Gold-NHC-N-naphthamide complexes

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Abstract

Pure $S_oS$ and $R_oS$ atropoisomeric Au(I)- and Au(III)-NHC-complexes with benzimidazolyl N-(2-naphthamide) frameworks were prepared from appropriate axially chiral pre-ligands. The catalytic capacity of gold-NHC-N-naphthyl complexes was studied in cyclopropanation reactions. In contrast to corresponding unsuccessful Au(I)-NHC-N-naphthyl-oxazolyl complexes, all tested $S_oS$ and $R_oS$ diastereomers of Au(I) and Au(III)-NHC-N-naphthamide complexes were excellent catalysts to give both successful cyclopropanation (up to 99%, 15 min), as well as subsequent rapid in situ cis-to-trans isomerization. The results demonstrate that the new axially chiral Au(I)-/Au(III)-NHC-benzimidazolyl-N-naphthamide complexes represent an interesting group of gold catalysts with specific properties, affording fast cyclopropanation, excellent product yields and predictable trans-stereoselectivity (>99% yield; >99% trans in 15 min).

Keywords: Gold-NHC-naphthamide; Au(I)/Au(III) complexes; catalytic active, cyclopropanation
Introduction

Gold catalysis has been a rapidly emerging field within transition metal catalysis in the past two decades to promote a great variety of organic scaffolds from unsaturated substrates. Gold has a high affinity towards carbon-carbon multiple bonds, especially alkynes, which may be activated towards nucleophilic attack. Coupled with high functional group tolerance, usually mild reaction conditions allow for diverse gold catalyzed transformations to be achieved, also including enantioselective reactions. A broad review on the status of gold chemistry has lately been published as a thematic issue edited by Hashmi. Gold(I) catalysis is by far more developed and understood compared to gold(III) catalysis, as evidenced by the large number of reported ligated gold(I) complexes. The last years have witnessed a revival of gold(III) chemistry. The challenge of gold(III) complexes is the possible reduction to gold(I) or gold(0) species. While the stability of gold(III) ions increases upon ligand coordination, stable gold(III) complexes generally show poorer catalytic activity. Thus, the aim for successful development of gold(III) catalysts is to find the balance between stability and catalytic activity. The development of gold(III) complexes and the applications of gold(III) in synthesis and catalysis, including mechanistic aspects, have recently been reviewed. The interest toward the synthesis of chiral gold(III) complexes is also steadily growing and the progress achieved in the synthesis of well-defined chiral gold(III) complexes has lately been summarized.

We have previously reported studies on the gold(III) coordination ability of different ligands to give a variety of polydentate Au(III) complexes, including oxazole and NHC based chiral Au(III) catalysts. The N,N-BOX-Au(III) complexes I (Scheme 1) based on bis-oxazoline ligands (BOX), were shown to represent an interesting group of Au(III) catalysts with specific catalytic properties. Our experimental and theoretical studies on Au(III) bidentate coordination of a series of pyridine-oxazoline and quinoline-oxazoline II based ligands, concluded that the superior activity of the N,N-Au(III)-pyridine-oxazolyl complexes II is caused by de-coordination of the pyridine-N ligand as a crucial step for efficient generation of catalytic activity. Further mechanistic studies (NMR, X-ray, DFT) of Au(III)-bidentate pyridine-oxazoline II mediated alkoxycyclization, also demonstrated that de-coordination of the pyridine nitrogen is involved as the rate-limiting step. Based on our successful synthesis of P,N-Au(III)-phosphine-oxazoline complexes III, as well as the efficient coordination affinity of oxazoline-nitrogen to generate N,N-Au(III)-bis-heterocyclic structures II, we synthesized oxazoline functionalized Au(III)-NHC complexes IV. These Au(III) complexes were too unstable for proper isolation and spectroscopic characterization, but selective 15N NMR techniques provided valuable proofs of N-coordination by formation of N-ligated Au(III) complexes. The changes in 15N-shift values (Δδ15N), observed by 1H,15N-HMBC 2D NMR studies, going from Au(I)Cl, via Au(III)Cl3 to the C,N-Au(III)-NHC-oxazolyl complexes, afforded important evidence that oxazoline-N-coordination to Au(III) took place. In particular, the huge up-field shift of the oxazoline-N (Δδ15Noxaz) undoubtedly confirmed that the target six-membered bidentate C,N-Au(III)-NHC-oxazoline chelated complex IV was formed. Other studies showed that chiral alcohol functionalized Au(III)-NHC complexes V failed to generate bidentate C,O-Au(III)-NHC-alcohol complexes.

Several axially chiral Au(I) complexes, based on a binaphthyl scaffold have been synthesized. Such Au(I) complexes, formed as atropoisomeric diastereomers with an axis of chirality, have also been designed as binaphthyl ligands connected to various N-heterocyclic carbene ligands. These synthesized axially chiral Au(I)-NHC complexes were, in general, reported to provide moderate to high catalytic activities and modest chiral inductions in asymmetric intramolecular cyclizations.
No examples of axially chiral gold(III) complexes with binapthyl based ligands have been reported. Likewise, the use of stabilizing NHC ligands in gold(III) chemistry is much less developed than the NHC-gold(I) complexes, which have proved to be powerful catalysts. By replacing one naphthyl group in the binapthyl scaffold with a benzimidazolium unit, the NHC functionality becomes incorporated in the axially chiral bisaryl structure (e.g. 9-14, Schemes 1 and 2). The aim of this project was to synthesize new axially chiral atropoisomeric NHC pre-ligands to allow the formation of modified axially chiral Au(I)/(III)-NHC complexes based on an N-naphthyl structure.

We are presently reporting the synthesis of novel axially chiral Au(I) and Au(III) complexes (9-12) (Schemes 1 and 2) with a benzimidazolyl N-(2-naphthamide) framework. The corresponding Au(I) complexes with the N-(2-oxazolyl) moiety (13, 14) were attempted oxidized to provide Au(III)-NHC-(2-oxazolyl) complexes (13', 14') (Scheme 2), with a C_N-bidentate Au(III)-NHC-(2-oxazolyl) metalacyclic structure, including both NHC and N-oxazoline Au(III)-coordination sites. The catalytic potential of the novel Au(I) and Au(III)-NHC-N-naphthamide complexes (9-12), compared with the respective Au(I)-NHC-N-(2-oxazolyl) complexes (13, 14) in gold-catalyzed cyclopropanation was studied.

In addition to NMR (1H, 13C), IR and HRMS characterization of new N-naphthamide compounds 7-12, structures of selected products (5, 9, 11) shown with full assignment of 1H and 13C NMR data, based on 2D NMR studies (COSY, HSQC, HMBC), are available in the Supporting Information.

