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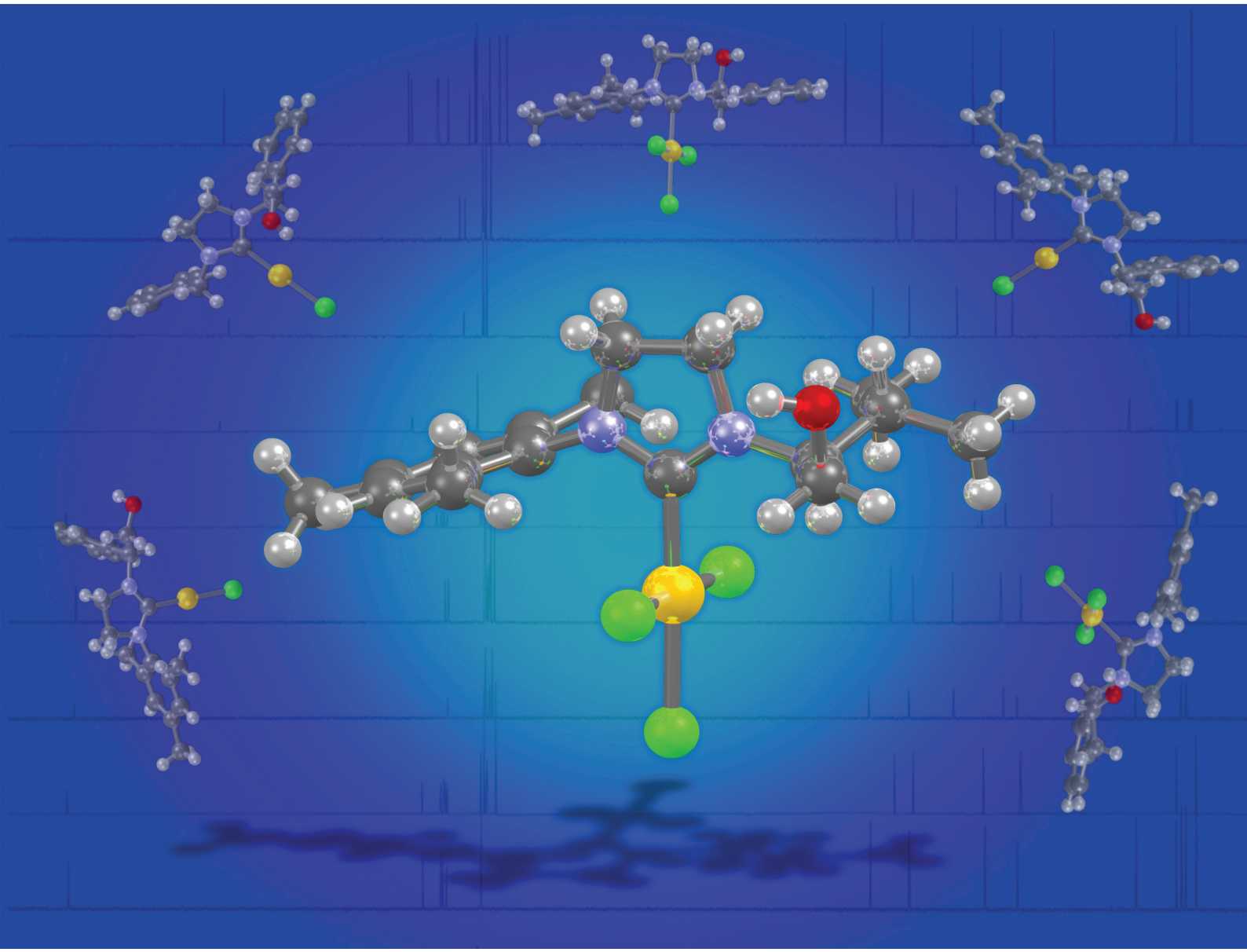

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Studies on gold(I) and gold(III) alcohol functionalised NHC complexes†

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Five pairs of novel chiral alcohol functionalised gold(I) and gold(III) NHC complexes derived from chiral amino alcohols, were synthesized and characterised (NMR, IR, HRMS). Single crystal X-ray diffraction data of gold(I) and gold(III) complexes are reported and discussed. The chiral imidazolium preligands were readily synthesized *via* the oxalamides, subsequent reduction and final orthoformate condensation. An improved method was used for generation of gold(I) NHC complexes (up to 92%) and further oxidation afforded the corresponding gold(III) NHC complexes (up to 99%). All the Au(I) and Au(III) NHC complexes proved far more catalytically active in a 1,6-enyne alkoxycyclization test reaction than our previously tested *N,N*- and *P,N*-ligated Au(III) complexes. Comparative gold(I) and gold(III) catalytic studies demonstrated different catalytic ability, depending on the NHC ligand flexibility and bulkiness. Excellent yields (92–99%) of target alkoxycyclization product were obtained with both gold(I) and gold(III) complexes with the bulky N^1-Mes-N^2-ethanol based NHC ligand.

