraeus Group for the generous donation of [HAuCl$_4$]. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: anthracene · cycloaddition · NHC ligands · transition metals · triptycene

[1] a) J. H. Chong, M. J. MacLachlan, *Chem. Soc. Rev.* **2009**, *38*, 3301–3315; b) C. F. Chen, Y. X. Ma, in *Iptycenes Chemistry: From Synthesis to Applications*, Springer Verlag, Berlin, **2012**; c) T. M. Swager, *Acc. Chem. Res.* **2008**, *41*, 1181–1190.
[2] R. Savka, S. Foro, H. Plenio, *Dalton Trans.* **2016**, *45*, 11015–11024.
[3] M. Heidrich, M. Bergmann, D. Müller-Borges, H. Plenio, *Adv. Synth. Catal.* **2018**, *360*, 3572–3578.
[4] M. Heidrich, H. Plenio, *Beilstein J. Org. Chem.* **2020**, *16*, 2080–2086.
[5] Y. Kanai, S. Foro, H. Plenio, *Organometallics* **2019**, *38*, 544–551.
[6] R. Vasiuta, A. Stockert, H. Plenio, *Chem. Commun.* **2018**, *54*, 1706–1709.
[7] R. Savka, M. Bergmann, Y. Kanai, S. Foro, H. Plenio, *Chem. Eur. J.* **2016**, *22*, 9667–9675.
[8] M. Bergmann, R. Savka, S. Foro, H. Plenio, *Eur. J. Inorg. Chem.* **2017**, *2017*, 3779–3786.
[9] J. Mathew, N. Koga, C. H. Suresh, *Organometallics* **2008**, *27*, 4666–4670.
[10] M. Hashmat Ali, M. Niedbalski, G. Bohnert, D. Bryant, *Synth. Commun.* **2006**, *36*, 1751–1759.
[11] R. C. Cambie, N. D. Renner, P. S. Rutledge, P. D. Woodgate, *Aust. J. Chem.* **1990**, *44*, 61–75.
[12] a) R. Adams, J. D. Edwards, *J. Am. Chem. Soc.* **1952**, *74*, 2605–2607; b) M. P. Uliana, B. M. Servilha, O. Alexopoulos, K. T. de Oliveira, C. F. Tormena, M. A. B. Ferreira, T. J. Brocksom, *Tetrahedron* **2014**, *70*, 6963–6973; c) S. K. Jackson, S. C. Banfield, M. A. Kerr, *Org. Lett.* **2005**, *7*, 1215–1218.
[13] T. Fukuyama, C.-K. Jow, M. Cheung, *Tetrahedron Lett.* **1995**, *36*, 6373–6374.
[14] Initially, N-toslyated triptycenes were prepared, but the cleavage of the N-tosyl group requires very forcing reaction conditions, which are incompatible with most functional groups.
[15] a) X.-Z. Zhu, C.-F. Chen, *J. Org. Chem.* **2005**, *70*, 917–924; b) J. Cao, H.-Y. Lu, C.-F. Chen, *Tetrahedron* **2009**, *65*, 8104–8112.
[16] S. Wolf, H. Plenio, *J. Organomet. Chem.* **2009**, *694*, 1487–1492.
[17] S. Leuthäußer, V. Schmidts, C. M. Thiele, H. Plenio, *Chem. Eur. J.* **2008**, *14*, 5465–5481.
[18] a) G. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3–8; b) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
[19] a) R. Golden, L. M. Stock, *J. Am. Chem. Soc.* **1972**, *94*, 3080–3088; b) F. Ulatowski, K. Melaniuk, *Eur. J. Org. Chem.* **2018**, *47*, 6629–6633; c) N. P. Tsvetkov, E. Gonzalez-Rodriguez, A. Hughes, G. Dos Passos Gomes, F. D. White, F. Kuriakose, I. V. Alabugin, *Angew. Chem. Int. Ed.* **2018**, *130*, 3651–3655; d) M. Goichi, K. Segawa, S. Suzuki, S. Toyota, *Synthesis* **2005**, *13*, 2116–2118; e) S. Ikedu, Y. Nishimura, T. Arai, *J. Phys. Chem. A* **2011**, *115*, 8227–8233; f) A. Kišić, M. Stephan, B. Mohar, *Org. Lett.* **2013**, *15*, 1614–1617; g) D. Kato, H. Sakai, N. V. Tkachenko, T. Hasobe, *Angew. Chem. Int. Ed.* **2016**, *55*, 5230–5234; *Angew. Chem.* **2016**, *128*, 5316–5320; h) U. Kraft, J. E. Anthony, E. Ripaud, M. A. Loth, E. Weber, H. Klauk, *Chem. Mater.* **2015**, *27*, 998–1004; i) H. Quast, J. Schulze, *Liebigs Ann. Chem.* **1990**, *1990*, 509–512; j) R. Camenzind, B. Rickborn, *J. Org. Chem.* **1986**, *51*, 1914–1916; k) A. Lohr, T. M. Swager, *J. Mater. Chem.* **2010**, *37*, 8107; l) J. Bouffard, R. F. Eaton, P. Müller, T. M. Swager, *J. Org. Chem.* **2007**, *72*, 10166–10180; m) F. Xu, L. Zhang, Y. Jia, X. Wang, X. Li, Q. Wen, Y. Zhang, W. Xu, *Eur. J. Med. Chem.* **2013**, *69*, 191–200.

Manuscript received: March 30, 2023
Revised manuscript received: April 14, 2023