Results and Discussion

Preparation of gold-NHC-N-naphthamide complexes
1. Pre-ligand preparation. In order to prepare novel axially chiral Au(I)- and Au(III)-NHC-naphthamide complexes (9, 10 and 11, 12) (Scheme 2), the appropriate chiral β-hydroxyamide-NHC pre-ligands 7 and 8 with a benzimidazolium-N-naphthyl framework, were synthesized from the respective benzimidazole precursors 5.
and 6, which were prepared in five steps as reported previously.\textsuperscript{27} Pd-catalyzed Buchwald-Hartwig amination of 2-nitroaniline with the phenol 1 triflate (98%), nitro reduction with iron powder (97%) and final ring closure (trimethyl orthoformate, TsOH, cat.) afforded the benzimidazole-naphthoate 2 by heating (91%) (Scheme 2). Subsequent reactions of ester 2 with enantiomerically pure aminoalcohols (S)-2-amino-2-phenylethan-1-ol 3 and (S)-2-amino-3-methylbutan-1-ol 4, gave respectively naphthamides 5 (64%) and 6 (65%) (Scheme 2). \textsuperscript{1}H and \textsuperscript{13}C NMR showed that the bis-aryl product 6 with the bulky α-isopropylamide moiety (R = iPr) was formed as an approximately 1:2 mixtures of axially chiral S\textsubscript{a}S-6 and R\textsubscript{a}S-6 diastereomers, demonstrating the restricted rotation along the N-C connecting bond in the bis-aryl benzimidazole-naphthalene product 6. The structures of the two diastereomeric α-isopropylamides 6 were calculated (ORTEP, Scheme 2) and show that the atropoisomeric diastereomers with an axis of chirality are chemically non-equivalent, which explains the two unique set of \textsuperscript{1}H and \textsuperscript{13}C NMR signals. The diastereomers of amides 6 were not isolated but used in a mixture in the next step. In contrast, \textsuperscript{1}H and \textsuperscript{13}C NMR of the less bulky α-phenylamide 5 (R = Ph) did not show diastereomers.

**Scheme 2.** Synthesis of axially chiral gold(I)- and gold(III)-NHC-N-naphthamide complexes 9-12 and Au(I)-NHC-N-naphthyl-oxazolyl complexes 13-14.
The chiral N-naphthyl-benzimidazolium pre-ligands 7 (93%) and 8 (99%) were obtained by benzimidazole N-methylation (Mel) of amides 5 and 6, producing the characteristic change of 1H NMR shift values of the H2 imidazole protons from δ ~8 ppm (imidazoles 5, 6) to δ ~10 ppm (imidazolium salts 7, 8). Both reactions afforded diastereomeric mixtures of the respective benzimidazolium salts 7 and 8, as shown by NMR (1H, 13C). As mixture of atropoisomeric pre-ligands Sα-S-7 and Rα-S-7 (R = Ph; 1:1.3 ratio; 1H NMR) were formed from non-diastereomeric benzimidazole 5, the observed axial chirality seems to arise by internal restrictions generated by benzimidazolium formation in this case. Differently, axial chirality occurred for the bulkier isopropylamide 6 (R = iPr) in the previous amidation step of chiral α-isopropylamine 4. The inseparable Sα-S-7 and Rα,S-7 α-phenylamide benzimidazolium diastereomers were characterized in a mixture, while the Sα,S-8 and Rα,S-8 α-isopropylamide diastereomeric pre-ligands were separated by chromatography (Sα,S-isomer eluting first) for individual characterization (NMR, HRMS). Benzimidazolium salts (7, 8) were further used in a mixture for coordination to Au(I).

2. Gold(I) coordination. Coordination of the diastereomeric mixture of Sα,S-7 and Rα,S-7 benzimidazolium salts (R = Ph) to gold(I) by optimized conditions (Me2SAuCl (1 eq), NaOAc (3 equiv), acetonitrile, rt 22 h) yielded the corresponding mixture of the target gold(I)-NHC-naphthalamide complexes 9. Chromatographic separation (Scheme 2) afforded the pure axially chiral gold(I)-NHC complexes Sα,S-9 as an oil (29%) and Rα,S-9 as a white solid (22%). Likewise, the pure Sα,S-10 (16%) and Rα,S-10 (17%) gold(I)-NHC complexes (R = iPr) were obtained from the Sα,S-8 and Rα,S-8 benzimidazolium salt mixtures by gold(I) coordination (Me2SAuCl (1 equiv), K2CO3 (1 equiv) in acetonitrile, reflux, 2 h) and subsequent flash chromatography. The somewhat lower yields of gold(I)-NHC-naphthalamide complex 10 (R = iPr) than complex 9 (R = Ph) indicates that the complexation is more restricted by the more sterically demanding iPr substituent. An even stronger steric effect was seen in imidazolium-based Au(I) and Au(III)-NHC-oxazolyl complexes IV,12 as different bulkiness of (iPr vs t-Bu) NHC substituents gave great variation in successful transformations (69% vs 18%) and stability of Au-NHC complexes. Likewise, it has been seen that steric hindrance of bulky t-Bu-oxazoline-imidazolium pre-ligands prevented iridium complexation28 and resulted in less successful transformation to similar Ir-NHC complexes. This effect is also discussed below for Au(I)-NHC-(2-oxazolyl) complexes 13, 14 (Scheme 2).

Strong bases, high temperature and prolonged silica exposure seemed to lower the yields by decomposition of the gold(I)-NHC complexes. Thus, by avoiding the above described chromatographic separation of the diastereomeric mixture, the yield of gold(I) complex Sα,S-10 (58%) was improved (from 16%) by gold(I) coordination of the isolated pure Sα,S-8 benzimidazolium salt. The identity of the novel gold(I) complexes 9 and 10 were confirmed by HRMS, and the structures of the individual diastereomeric Sα,S-9, Rα,S-9, Sα,S-10 and Rα,S-10 complexes were proved by 1H and 13C NMR and 2D NMR (COSY, HSQC, 1H-13C-HMBC) characterization.

3. Gold(I)-to-gold (III) oxidation. The Au(III)-NHC complexes 11 and 12 were prepared by oxidation of the respective diastereomeric Au(I) complexes 9 and 10 with PhlCl2 in CH2Cl2 at rt (Scheme 2).29 Crystalline complexes were obtained by pentane addition to the final reaction mixture. The diastereomERICALLY pure Sα,S-9, Rα,S-9, Sα,S-10 and Rα,S-10 gold(I) complexes were oxidized separately to give crystalline Sα,S-11 (41%), Sα,S-12 (34%) and Rα,S-12 (30%) gold(III)-NHC complexes, while pure Rα,S-11 gold(III)-NHC could not be isolated from the respective product mixture.