Introduction

Homogenous gold catalysis is one of the fastest growing fields within homogenous transition metal catalysis. Gold catalysts display excellent selectivity towards the activation of carbon–carbon multiple bonds, allowing for a wide array of transformations.[1–8] Moreover, in the span of two decades gold catalysis has gone from a novelty to a widely recognised and useful tool in organic synthesis and has found application in the total synthesis of several complex natural products.[9–11] *N*-Heterocyclic carbenes (NHCs) have likewise become ubiquitous ligands in transition metal catalysis[12] since the first isolation of a free NHC in 1991 by Arduengo.[13] Their properties as strong σ-donors, even stronger than the widely used phosphines, lead to the formation of strong bonds to most transition metals, gold among them.[14] Gold(I) NHC complexes have widely been adopted as catalysts,[15,16] also within asymmetric gold(I) catalysis.[17–19] Even though gold(III) NHC complexes are easily prepared from the analogous gold(I) NHC complexes,[20] their use as catalysts is so far limited, despite their potential catalytic activity.[21–26] Reports of chiral gold(III) NHC complexes have been scarce, though a chiral cyclometallated NHC complex developed by Toste achieved excellent kinetic resolution of a 1,5-cycloisomerization.[27] Additionally, the study of the biological activity, especially anticancer, of both gold(I) and gold(III) NHC complexes is an active field.[28]

In contrast to the linear coordination mode of gold(I), gold(III) forms tetracoordinate, square planar complexes, which presents an opportunity for additional chelating or hemilabile functionalities on the NHC ligand.[21,29] Such ligated Au(III) catalysts might bring a prochiral reacting substrate closer to the chiral environment of the ligand, improving the enantioselectivity of the reaction. Alcohol-functionalised NHC ligands have been successfully employed in copper catalysed conjugate addition of enones.[30] Additionally, we have previously reported a series of chiral, alcohol functionalised gold(I) NHC complexes, catalytic active in cyclopropanation reactions.[31] The direct and modular template synthesis of NHC–gold complexes with a free hydoxy group has also been reported.[32] Herein, we report the synthesis and structure of novel alcohol functionalised gold(I) and gold(III) NHC complexes and their catalytic activity in alkoxycyclisation of 1,6-enynes.

Results and discussion

Preparation of imidazolium preligands

The imidazolinium chloride preligands **7a–e** were readily available through a slightly modified four-step synthetic method (Scheme 1a).[30] Oxalamide ethyl esters **3a,b** were prepared in quantitative yield from mesityl/benzyl amines **2a,b** and ethyl chlorooxoacetate **1**. Subsequent condensation with chiral amino-

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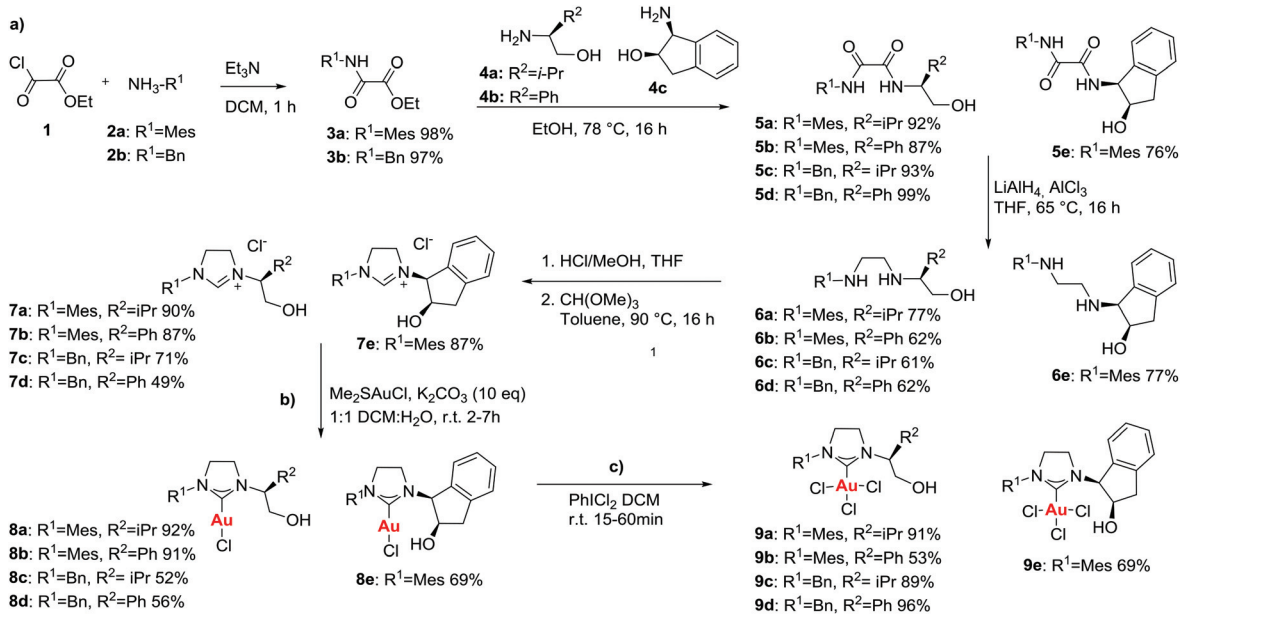
†Electronic supplementary information (ESI) available: Copies of ^{1}H and ^{13}C NMR spectra. CCDC 2056822, 2056823, 2056825, 2056827, 2056945 and 2056946. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1dt00387a



Scheme 1 Synthesis of (a) imidazolium chloride preligands **7a–e**; (b) Au(I)NHC complexes **8a–e** and (c) Au(III)NHC complexes **9a–e**.

alcohols **4a–c** in refluxing ethanol yielded the asymmetric oxalamides **5a–e** (76–99%), which were reduced with $LiAlH_4$ to give the corresponding N^1-Mes/Bn-N^2-(iPr/Ph)-ethanol diamines **6a–d** (61–77%) and N^1-Mes-N^2-indanol diamine **6e** (77%). Finally, protonation by anhydrous HCl (1 eq.) followed by cyclocondensation with trimethylorthoformate yielded the respective imidazolinium chlorides **7a–e** in moderate to high yields (49–90%).