13C NMR studies of all Sα,S and Rα,S-diastereomeric oxidation products (11, 12) confirmed successful Au(I) to Au(III) oxidation. A 13C NMR carbene approach has been established to confirm successful formation.
of imidazole-based Au(III)-NHC carbene complexes.\textsuperscript{30-33} \textsuperscript{13}C NMR shift values of the C2 carbon in imidazole-based compounds are characteristic and can readily be used to identify actual products in synthesis sequences from imidazolium pre-ligands via gold(I)-NHC to gold(III)-NHC complexes.\textsuperscript{5-11,32,34,35} Hence, the transformations of imidazolium salts to Au(I)-NHC complexes were verified by the extensive down-field changes of C2 \textsuperscript{13}C NMR chemical shift (\textit{\Delta}\textit{δC} ~ 45 ppm), going from \textit{δ} ~ 143 ppm (N-CH-N) in imidazolium salts 7 and 8 to \textit{δ} ~ 189 ppm (carbene-C2) in Au(I)-NHC 9 and 10. Subsequent oxidation was confirmed by significant characteristic up-field \textsuperscript{13}C NMR shifts (\textit{\Delta}\textit{δC} ~ -35 ppm) of the carbene signals from the respective Au(I)-NHC carbene precursors 9 and 10 (\textit{δ} ~ 189 ppm) to the Au(III)Cl\textsubscript{3}-NHC complexes 11 and 12 (\textit{δ} ~ 153 ppm). The up-field shift generated by oxidation is explained by the higher Lewis acidity of the Au(III) vs. Au(I) metal center, which induces a greater delocalization of the electron density from the benzimidazole ring to the carbene carbon atom. Our observed values are in accordance with literature values of chlorido gold(III) complexes of typical NHCs.\textsuperscript{30-33}

The identity of the \textit{S_0,S}-11 and \textit{S_0,S}, \textit{R_0,S}-12 Au(III)-NHC complexes was also confirmed by (ESI) HRMS. The \textit{S_0,S}-11 complex (R = Ph) revealed the characteristic HRMS isotope ($^{35}$Cl/$^{37}$Cl) pattern of the Cl\textsubscript{2} compound, Au(III)Cl\textsubscript{3}-NHC (\textit{~20:20:6:1 ratio}) for the M+H (\textit{m/z} 724/726/728) molecular ion, as well as for the M+Na (\textit{m/z} 746/748/750) and the M+K (\textit{m/z} 762/764/766) adducts. HRMS of the corresponding \textit{S_0,S} and \textit{R_0,S}-12 Au(III) complexes (R = iPr) showed the molecular ions and fragments of the respective bis-NHC Au(III) derivative Au(III)Cl\textsubscript{2}(NHC)\textsubscript{2} (Scheme 2). ESI-HRMS spectra of similar benzimidazole based gold(III)-NHC complexes are known to be complicated, as ESI-MS conditions may give rise to dinuclear species.\textsuperscript{32} Only the non-chloro HRMS bis-NHC molecular ion (M$^+$-2Cl; Au(III)(NHC)\textsubscript{2}, \textit{m/z} 971) was observed for the \textit{S_0,S}-12 Au(III) complex. However, for the \textit{R_0,S}-12 isomer, the characteristic Cl\textsubscript{2} isotope ($^{35}$Cl/$^{37}$Cl) pattern (\textit{~3 : 2 : 1 ratio}) of the bis-NHC adduct, Au(III)Cl\textsubscript{2}(NHC)\textsubscript{2}, was registered for both M$^+$ (\textit{m/z} 1041/1043/1045) and for M$^+$+H (\textit{m/z} 1042/1044/1046). Also, the de-chlorinated bis-NHC molecular ion of the non-chloro fragment (M$^+$- 2Cl; \textit{m/z} 971) was seen, in accordance with literature.\textsuperscript{34}

Attempts to prepare single crystals of Au-NHC-naphthamide complexes 9-12, suitable for X-ray diffraction analysis, were not successful.

**Preparation of gold-NHC-N-naphthyl-oxazolyl complexes**

The Au(I)-NHC complexes 13,14 with the N-naphthyl-2-oxazolyl framework were synthesized in four steps from amides 5,6 (Scheme 2), according to the literature.\textsuperscript{27,36} Oxazole cyclization (80-90%, SOCl\textsubscript{2}), diastereomer separation (35-45% of each \textit{S_0,S} and \textit{R_0,S}) and individual imidazolium salt formation (100%, Mel), afforded the \textit{S_0,S} and \textit{R_0,S} Au(I)-NHC complexes (13,14;~90%, Me\textsubscript{2}SAuCl, base). The pure \textit{S_0,S}-diastereomers were most successfully isolated and \textit{S_0,S}-13, and \textit{S_0,S}-14 were obtained in 37% and 28% overall yields over four steps from diastereomeric amide (5, 6) mixtures.

Oxidation of gold(I)-NHC complexes 13, 14 with PhiCl\textsubscript{2} failed to give the corresponding \textit{C,N}-bidentate gold(III)-NHC-N-naphthyl-(2-oxazolyl) complexes. The observed complex decomposition may be due to a less favored seven-membered metallacyclic structures 13$^\prime$, 14$^\prime$ (Scheme 2) with a strained planar Au(III) center by including oxazole \textit{N}-coordination. The Au(I)-to-Au(III) oxidation may also provide an unstable oxazoline group, caused by the increased electron-withdrawing effect of Au(III), which might activate for nucleophilic attack on the oxazoline C-N bond. Previous attempts to prepare similar Au(III)-NHC-oxazolyl seven-membered \textit{C,N}-bidentate complexes by Selectfluor oxidation of Au(I) precursors were unsuccessful,\textsuperscript{36} while the more favored six-membered \textit{P,N}-Au(III)Cl\textsubscript{2}[SbF\textsubscript{6}] phosphine-oxazolyl complexes \textit{III} (Scheme 1) and the corresponding Au(I)Cl precursors were stable and no oxazoline decomposition was detected. In contrast, the oxazolyl moiety caused low stability of the \textit{C,N}-Au(III)Cl\textsubscript{2}[SbF\textsubscript{6}]-NHC-oxazolyl complexes IV.\textsuperscript{12} However, significant evidences for oxazoline-N-Au(III) coordination by formation of the six-membered bidentate \textit{C,N}-Au(III)-NHC-oxazoline
chelated complex IV (Scheme 1) was obtained by $^1$H, $^{15}$N-HMBC 2D NMR, in particular, by the large up-field shift of the oxazoline-N ($\Delta \delta^{15}\text{N}_{\text{oxaz}}$: -71.3 ppm). The related stable $C,N$-Ir(cod)$_2$ and $C,N$-PtBr$_2$ NHC-oxazolyl complexes have been prepared in low to moderate yields, but bulkier t-Bu-oxazoline groups in $C,N$-Ir-NHC complexes prevented metal complexation. Such steric effects may also explain the challenging lack of stability of the $C,N$-Au(III)Cl$_2$SbF$_6$ NHC-oxazolyl complexes IV and the $C,N$-bidentate gold(III)-NHC-N-naphthyl-(2-oxazolyl) complexes (13', 14').

**Catalytic properties of gold-NHC-N-naphthyl complexes in gold-catalyzed cyclopropanation**

The catalytic potential of the Au(I) and Au(III)-NHC-N-naphthyl complexes 9-14 was studied in the gold-catalyzed cyclopropanation reaction of propargyl ester I and styrene II (Table 1). We have previously used this model reaction for evaluation of catalytic ability of other novel gold(I) and gold(III) catalysts, hence, providing a solid and well-established background for comparison. The reactions were performed by addition of a silver salt (AgSbF$_6$, 5 mol %) to a CH$_2$Cl$_2$ solution of the relevant Au complex (5 mol %, 9-14), to generate the catalytically active cationic gold species in the mixture of propargyl acetate I and styrene II. The yield and the stereoselectivity of the vinyl-cyclopropane product III were determined by $^1$H NMR. The stereoselectivity, measured as the cis / trans ratio, was based on the ratio of the singlet integrals for the respective vinylc protons ($\delta$ 5.90 and $\delta$ 6.08 ppm, structure III, Table 1).

In contrast to the initially established model for stereoselective cyclopropanations, which explains a favored cis selectivity by steric interactions, we have previously shown that the stereoselective outcome is not fixed, since a more complex situation controls the stereochemistry of propargyl cyclopropanations. Our results demonstrated that the amounts of formed cis and trans isomers varies by cis-to-trans isomerization over time, and the stereoselective outcome is affected by the electronic properties, the bulkiness of substrates as well as the catalytic activity of the Aul or AuIII catalyst. Some Au catalysts (e.g. BOX-Au(III) complexes I) (Scheme 1) were excellent for both fast cyclization into initial selective cis-cyclopropanes as well as subsequent complete in situ cis-to-trans isomerization. Thus, proper choice of Au catalyst successfully enabled highly selective formation of either cis or trans products (dr > 99%), and separate gold catalyzed (JohnPhosAu(I)SbF$_6$) isomerization allowed the preparation of pure trans diastereomers (up to 98% yield) from corresponding pure cis substrates. The formation of trans isomers is proposed to proceed by Au-catalyzed ring-opening through different relevant intermediates, as shown in the suggested cis-to-trans isomerization pathways and a more detailed discussion presented in or previous work.

In the present studies, all the tested diastereomers of gold(I)-NHC (9, 10) and gold(III)-NHC (11, 12) N-naphthamide complexes were strong catalysts to afford cyclopropanation, as shown by complete conversion of propargyl substrate I into the target vinylcyclopropyl product III (100%, Table 1, entries 1-6) by vigorous stirring in 5-15 min. Also, predictable trans-stereoselectivitivon p. 7) of most reactions was excellent, as shown by up to 1:99 ratios of cis / trans cyclopropane III products (Table 1, entries 1-5). The results prove the combined ability of both the Au(I) and Au(III)-naphthamide complexes ($S_{\alpha}$S- and $R_{\alpha}$S-Au(I)-9; $S_{\alpha}$S-Au(I)-10, $S_{\alpha}$S-Au(III)-11 (R = Ph) and $S_{\alpha}$S-Au(III)-12 (R = iPr) to strongly activate for initial cyclopropanation as well as immediate in situ cis-to-trans-isomerization. The catalyst efficiency was demonstrated by the high-yielding preparation and isolation of the pure trans-isomer (91% isolated, >99% trans product III, Table 1, entry 1) provided by the $S_{\alpha}$S-Au(I)-9 (R = Ph) catalyst. The diastereomeric $R_{\alpha}$S-Au(III)-12 complex (R = iPr afforded slight isomerization and low trans-selectivity, in contrast to the $S_{\alpha}$S-12 isomer. The initial product mixture (cis / trans ratio 30:70, 15 min) did undergo slow isomerization over time (10:90 ratio, 2 h) to give the pure trans product (>99%) after 16 h (Table 1, entry 6). The results may indicate that the $R_{\alpha}$S-stereochimistry and the bulkiness (R = iPr) reduce the cis-to-trans isomerization ability of the $R_{\alpha}$S-12 complex. The corresponding $R_{\alpha}$S-
complex (R = Ph) could not be isolated from the oxidation reaction (Scheme 2) and was not available for comparison.

Interestingly, the related oxazoline complexes (R = Ph, iPr) S\textsubscript{o},S\textsubscript{13}-Au(I)-NHC and S\textsubscript{o},S\textsubscript{14}-Au(I)-NHC mainly failed to catalyze cyclopropanation. Full substrate conversion was seen, but polymers were mainly observed (Table 1, entries 7,8).

Despite the axially chiral nature of the applied new gold catalysts 9-12, no enantioselectivity was obtained (chiral HPLC) in the cyclopropanation reaction. The lack of stereocontrol is most likely due to the chiral environment provided by the ligand being too far from the reaction center.

**Table 1. Catalytic studies of novel Au-NHC-N-naphthyl complexes**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Gold catalyst</th>
<th>Functionality</th>
<th>Product III</th>
<th>cis : trans ratio\textsuperscript{a}</th>
<th>% yield\textsuperscript{b} (% trans\textsuperscript{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S\textsubscript{o},S\textsubscript{-Au(I)-9}</td>
<td>amide / R = Ph</td>
<td>&gt; 99% (&gt; 99% trans\textsuperscript{a})</td>
<td>1 : 99</td>
<td>91% yield\textsuperscript{c} (&gt; 99% trans\textsuperscript{c})</td>
</tr>
<tr>
<td>2</td>
<td>R\textsubscript{o},S\textsubscript{-Au(I)-9}</td>
<td>amide / R = Ph</td>
<td>&gt; 99%</td>
<td>3 : 97</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>S\textsubscript{o},S\textsubscript{-Au(I)-10}</td>
<td>amide / R = iPr</td>
<td>&gt; 99%</td>
<td>3 : 97</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>S\textsubscript{o},S\textsubscript{-Au(III)-11}</td>
<td>amide / R = Ph</td>
<td>&gt; 99%</td>
<td>4 : 96</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>S\textsubscript{o},S\textsubscript{-Au(III)-12}</td>
<td>amide / R = iPr</td>
<td>&gt; 99%</td>
<td>3 : 97</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>R\textsubscript{o},S\textsubscript{-Au(III)-12}</td>
<td>amide / R = iPr</td>
<td>&gt; 99%; 15 min</td>
<td>30 : 70</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>S\textsubscript{o},S\textsubscript{-Au(I)-13}</td>
<td>oxazole / R = Ph</td>
<td>&lt;</td>
<td>99% (&gt; 99% trans\textsuperscript{a}); 16 h</td>
<td>1 : 99</td>
</tr>
<tr>
<td>8</td>
<td>S\textsubscript{o},S\textsubscript{-Au(I)-14}</td>
<td>oxazole / R = iPr</td>
<td>&lt;</td>
<td></td>
<td></td>
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</table>