Synthesis of gold(I) and gold(III) NHC complexes

The NHC ligated gold(I) complexes **8a–e** were prepared from imidazolinium chloride preligands **7a–e**. Initially, the most commonly used route towards gold(I) NHC complexes[33] *via* transmetalation of a silver(I) NHC complex, usually generated *in situ*, was applied. The reaction of imidazolinium chlorides **7a,b,e** with Ag_2O (0.5–1 eq.) in DCM for 3–24 h, followed by addition of Me_2SAuCl, provided gold(I) NHC complexes **8a,b,e** in moderate yields (48–69%). However, due to unreacted Me_2SAuCl, the product isolation required chromatographic purification. A more convenient and atom-efficient method to generate gold(I) NHC complexes is based on treatment of the imidazolinium salt (Scheme 1b) by a weak base, such as K_2CO_3, in either refluxing acetone[34] or in DCM at room temperature.[35] Stirring imidazolinium salts **7a,e** in refluxing acetone with K_2CO_3 (1 eq.) and Me_2SAuCl gave full conversion of imidazolinium salts **7a,e** in 2 hours, but only low yields of Au(I) complexes **8a,e** (50–56%) and formation of a dark precipitate, indicating significant decomposition to gold(0). The similar reaction of imidazolinium choride **7b** in DCM at room temperature with increased amount of K_2CO_3 (10 eq.) was slow (<35% conversion to complex **8b** in 12 hours; ^{1}H NMR). However, fast conversion (<2 h) and excellent yield (up to 91% of **8b**) was obtained for the corresponding reaction in a mixture of DCM and water (1 : 1) by vigorous stirring and simple work-up (brine washing of organic phase and filtering through short silica plug). This method was used for the synthesis of all gold(I) NHC complexes **8a–e** (Scheme 1b). The flexible N^1-Mes-N^2-(iPr/Ph)-ethanol–NHC gold(I) complexes **8a,b** were more successfully prepared (91–92%) than the corresponding rigid N^1-Mes-N^2-indanol complex **8e** (69%). The N^1-Bn complexes **8c** and **8d** proved less stable under the reaction conditions. Hence, lower isolated yields (52–56%) were obtained, due to significant decomposition during the course of the reaction.

^{1}H NMR studies readily illustrate the course of the K_2CO_3-Me_2SAuCl reaction (Scheme 1b) with imidazolinium chloride **7e** to give the gold(I) NHC complex **8e** (Fig. 1). As reported by both Nolan[34] and Gimeno,[35] this reaction proceeds through an intermediate anion exchange of imidazolinium chloride to Me_2SAuCl, giving the new $AuCl_2^-$ imidazolinium counterion. The chloride counterion exchange is observed by ^{1}H NMR spectroscopy, in particular by a shielding effect for the H^2 proton (from 8.65 to 8.40 ppm for **7e**, Fig. 1a and b). The formation of the desired Au(I) complex is clearly verified by the disappearance of the acidic H^2 proton (Fig. 1c). The formation of Au(I) NHC was also seen by the large change in chemical shift of the original imidazolium (**7e**) C^2 ^{13}C NMR signal at ~140 ppm, appearing as a NHC carbenic carbon resonance at ~195 ppm (**8e**, which is characteristic for gold(I) NHC complexes with a saturated imidazoline backbone.[33] ^{1}H NMR also demonstrates that most aliphatic indanol protons are clearly affected and mostly experience a shielding effect by ligand coordination and formation of the target Au(I) NHC complex **8e**.

The Au(III) NHC–alcohol complexes **9a–e** were readily prepared by oxidation of the respective (AuI) complexes **8a–e** with dichloroiodobenzene, $PhICl_2$, in DCM at room temperature (Scheme 1c).[20] The reactions proceeded smoothly and afforded

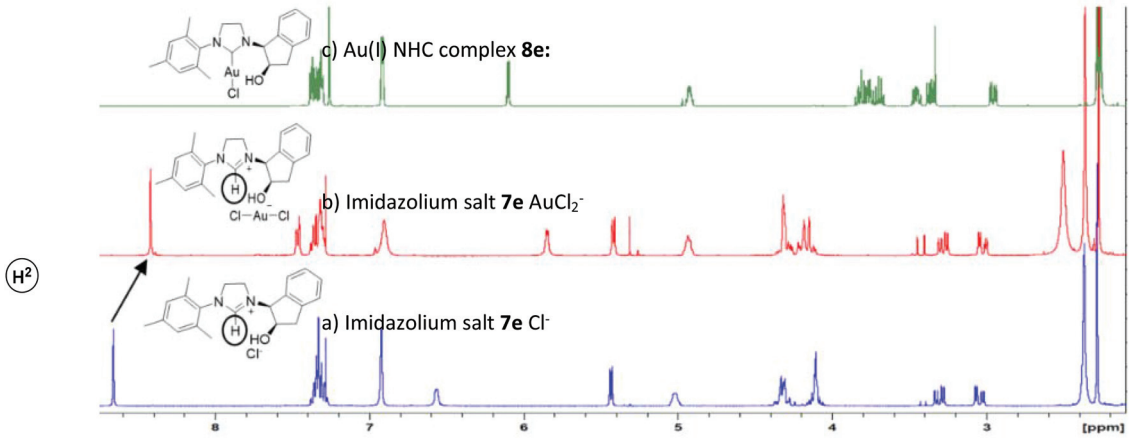


Fig. 1 ^{1}H NMR studies; formation of (c) Au(I) NHC complex **8e** from K_2CO_3, Me_2SAuCl and (a) preligand **7e** (Scheme 1b), *via* (b) imidazolium $AuCl_2^-$ salt.

high yields of complexes **9a** and **9c–e** (89–96%). The lower yield of complex **9b** (53%) was due to solubility issues and challenging product isolation. The successful Au(I)-to-Au(III) oxidation of complexes **8a–e** was verified by the significant change of chemical shift of the carbenic ^{13}C NMR resonance from ~195 ppm to ~170 ppm, which is characteristic for gold(I)- and gold(III) NHC complexes of saturated imidazolines, respectively.[36]

XRD, structural discussion

All the gold(I) and gold(III) complexes **8a–e** and **9a–e** were air stable, crystalline solids, and could be stored indefinitely in the freezer under normal atmosphere and were stable for several days in NMR tubes in $CDCl_3$. Crystals for single crystal X-ray diffraction were obtained for complexes **8b,d,e** and **9a,b,e** by slow diffusion of diethyl ether into saturated dichloromethane solutions of the complexes (solid state structures Fig. 2).

Selected bond lengths and bond angles for the analysed structures are reported in Table 1. The Au–C bond in the Au(I) complexes **8a,b,e** is in average significantly shorter (<2.0 Å) compared to that found in the corresponding Au(III) species **9a,b,e** (>2.05 Å). This is in line with reported Au(I) and Au(III) NHC complexes, which have average NHC-Au(I) and Au(III) distances of 1.984 ± 0.022 Å (range 1.897–2.151 Å)[37] and 2.004 ± 0.012 Å (range 1.986–2.039 Å).[23,38] Notably, **9b** shows the longest NHC–Au(III) distance (2.055 Å) reported so far. Interestingly, in this series the chloride atom *trans* to the carbene centre shows significantly shorter Au–Cl distances in case of Au(I) (2.28–2.29 Å) compared those in Au(III) (2.32 Å) complexes. In comparison with literature reported Au(III)–Cl_{trans} distances the average is slightly longer (2.314 ± 0.010 Å, range 2.291–2.338 Å)[39] compared to the Au(I)–Cl distances (2.286 ± 0.015 Å, range 2.253–2.350 Å),[40] however both classes

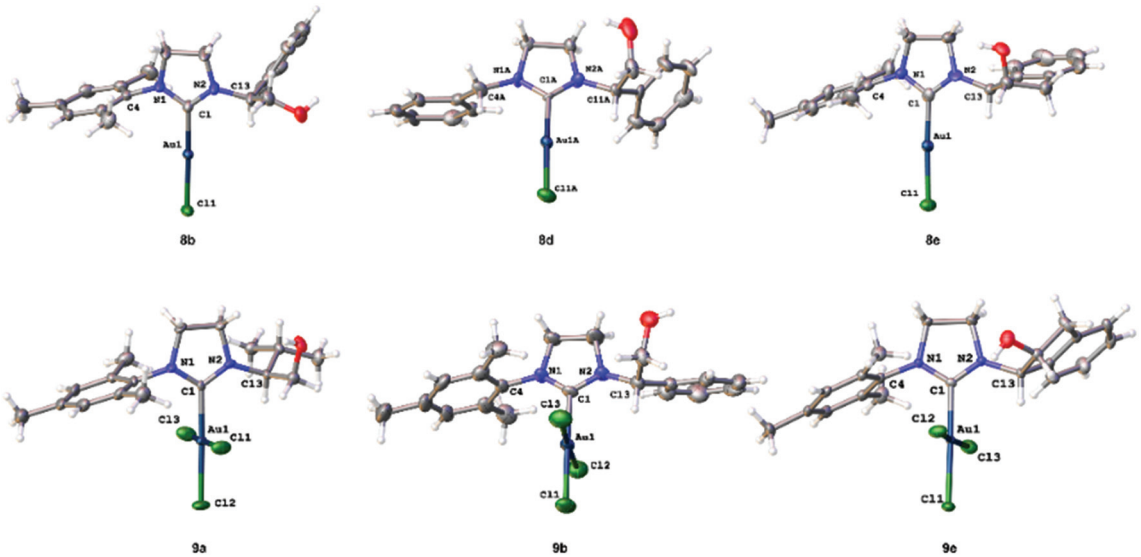


Fig. 2 Solid state structures of gold(I) and gold(III) NHC complexes **8b,d,e** and **9a,b,e** obtained by X-ray crystallographic analysis.