\textsuperscript{a} General procedure: Gold catalyst (5 mol%) in CH\textsubscript{2}Cl\textsubscript{2} was added to a mixture of propargyl ester I, styrene II, and AgSbF\textsubscript{6} (5 mol %) and stirred vigorously until full conversion of propargyl ester I within 15 min. The cis / trans cyclopropyl III ratio was determined by \textsuperscript{1}H NMR (ratio of integrals for singlets \(\delta 5.90 / \delta 6.08\) ppm). \textsuperscript{b} Yield of target product III obtained at full conversion, determined by \textsuperscript{1}H NMR. \textsuperscript{c} Isolated product; yield and \textsuperscript{1}H NMR. \textsuperscript{d} Undefined polymer mixture.
Conclusions

A series of new pure \( S_{\alpha}S \) and \( R_{\alpha}S \) atropoisomeric diastereomers of Au(I) and Au(III)-NHC-N-naphthamide complexes (9-12; with iPr and Ph groups) were prepared from appropriate axially chiral pre-ligands.

The catalytic capacity of gold-NHC-N-naphthyl complexes was studied in cyclopropanation. In contrast to the unsuccessful \( S_{\alpha}S \)-Au(I)-NHC-oxazole complexes 13 and 14, the \( S_{\alpha}S \) and \( R_{\alpha}S \) diastereomers of Au(I) and Au(III)-NHC-N-naphthamide complexes 9-11 and \( S_{\alpha}S \)-12 were excellent catalysts to give successful cyclopropanation (> 99% yield, 15 min). Additionally, subsequent rapid \textit{in situ} cis-to-trans isomerization took place, thus affording predictable stereoselective trans-cyclopropyl products (\textit{trans} > 99%) in 15 min. The \( R_{\alpha}S \)-Au(III)-12 (iPr) complex also gave immediate cyclopropanation, but afforded slow isomerization into pure trans (>99%, 16 h), indicating that the \( R_{\alpha}S \)-12 iPr-structure reduces the isomerization ability. No enantioselectivity was obtained in the reaction catalyzed with the axially chiral gold complexes.

The results demonstrate that the novel axially chiral Au(I)- as well as the Au(III)-NHC-N-naphthamide complexes (9-12) represent an interesting group of gold catalysts with specific catalytic properties.

Experimental Section

General. Commercial grade reagents were used without any additional purification. Dry solvents were collected from a MB SPS-800 solvent purification system. Preparation of sensitive compounds was performed under dry conditions and in an inert atmosphere. All reactions were monitored by NMR and/or thin-layer chromatography (TLC) using silica gel 60 F254 (0.25 mm thickness). TLC plates were developed using UV-light (254 nm) and/or phosphomolybdenic acid with heating. Flash chromatography was performed with Merck silica gel 60 (0.040-0.063 mm). \(^1\)H and \(^{13}\)C NMR spectra were recorded either on a Bruker Avance DPX 400 MHz or a Bruker Avance III 600 MHz spectrometer. Chemical shift values for \(^1\)H and \(^{13}\)C NMR are reported in ppm (δ) down-field from tetramethylsilane (TMS) as an internal standard. Coupling constants (\(J\)) are reported in Hz. \(^1\)H and \(^{13}\)C NMR assignments of \( S_{\alpha}S \)-9, \( R_{\alpha}S \)-9 and \( S_{\alpha}S \)-11, based on 2D NMR studies (COSY, HSQC, HMBC) are available in Supp. Material. Accurate mass (HRMS) determination was performed on a “Synapt G2-S” Q-TOF instrument from Waters. Samples were ionized with an ESI probe with no chromatography separation performed before mass analysis. Calculated exact mass and spectra processing was done by Waters TM Software Masslynx V4.1 SCN871. IR spectra were recorded with a Bruker Alpha FT-IR spectrometer and OPUS V7.5 software was used for spectra analysis. Compounds 5, 6, 13, 14 were prepared according to literature.\(^{27}\)

Synthesis of benzimidazolium salts (7,8)

1-(2-Hydroxy-1-phenylethyl)carbamoyl)naphthalen-1-yl)-3-methyl-1H-benzo[d]imidazol-3-ium iodide (7). Amide 5 (117.2 mg, 0.29 mmol) and iodomethane (0.180 mL, 2.89 mmol) were dissolved in CH\(_3\)CN (10 mL) and stirred for 8h. The solvent was removed under reduced pressure to yield a diastereomeric mixture of benzimidazolium salt 7 (147.4 mg, 93%) as a pale yellow solid. \(^1\)H NMR (600 MHz, CDCl\(_3\)): δ (ppm) 11.20 (s, 1H, N=CH-N), 10.70 (s, 1.3H, N=CH-N), 8.39 (d, J 7.1 Hz, 1H, Ar), 8.22 (t, J 8.7 Hz, 2H, Ar), 8.08 (d, J 8.3 Hz, 1H, Ar), 8.06 (d, J 8.3 Hz, 1H, Ar), 7.97 (d, J 8.0 Hz, 1H, Ar), 7.92 (d, J 8.5 Hz, 1H, Ar), 7.82 (d, J 8.5 Hz, 1H, Ar), 7.75-7.72 (m, 2H, Ar), 7.70-7.62 (m, 5H, Ar), 7.62-7.48 (m, 5H, Ar), 7.35-7.29 (m, 6H, Ar), 7.17-7.13 (m, 8H, Ar), 5.06-5.02 (m, 1H, NH), 4.93-4.89 (m, 1.3H, NH), 4.35 (s, 3H, CH\(_3\)), 4.16 (s, 4H, CH\(_2\)), 4.06-3.98 (m, 2H, CH\(_2\)), 3.88 (t, J 6.6 Hz, 1H, OH), 3.77-3.73 (m, 1.3H, CH\(_2\)), 3.71-3.67 (m, 1H, CH\(_2\)), 2.96 (t, J 6.7 Hz, 1.3H, OH). \(^{13}\)C NMR (600 MHz, CDCl\(_3\)): δ (ppm) 166.2 (C=O), 165.9 (C=O), 143.3 (N=CH-N), 143.1, 132.58 (C\(_6\)), 132.57 (C\(_7\)), 131.6 (C\(_8\)), 131.3
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1-[1-Hydroxy-3-methylbutan-2-yl]carbamoylnaphthalen-1-yl]-3-methyl-1H-benzo[d]imidazol-3-ium iodides (8). A diastereomeric mixture of amides Sₐ-S-6 and Rₐ-S-6 (365 mg, 977 mmol) and iodomethane (1368 mg, 9.64 mol, 600 mL) were dissolved in CH₃CN (10 mL) and stirred at reflux for 18 h. The product was crystallized from CH₂Cl₂/pentane to yield a diastereomeric mixture of imidazolium compounds 8 (99%). The Sₐ-S-8 diastereomer was isolated by flash column chromatography (CH₂Cl₂/MeOH = 20:1), while the Rₐ-S-8 diastereomer could be enriched for characterization.