Table 1 Structural parameters of crystallographically characterized gold(I) and gold(III) NHC complexes

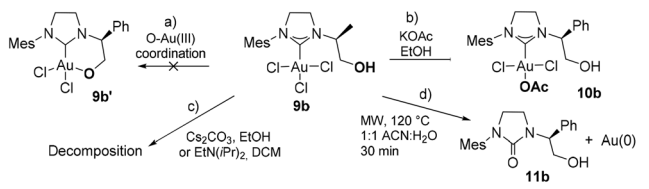
	Au(I)			Au(I)		
	8b	**8d**[a]	**8e**	**9a**	**9b**	**9e**
C1–Au	1.980(5)	1.99	1.972(12)	2.016(6)	2.055	2.009(5)
Au–Cl_{trans}	2.2870(13)	2.28	2.295(3)	2.3269(17)	2.324	2.3290(12)
C–Au–Cl_{trans}	177.61(16)	178.3	178.3(3)	178.1(2)	178.7	177.26(13)
$AuCl_{cis}$	—	—	—	2.275(2)	2.27	2.2876(13)
$AuCl_{cis}$	—	—	—	2.265(2)	2.278	2.2845(12)
C–Au–Cl_{cis}	—	—	—	88.39(19)	88.6	87.72(13)
C–Au–Cl_{cis}	—	—	—	91.39(19)	90.3	91.10(13)
Cl–Au–Cl	—	—	—	176.05(9)	176.7	174.61(6)
C4–N1–C1	126.2(4)	125.7	124.2(9)	127.3(5)	129.2	125.8(4)
C13–N2–C1	124.7(4)	125.3	122.1(10)	127.4(5)	127.3	125.4(4)
Angle of planes[b]	—	—	—	89.8(2)	85.5	100.4(1)

[a] Average value of two independent molecules. [b] Dihedral angle between the least square planes spanned by the NHC backbone and the C·$AuCl_3$ motif.

cover a wide ranges of Au–Cl_{trans} distances. The *cis*-chlorides in the Au(III) complexes have shorter Au–Cl distances (2.26–2.28 Å), which is not reflected in the structurally reported Au(III) complexes (range 2.227–2.382; average 2.280 ± 0.023 Å).[41] There is no noticeable deviation from linearity for the Au(I) complexes nor from an ideal square planar Au(III) configuration. The latter plane is significantly distorted from the least squares plane spanned by the NHC backbone (**9b**: 85.5°; **9a**: 89.8°: **9e**: 100.4°) to accommodate for the steric demand of the *N*-substituents, which is not uncommon for this class of complexes.[42–45]

Attempted O–Au(III) coordination

Several approaches were attempted to give a bidentate *C*,*O*-Au(III) complex (*e.g.* **9b′**, Scheme 2a) by *O*-Au(III) coordination of the alcohol moiety of gold(III) NHC complexes **9a–e**. KOAc treatment for OH deprotonation[46] of complex **9b** in EtOH gave the unstable gold(III) acetate derivative **10b** (Scheme 2b), by chloride–acetate counterion exchange, as shown by IR (OH-stretch) and ^{1}H NMR (OAc), while non-coordinating bases (Cs_2CO_3 in EtOH) or Hünig's base (EtN(i-Pr)$_2$ in DCM) led to black mixtures of unidentified products (Scheme 2c), presumably due to reduction to gold(0). As microwave assisted methods have been successfully applied in the synthesis of gold(III) complexes, *e.g.* cyclometallated complexes by C–H activation,[47] thermal activation (70–120 °C) was tested for *O*-Au(III) coordination. No reaction took place in CH_3CN. However, in CH_3CN–water (1 : 1, 30 min, 120 °C), the white, crystalline imidazolinone product **11b** (Scheme 2d) was formed by C2 oxidation along with reduction to elemental gold, as proven by IR (broad OH and new urea C=O (1672 cm^{-1}) signal) and ^{13}C NMR (urea C=O at 165.0 ppm). Lowering the reaction temperature slowed down the unwanted NHC-oxidation, but still no coordination was observed.



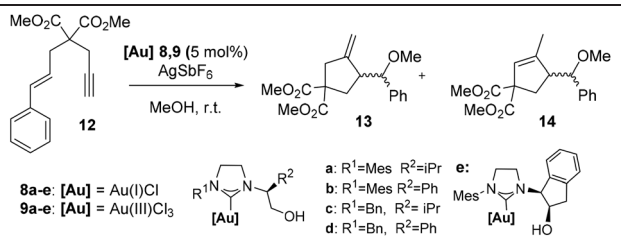
Scheme 2 Attempts to coordinate the OH functionality of Au(III) NHC complex **9b**.

Catalytic activity of Au NHC complexes

The alkoxycyclisation of a 1,6-enyne[8,48,49] is known to be catalysed by gold(I) NHC catalysts[17–19,50–52] and also by gold(III) complexes.[53,54] Our previous studies on the mechanism[55,56] of the this gold catalysed reaction[54] show that initial gold–alkyne coordination activates towards nucleophilic intramolecular attack by the alkene, and yields a carbocation which undergoes nucleophilic attack by methanol. Final proton transfer and deauration yields the 3-methylene-cyclopentane target product **13** from enyne substrate **12** (Table 2). The exocyclic double bond of **13** may isomerise to give the endocyclic double bond isomer **14**. The alkoxycyclisation of 1,6-enyne **12** into cyclopentane product **13** was chosen as a model reaction to test the catalytic activity of the new gold(I)- and gold(III) NHC complexes **8a–e** and **9a–e** (Table 1). To the best of our knowledge, the reaction has not previously been catalysed by gold(III) NHC complexes.

The reactions were performed at room temperature with enyne **12** in MeOH, acting both as a solvent and nucleophile. For the Au(I) catalyzed reactions (4–6 h, entries 1–5), $AgSbF_6$ (5 mol%) was used for counterion exchange of the non-active gold(I) NHC–Cl complex (**8a–e**, 5 mol%). No reaction was observed in the absence of the silver salt additive. Likewise, no reaction took place with the silver salt alone. All the Au(I) NHC complexes **8a–e** proved catalytically active and gave the alkoxycyclization product **13** in high to excellent yields (66–99%, entries 1–5). The N^2-ethanol based complexes **8a–d** were more catalytic active (77–99% of **13**, 4 h, entries 1–4) than the rigid cyclic N^2-indanol complex **8e** (66%, 6 h, entry 5). The two bulky N^1-Mes Au(I)NHC complexes **8a,b** gave highest yields of product **13** (99% and 89%; entries 1,2). Complex **8b** also gave minor amounts of the not previously reported isomer **14** (7%) with an endocyclic double bond, most likely formed by isomerization of the originally formed product **13**. Au(I) NHC com-

Table 2 Catalytic testing of gold(I) and gold(III) NHC complexes (**8a–e** and **9a–e**) in gold catalysed alkoxycyclization of 1,6-enyne **12**[a]



Entry	[Au] catalyst (ratio $AgSbF_5$: [Au])	Time[b]	Yield[c]
1	**8a** (1 : 1)	4 h	99% (**13**)
2	**8b** (1 : 1)	4 h	89% (**13**) + 7% (**14**)
3	**8c** (1 : 1)	4 h	79% (**13**)
4	**8d** (1 : 1)	4 h	77% (**13**)
5	**8e** (1 : 1)	6 h	66% (**13**)
6	**9a** (1 : 1)	2 h	44% (**13**)
7	**9a** (2 : 1)	2 h	92% (**13**)
8	**9a** (3 : 1)	2 h	38% (**13**) + 9% (**14**)
9	**9b** (2 : 1)	2 h	15% (**13**) + 32% (**14**)
10	**9c** (2 : 1)	2 h	22% (**13**) + 15% (**14**)
11	**9d** (2 : 1)	2 h	38% (**13**) + 10% (**14**)
12	**9e** (2 : 1)	2 h	49% (**13**) + 9% (**14**)

[a] Reactions were performed on a 0.1 mmole scale in 3 mL MeOH with 5 mol% [Au] and 5–15 mol% $AgSbF_6$. [b] Full conversion. [c] Isolated yields.

plexes **8c,d**, with the more flexible and less sterically hindered N^1-benzyl substituent, gave product **13** in good yields (79 and 77%, entries 3,4).

Thus, our Au(I) NHC complexes gave similar to better yields and reaction rates in this reaction compared to previously reported Au(I) NHC complexes (48–99% yields, 1–48 h).[17–19,50–52]

The study of the corresponding gold(III) NHC complexes were initiated by optimizing the ratio of silver salt additive to gold(III) complex **9a** (entries 6–8). A 3 : 1 ratio of silver salt/gold(III) catalyst has been used in previous gold(III) catalyzed alkoxycyclisations.[53] A large increase in yield in $AuCl_3$ catalyzed hydroarylation of alkenes has also been seen by increasing the number of equivalents of $AgSbF_6$ from 1 to 3, presumably due to generation of a more electrophilic gold(III) species.[57] Screening for optimum amount of silver salt to be used with the present gold(III) complex **9a**, showed that a highly increased selectivity (from 44% to 92%) towards the main product **13** was obtained going from 1 : 1 to 2 : 1 ratio of $AgSbF_6$/Au(III) catalyst (entries 6 and 7). Further increased ratio (3 : 1) had negative impact on the yield and selectivity (entry 8). In general, the other gold(III) NHC complexes **9a–e** afforded faster conversion (100% in 2 h, entries 6–12) than the corresponding gold(I) complexes (4–6 h, entries 1–5), and gave definitely, more rapid reactions than our previously studied pyridine-oxazoline-Au(III)[51] and *P,N*-chelated gold(III)[51] complexes (14–62% conversion in 24 h). However, in contrast to Au(I) NHC complexes **8a–e**, the gold(III) NHC **9b–e** catalyzed reaction were less selective, giving poorer yields of target product **13** (15–49%, entries 9–12), as significant amounts of isomer **14** were formed (9–32%). This result is consistent with our previous studies on gold(III) catalysed alkoxycyclisations of 1,6-enynes, with gold(III) being less suited for this reaction than their gold(I) counterparts.[54,58] The lower selective may be explaned by the ability of gold(III) complexes to give competing alkyne hydration, which was supported by the observation of the ketone byproduct (dimethyl 2-cinnamyl-2-(2-oxopropyl)malonate) in some reactions, together with other non-identified biproducts. High yield of product **13** (92%) was, however, obtained with the most bulky N^1-Mes-N^2-(iPr)ethanol NHC–gold(III) complex **9a**.

The bulky N^1-Mes Au(I) and Au(III) NHC complexes (**8a,b,e** and **9a,b,e**) gave minor enantioselectivity. The Au(III) catalysts **9a,b,e** afforded slightly higher values (5–6% ee) than the Au(I) **8a,b,e** analogues (3–5% ee). The more flexible and less sterically hindered N^1-benzyl Au(I) and Au(III) NHC complexes (**8c,d** and **9c,d**) did not induce enantioselectivity. The lack of stereocontrol is most likely due to the chiral environment provided by the ligand being too far from the reaction centre.