Sₐ-S-8: ¹H NMR (600 MHz, CDCl₃) δ 11.27 (s, 1H), 8.24 (dd, J 8.6, 0.9 Hz, 1H), 8.09 (d, J 8.5 Hz, 1H), 7.81 (dt, J 8.5, 0.9 Hz, 1H), 7.75 (d, J 8.4 Hz, 1H), 7.73 (ddd, J 8.4, 7.3, 1.0 Hz, 1H), 7.69 (ddd, J 8.2, 6.8, 1.1 Hz, 1H), 7.60 (ddd, J 8.4, 7.3, 1.0 Hz, 1H), 7.56 (ddd, J 8.3, 6.8, 1.2 Hz, 1H), 7.32 (d, J 8.4 Hz, 1H), 7.26 (d, J 5.3 Hz, 5H), 7.18 (d, J 8.9 Hz, 1H), 4.37 (d, J 0.7 Hz, 3H), 3.87 - 3.76 (m, 2H), 3.58 (ddd, J 11.3, 5.5, 2.8 Hz, 1H), 3.48 (t, J 6.0 Hz, 1H), 1.93 (h, J 6.8 Hz, 1H), 0.99 (d, J 6.8 Hz, 3H), 0.95 (d, J 6.8 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 166.8, 143.4, 135.4, 134.6, 133.7, 132.6, 131.3, 129.3, 129.2, 128.7, 128.4, 128.2, 127.7, 125.3, 124.0, 121.7, 114.5, 112.7, 61.7, 57.8, 33.9, 29.6, 19.8, 19.2. IR (CDCl₃, cm⁻¹): 3348 (b), 3051 (w), 2962 (m), 2874 (w), 1733 (w), 1650 (s), 1564 (m), 1534 (m), 1461 (m), 1378 (m), 1258 (m), 918 (m), 751 (s), 731 (s). HRMS (ESI, m/z): calcd for C₂₄H₂₆N₃O₂ [M- I] 388.2025; found 388.2026.

Rₐ-S-8: analyzed in an approx. 1:8 mixture of Sₐ-S-8 and Rₐ-S-8 diastereomers: ¹H NMR (600 MHz, CDCl₃) δ 10.38 (s, 1H), 8.16 (d, J 9.5 Hz, 1H), 8.00 (d, J 8.4 Hz, 1H), 7.82 (dd, J 13.6, 8.5 Hz, 2H), 7.69 - 7.61 (m, 3H), 7.55 - 7.51 (m, 2H), 7.41 - 7.34 (m, 2H), 4.31 (s, 3H), 3.55 - 3.42 (m, 2H), 3.40 (s, 1H), 3.37 - 3.32 (m, 1H), 3.03 (t, J 6.2 Hz, 1H), 1.86-1.77 (m, 1H), 0.70 (d, J 6.7, 1.3 Hz, 6H).

Synthesis of axially chiral Au(I)-NHC-N-naphthamide complexes (9,10)

1-[2-(2-Hydroxy-1-phenylethyl)carbamoylnaphthalen-1-yl]-3-methyl-2,3-dihydro-1H-benzo[d]imidazol-2-yl]gold(I) iodides; Sₐ-S-9 and Rₐ-S-9. A diastereomeric mixture of benzimidazolium salt 7 (47.2 mg, 0.08 mmol), AuCl·SMOE₂ (25.4 mg, 0.08 mmol), and sodium acetate (22.8 mg, 0.28 mmol) were dissolved in CH₃CN (6 mL) and stirred for 22 h at rt. After removal of the solvent under reduced pressure, the residue was purified by flash chromatography (EtOAc : n-pentane = 1:1) to afford axially chiral Au(I) complexes Sₐ-S-9 (18.5 mg, 29%) as a brown oil and Rₐ-S-9 (13.8 mg, 22%) as a white solid. ¹H and ¹³C NMR assignments of Sₐ-S-9 and Rₐ-S-9, based on 2D NMR studies (COSY, HSQC, HMBC) are available in SI).

Sₐ-S-9: ¹H NMR (600 MHz, CDCl₃) δ (ppm) 8.14 (d, J 8.5 Hz, 1H, Ar), 8.04 (d, J 8.3 Hz, 1H, Ar), 7.73 (d, J 8.5 Hz, 1H, Ar), 7.66-7.63 (m, 1H, Ar), 7.60 (d, J 8.3 Hz, 1H, Ar), 7.52-7.47 (m, 2H, Ar), 7.41 (m, 2H, Ar), 7.38-7.32 (m, 3H, Ar), 7.31-7.28 (m, 1H, Ar), 7.21 (d, J 8.5 Hz, 1H, Ar), 6.99 (d, J 8.2 Hz, 1H, NH), 6.94 (d, J 8.2 Hz, 1H, Ar), 5.11 (m, 1H, CH), 4.22 (s, 3H, CH₃), 3.96 (dd, J 4.1, 11.5 Hz, 1H, CH₂), 3.91 (dd, J 5.3, 11.4 Hz, 1H, CH₂), 2.47 (s, br, 1H, OH). ¹³C NMR (600 MHz, CDCl₃) δ (ppm) 188.7 (C-Au), 166.6 (C=O), 138.8 (C₉), 135.5 (C₉), 134.9 (C₉), 133.7 (C₉), 132.9 (C₉), 131.2 (C₉), 130.8 (C₉), 129.9 (C₉), 128.9 (2C, C₉), 128.77 (C₉), 128.72 (C₉), 128.3 (C₉), 127.9 (C₉), 127.0 (2C, C₉), 125.5 (C₉), 125.1 (C₉), 124.1 (C₉), 122.9 (C₉), 122.9 (C₉), 111.5 (C₉), 65.4 (CH₂), 55.6 (CH), 35.1 (CH₃). IR (CDCl₃, cm⁻¹): 3410 (b), 3060 (w), 2927 (w), 1658 (s), 1503 (m), 1440 (w), 1375 (m), 1047 (m), 910 (m), 732 (s). HRMS (ESI) calcd for C₂₄H₂₄N₃O₂Au [M+H] 746.0579; found 746.0591.