Conclusions

Five pairs of chiral gold(I) and gold(III) NHC complexes (**8a–e** and **9a–e**), derived from chiral amino alcohols, were synthesized and characterised (NMR, IR, HRMS). The chiral imidazolium preligands **7a–e** were readily synthesized *via* the oxalamides, prepared from the respective chiral aminoalcohols and chlorooxoacetate; subsequent reduction and final orthoformate condensation. An improved method was used for generation of gold(I) NHC complexes (**8**, up to 92%) and further oxidation afforded the corresponding gold(III) NHC complexes (**9**, up to 99%). Single crystal X-ray diffraction was obtained for six gold(I) and gold(III) complexes. Attempts to coordinate the pendant alcohol functionality to the gold(III) centre was not successful.

The synthesised gold(I) and gold(III) NHC complexes (**8**, **9**) were studied in an alkoxycyclisation test reaction. All complexes were far stronger catalysts than our previously tested *N,N*- and *P,N*-ligated Au(III) complexes in this reaction. Gold(I) complexes (**8a–e**) were most efficient and selective (66–99% yield of target product **13**, 4 h, r.t.). The gold(III) complexes (**9b–e**) gave fastest conversion, but were less selective, due to competing alkyne hydration. However, excellent yields of target product **13** (92–99%) were obtained with both gold(I) and gold(III) complexes (**8a**, **9a**) with the bulky N^1-Mes-N^2-ethanol based NHC ligand. Only minor enantioselectivity (up to 6% ee) was obtained with the most bulky N^1-Mes Au(I) and Au(III)NHC complexes (**8a,b,e** and **9a,b,e**).

Experimental

General

Commercial grade reagents were used without any additional purification. Dry solvents were collected from a MB SPS-800 solvent purification system. All reactions were monitored by

NMR and/or thin-layer chromatography (TLC) using silic a gel 60 F254 (0.25 mm thickness). TLC plates were developed using UV-light and/or *p*-anisaldehyde stain. Flash chromatography was performed with Merck silica gel 60 (0.040–0.063 mm). ^{1}H and ^{13}C NMR spectra were recorded either a Bruker Avance DPX 400 MHz or a Bruker Avance III 600 MHz spectrometer. Chemical shifts are reported in ppm (δ) downfield from tetramethylsilane (TMS) as an internal standard. Melting points (mp) were determined using a Stuart SMP40 apparatus and are uncorrected. Accurate mass determination was performed on a "Synapt G2-S" Q-TOF instrument from Waters. Samples were ionized with an ASAP probe with no chromatography separation performed before mass analysis. IR spectra were recorded with a Nicolet 20SXC FT-IR spectrometer using EZ OMNIC software to analyse the spectra and a Bruker Alpha FT-IR spectrometer using OPUS V7 software to analyse the spectra. Single crystal X-ray data were collected on a Bruker D8 APEX-II diffractometer equipped with a CCD camera using Mo Kα radiation (λ = 0.71073 Å).

CCDC ID: 2056822, 2056823, 2056825, 2056827, 2056945, 2056946;† CCDC also included under each complex (**8b,d,e** and, **9b,d,e**) below.

General procedure for the synthesis of oxalamide ethyl esters

To a solution of amine **2** (1 eq.) and triethylamine (1 eq.) in dry DCM (40 mL) was added ethyl chlorooxoacetate **1** (1 eq.). The resulting solution was stirred at room temperature for 1 hour. The solution was then diluted with 30 mL DCM and washed with $NaHCO_3$ solution (saturated, 2 × 25 mL) and brine (25 mL). The organic layer was dryed over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to afford the products as white solids.

Ethyl 2-(mesitylamino)-2-oxoacetate (3a). Following the general procedure, mesityl amine (**2a**, 1.734 g, 12.8 mmol), triethylamine (1.785 g, 12.8 mmol) and ethyl chlorooxoacetate (**1** 1.433 g) gave target product **3a** as a white solid in 94% yield (2.843 g, 12.08 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.33 (s, 1H, NH), 6.92 (s, 2H, CH_{Ar}), 4.43 (q, J = 7.0 Hz, 2H, CH_2), 2.28 (s, 3H, CH_3), 2.20 (s, 6H, CH_3), 1.45 (t, J = 7.0 Hz, 3H, CH_3).

Ethyl 2-(benzylamino)-2-oxoacetate (3b). Following the general procedure, benzyl amine (1293 mg, 12.06 mmol), triethylamine (1221 mg, 12.06 mmol) and ethyl chlorooxoacetate (1647 mg, 12.06 mmol) gave target product **3b** as a white solid in 97% yield (2146 mg, 11.70 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.50 (s, 1H, NH), 7.27–7.35 (m, 5H, CH_{Ar}), 4.50 (d, J = 6.0 Hz, 1H, CH_2), 4.32 (q, J = 7.1 Hz, 2H, CH_2), 1.36 (t, J = 7.1 Hz, 3H, CH_3).

General procedure for the synthesis of oxalamides

To a solution of oxalamide ethyl ester **3** (1 eq.) in ethanol (10 mL) was added aminoalcohol **4** (1 eq.) and the solution stirred at reflux for 16 hours. The solvent was decanted off and the solid residue was washed with EtOH (2 × 5 mL). The solid was then dried *in vacuo* to yield the oxalamides as white solids.