Rₐ-S-9: ¹H NMR (600 MHz, CDCl₃) δ (ppm) 8.17 (d, J 8.5 Hz, 1H, Ar), 8.03 (d, J 8.4 Hz, 1H, Ar), 7.87 (d, J 8.5 Hz, 1H, Ar), 7.65-7.61 (m, 1H, Ar), 7.49-7.45 (m, 3H, Ar), 7.34-7.30 (m, 1H, Ar), 7.30-7.27 (m, 3H, Ar), 7.17 (dd, J
7.8, 9.3 Hz, 2H, Ar), 7.11 (d, J 8.6 Hz, 1H, Ar), 7.01 (d, J 7.3 Hz, 1H, NH), 6.92 (d, J 8.2 Hz, 1H, Ar), 4.89 (q, J 1H, CH), 3.91 (s, 3H, CH₃), 3.90-3.86 (m, 2H, CH₂), 2.28 (t, J 5.7 Hz, 1H, OH). ¹³C NMR (600 MHz, CDCl₃) δ (ppm) 189.0 (C-Au), 166.7 (C-O), 138.0 (C₉), 135.4 (C₈), 135.0 (C₇), 133.4 (C₆), 132.6 (C₅), 131.3 (C₄), 130.3 (C₃), 129.9 (C₂), 128.9 (C₁), 128.73 (C₁ₓ), 128.69 (C₁ᵧ), 128.4 (C₂), 127.8 (C₃), 127.1 (C₁ₓ), 125.6 (C₃), 125.2 (C₀), 124.9 (C₁), 122.7 (C₁ₓ), 112.7 (C₂), 111.2 (C₃), 65.9 (CH₂), 56.5 (CH), 34.8 (CH₃). IR (CDCl₃, cm⁻¹): 3474 (b), 3288 (b), 3057 (w), 2931 (w), 1655 (s), 1526 (m), 1387 (m), 1048 (m), 910 (m), 825 (s). HRMS (ESI) calcd for C₂₇H₂₃N₂O₂Au [M + H] 746.0579; found 746.0588.

1-[2-(1-Hydroxy-3-methylbutan-2-yl)carbamoyl]naphthalen-1-yl]-3-methyl-2,3-dihydro-1H-benzo[d]imidazol-2-yl)gold(II) iodides; S₀₋S-10 and R₀₋S-10.

i) Diastereomerically pure S₀₋S-10 and R₀₋S-10. ¹H NMR (600 MHz, CDCl₃) δ 8.17 (d, J 8.6, 1H), 8.08 - 8.03 (m, 1H), 7.75 (d, J 8.5 Hz, 1H), 7.65 (ddd, J 8.2, 6.8, 1.1 Hz, 1H), 7.59 (d, J 8.3, 0.9 Hz, 1H), 7.52 - 7.46 (m, 2H), 7.34 (d, J 15.5 Hz, 1H), 7.20 (dd, J 8.5, 1.1 Hz, 1H), 6.95 (d, J 8.2 Hz, 1H), 6.51 (d, J 9.2 Hz, 1H), 4.19 (s, 3H), 3.86 - 3.79 (m, 1H), 3.74 (s, 2H), 3.03 - 1.96 (m, 1H), 1.00 (dd, J 14.3, 6.7 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 188.5, 166.9, 135.6, 134.8, 134.2, 132.8, 131.2, 130.8, 129.9, 128.8, 128.7, 128.2, 125.6, 125.0, 123.8, 122.9, 112.9, 111.5, 62.0, 56.9, 35.1, 29.4, 19.8, 19.5. IR (CDCl₃, cm⁻¹): 3348 (b), 3051 (w), 2962 (m), 2874 (w), 1733 (w), 1650 (s), 1564 (m), 1534 (m), 1461 (m), 1378 (m), 1258 (m), 918 (m), 751 (s), 731 (s). HRMS (ESI, m/z): calcd for C₂₄H₂₃N₂O₂AuNa [M + Na] 734.0555; found 734.0557.

R₀₋S-10: ¹H NMR (600 MHz, CDCl₃) δ 8.15 (dd, J 8.6, 0.9 Hz, 1H), 8.02 (dt, J 8.3, 0.9 Hz, 1H), 7.79 (d, J 8.5 Hz, 1H), 7.63 (ddd, J 8.2, 6.8, 1.1 Hz, 1H), 7.59 (d, J 8.3 Hz, 1H), 7.53 - 7.49 (m, 1H), 7.48 (ddd, J 8.2, 6.8, 1.2 Hz, 1H), 7.36 (ddd, J 8.3, 7.3, 1.0 Hz, 1H), 7.36 - 7.11 (m, 1H), 6.98 (dt, J 8.3, 0.9 Hz, 1H), 6.53 (d, J 8.2 Hz, 1H), 4.20 (s, 3H), 3.76 - 3.61 (m, 3H), 2.20 (t, J 5.5 Hz, 1H), 1.92 - 1.83 (m, J 6.7 Hz, 1H), 0.82 (dd, J 6.8, 4.7 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 189.2, 167.5, 135.6, 134.8, 134.2, 132.8, 131.2, 130.1, 129.9, 128.7, 128.3, 125.7, 125.3, 124.6, 122.7, 112.9, 111.3, 63.5, 58.2, 35.0, 29.0, 19.3. IR (CDCl₃, cm⁻¹): 3416 (b), 2959 (m), 2874 (w), 1651 (s), 1516 (s), 1460 (m), 1440 (m), 1388 (m), 1372 (m), 1238 (m), 911 (m), 744 (s). HRMS (ESI, m/z): calcd for C₂₄H₂₃N₂O₂AuNa [M + Na] 734.0555; found 734.0557.

Synthesis of axially chiral Au(III)Cl₃-NHC complexes (11, 12)

[1-(2-(2-Hydroxy-1-phenylethyl)carbamoyl)naphthalen-1-yl]-3-methyl-2,3-dihydro-1H-benzo[d]imidazol-2-yl)gold(III) trichloride; S₀₋S-11. S₀₋S-11: Diastereomerically pure gold(III) complex S₀₋S- 9 (15.8 mg, 0.02 mmol) and PhICl₂ (7.3 mg, 0.026 mmol) were dissolved in CH₂Cl₂ (2 mL) and stirred at rt for 15 min. n-Pentane (8 mL) was added to the solution and gave a yellow precipitate. The precipitate was filtered and washed with n-pentane (30 mL) and concentrated in vacuo. The crude product was purified by flash column chromatography (EtOAc/pentane = 1:1) and yielded Au(III)-NHC complex S₀₋S-11 (6.2 mg, 41%) as a yellow solid. ¹H and ¹³C NMR assignment of S₀₋S-11, based on 2D NMR studies (COSY, HSQC, HMBC) are available in SI. ¹H NMR (600 MHz, CDCl₃) δ (ppm) 8.23 (d, J 8.5 Hz, 1H, Ar), 8.05 (d, J 8.3 Hz, 1H, Ar), 7.87 (d, J 8.5 Hz, 1H, Ar), 7.72 (d, J 8.4 Hz, 1H, Ar), 7.68 (t, J 7.5 Hz, 1H, Ar), 7.60-7.55 (m, 3H, Ar, NH), 7.48 (d, J 8.6 Hz, 1H, Ar), 7.43 (t, J 7.8 Hz, 1H, Ar), 7.30 (t, J 7.6 Hz, 2H, Ar), 7.26-7.22 (m, 3H, Ar), 7.17 (d, J 8.4 Hz, 1H, Ar), 4.94 (m, 1H, CH₃), 4.37 (s, 3H, CH₃),...
3.55 (d, J 11.3 Hz, 1H, CH2), 3.21 (t, J 5.4 Hz, 1H, CH2). 13C NMR (600 MHz, CDCl3) δ (ppm) 165.5 (C=O), 152.7 (C-Au), 138.5 (C4), 136.2 (C4), 135.2 (C4), 133.8 (C4), 133.0 (C4), 132.4 (C4), 129.1 (C4), 128.99 (C4r), 128.93 (C4), 128.91 (C4), 128.6 (C4), 127.9 (2C, C4), 127.6 (C4), 126.62 (2C, C4r), 126.58 (C4r), 126.4 (C4r), 125.1 (C4), 124.1 (C4), 114.0 (C4), 111.8 (C4), 65.8 (CH2), 55.4 (CH), 35.6 (CH3). IR (CDCl3, cm⁻¹): 3338 (b), 3063, 2926 (w), 2853 (w), 1658 (s), 1503 (s), 1262 (w), 1148 (w), 1071 (w), 1027 (w), 748 (m), 707 (m). MS (ESI): Three set of molecular ion signals with Cl3 isotope pattern (~20 : 20 : 6 : 1 ratio): (M+H) (m/z 724/726/728), (M+Na) adduct (m/z 746/748/750) and (M+K) adduct (m/z 762/764/766). HRMS (ESI) calcd for C27H24N2O2Au35Cl3 [M + H] 724.0600; found 724.0602; calcd for C27H23N2O2Au35Cl3Na [M + Na] 746.0419; found 746.0424; calcd for C27H23N2O2Au35Cl3K [M + K] 762.0158; found 762.0161.

[1-{2-(1-Hydroxy-3-methylbutan-2-yl)carbamoyl]naphthalen-1-yl]-3-methyl-2,3-dihydro-1H-benzof[d]imidazol-2-yl]gold(III) trichlorides; Sα,S-12 and Rα,S-12. Sα,S-12: Diastereomerically pure gold(I) complex Sα,S-10 (15.4 mg, 22 mmol) and PhCl2 (12.4 mg, 45 mmol) were dissolved in CH2Cl2 (2.5 mL) and stirred at rt for 15 min. The product was crystallized from n-pentane and yielded product Sα,S-12 (5.8 mg, 34%). 1H NMR (600 MHz, CD2Cl2) δ 8.28 (d, J 8.5 Hz, 1H), 8.10 (d, J 8.4 Hz, 1H), 7.84 (d, J 8.5 Hz, 1H), 7.75 (dt, J 8.5, 0.9 Hz, 1H), 7.72 (dd, J 8.0, 6.8, 1.1 Hz, 1H), 7.59-7.63 (m, 2H), 7.53 (dd, J 8.5, 0.6 Hz, 1H), 7.46 (ddd, J 8.3, 7.3, 0.9 Hz, 1H), 7.20 (d, J 8.2 Hz, 1H), 7.0 (d, J 8.6 Hz, 1H), 4.34 (s, 3H), 3.50-3.54 (m, 1H), 3.31 (dt, J 11.5, 4.7 Hz, 1H), 2.87 (ddd, J 3.4, 7.1, 11.0 Hz, 1H), 1.77-1.86 (m, 1H), 1.43 (dd, J 6.8, 5.0 Hz, 1H), 0.89 (d, J 7.0 Hz, 3H), 0.87 (d, J 7.0 Hz, 3H). 13C NMR (151 MHz, CD2Cl2) δ 166.2, 136.6, 135.6, 134.4, 134.1, 132.6, 129.5, 129.1, 129.1, 128.9, 127.7, 126.8, 125.6, 124.6, 114.3, 112.3, 62.7, 57.4, 36.0, 29.5, 19.4, 19.2. HRMS (ESI) showed the Au(III)bis-NHC non-chloro molecular ion, Au(III)(NHC)2; calcd for C48H50N6O4Au [M⁺ - 2Cl] 971.3559; found 971.3554.

Rα,S-12: Following the same procedure as for Sα,S-12 above, PhCl2 oxidation of gold(I) complex Rα,S-10 afforded diastereomer Rα,S-12 (approx. 30% yield). 1H NMR (600 MHz, CDCl3) δ 8.23 (d, J 9.6 Hz, 1H), 8.08 - 8.00 (m, 1H), 7.84 (d, J 8.5 Hz, 1H), 7.78 - 7.65 (m, 2H), 7.62 - 7.55 (m, 2H), 7.48 - 7.43 (m, 2H), 7.24 - 7.20 (m, 1H), 6.95 (d, J 7.0 Hz, 1H), 4.37 (s, 3H), 3.62 - 3.48 (m, 3H), 1.70 - 1.63 (m, 1H), 0.69 - 0.55 (m, 6H). 13C NMR (151 MHz, CDCl3) δ 167.4, 153.0, 137.5, 136.2, 135.2, 133.6, 133.2, 132.5, 130.5, 130.3, 129.1, 129.1, 129.0, 128.6, 127.0, 126.8, 126.6, 125.2, 124.0, 114.1, 111.7, 63.5, 58.8, 35.6, 28.9, 18.7, 18.6. IR (CDCl3, cm⁻¹): 3393 (b), 3071 (w), 2960 (m), 1650 (s), 1522 (m), 1504 (m), 1457 (s), 1407 (m), 1377 (m), 909 (m), 730 (s). MS data showed the Au(III)bis-NHC adduct ([Au(III)Cl2(NHC)2Cl]2 for Rα,S-12 Au(III) with the AuCl2 isotope (35Cl/37Cl) pattern (~3 : 2 : 1 ratio): MS (ESI, m/z) for (M⁺): m/z 1041/1043/1045; and for (M⁺): m/z 1042/1044/1046. The non-chloro molecular ion, (M⁺- 2Cl) 971 was also seen. HRMS registered the Au(III)bis-NHC adduct M⁺: [Au(III)Cl2(NHC)2⁺]; HRMS (ESI, m/z): calcd for C48H50Au35Cl3N6O4 (M⁺) 1041.2936; found 1041.2936; calcd for C48H51Au35Cl3N6O4 (M⁺+H) 142.3014; found 142.2942; m/z); calcd for C48H50N6O4Au [M⁺ - 2Cl] 971.3559; found 971.3562.

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Supplementary Material

$^1$H and $^{13}$C NMR spectra of novel compounds 7-12, as well as structures of compounds 5, 9 and 11 shown with full $^1$H and $^{13}$C NMR assignments can be found in the Supplementary Material file.

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