(*S*)-*N*^{1}-(1-Hydroxy-3-methylbutan-2-yl)-*N*^{2}-mesityloxalamide (5a). Following the general procedure, ethyl 2-(mesitylamino)-2-oxoacetate (**3a**, 942 mg, 4.00 mmol) and (*S*)-2-amino-3-methylbutan-1-ol (**4a**, 413 mg, 4.00 mmol) gave target product **5a** as a white solid in 97% yield (1137 mg, 0.89 mmol). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.73 (s, 1H, NH), 7.67–7.68 (d, J = 5.4 Hz, 1H, NH), 6.92 (s, 2H, CH_{Ar}), 3.74–3.80 (m, 3H, CH + CH_2), 2.28 (s, 3H, CH_3), 2.19 (s, 6H, 2 × CH_3), 1.97–2.03 (m, 1H, CH), 1.01–1.02 (d, J = 6.9 Hz, 3H, CH_3), 0.98–0.99 (d, J = 6.9 Hz, 3H, CH_3). ^{1}H NMR corresponds to previously reported spectra.

((*S*)-*N*^{1}-(2-Hydroxy-1-phenylethyl)-*N*^{2}-mesityloxalamide (5b). Following the general procedure, ethyl 2-(mesitylamino)-2-oxoacetate (**3a**, 344 mg, 1.56 mmol) and (*S*)-2-amino-2-phenylethanol (**4a**, 214 mg, 1.56 mmol) gave target product **5b** as a white solid in 87% yield (422 mg, 1.36 mmol). ^{1}H NMR (400 MHz, $(CD_3)_2S{=}O$) δ (ppm) 10.06 (s, 1H, NH), 9.10 (d, J = 8.5 Hz, 1H, NH), 7.32–7.40 (m, 4H, CH_{Ar}), 7.25 (tt, J = 7.1, 1.2 Hz, 1H, CH_{Ar}), 6.89 (s, 2H, CH_{Ar}), 4.99 (t, J = 6.0 Hz, 1H, OH), 4.89–4.94 (m, 1H, CH), 3.73–3.79 (m, 1H, CH_2), 3.63–3.68 (m, 1H, CH_2), 2.23 (s, 3H, CH_3), 2.07 (s, 6H, CH_3).

((*S*)-*N*^{1}-Benzyl-*N*^{2}-(1-hydroxy-3-methylbutan-2-yl)oxalamide (5c). Following the general procedure, ethyl 2-(benzylamino)-2-oxoacetate (**3b**, 553 mg, 2.67 mmol) and (*S*)-2-amino-3-methylbutan-1-ol (275 mg, 2.67 mmol) gave target product **5c** as a white solid in 93% yield (653 mg, 2.48 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.88 (t, J = 6.3 Hz, 1H, NH), (d, J = 7.1 Hz, 1H, NH), 7.27–7.36 (m, 5H, CH_{Ar}), 4.43–4.53 (m, 2H, CH_2), 3.68–3.75 (m, 3H, CH + CH_2), 2.41 (t, J = 5.7 Hz, 1H, OH).

((*S*)-*N*^{1}-Benzyl-*N*^{2}-(2-hydroxy-1-phenylethyl)oxalamide (5d). Following the general procedure, ethyl 2-(benzylamino)-2-oxoacetate(**3b**, 554 mg, 2.67 mmol) and (*S*)-2-amino-2-phenylethanol (367 mg, 2.67 mmol) gave target product **5d** as a white solid in 99% yield (788 mg, 2.64 mmol). ^{1}H NMR (400 MHz, $(CD_3)_2S{=}O$) δ (ppm) 9.29 (t, 1H, J = 6.5 Hz, NH), 8.99 (t, 1H, J = 8.6 Hz, NH), 7.21–7.35 (m, 10H, CH_{Ar}), 4.97 (t, J = 5.7 Hz, 1H, OH), 4.82–4.87 (m, 1H, CH), 4.27–4.37 (m, 2H, CH_2), 3.68–3.74 (m, 1H, CH_2), 3.60 (m, 1H, CH_2). IR $\tilde{\nu}$ (cm^{-1}) 3293, 3062, 3031, 2929, 1651, 1515, 1073, 609. HRMS (ESI) m/z [M + H$^+$]: calcd for $C_{17}H_{19}N_2O_3$ 299.1396, found 299.1396.

(*N*^{1}-((1*S*,2*R*)-2-Hydroxy-2,3-dihydro-1*H*-inden-1-yl)-*N*^{2}-mesityloxalamide (5e). Following the general procedure ethyl 2-(mesitylamino)-2-oxoacetate (**3a**, 681 mg, 2.90 mmol) and (1*S*,2*R*)-1-amino-1*H*-inden-2-ol (**4c**, 432 mg, 2.90 mg) gave target product **5e** as a white solid in 76% yield (748 mg, 2.20 mmol). ^{1}H NMR (600 MHz, $(CD_3)_2S{=}O$) δ (ppm) 10.28 (s, 1H, NH), 8.25–8.27 (d, J = 8.6 Hz, 1H, NH), 7.21–7.28 (m, 4H, CH_{Ar}), 6.91 (s, 2H, CH_{Ar}), 5.48–5.49 (d, J = 4.9 Hz, 1H, OH), 5.22–5.25 (dd, J = 8.5, 5.2 Hz, 1H, CH), 4.50–4.54 (m, 1H, CH), 3.11–3.16 (dd, J = 16.2, 5.1 Hz, 1H, CH_2), 2.85–2.89 (dd, J = 16.2, 1.4 Hz, 1H, CH_2), 2.23 (s, 3H, CH_3), 2.11 (s, 6H, 2 × CH_3). ^{13}C (150 MHz, $(CD_3)_2S{=}O$) δ (ppm) 160.1 (C=O), 159.1 (C=O), 141.7 (C_{Ar}), 141.2 (C_{Ar}), 136.5 (C_{Ar}), 135.2 (C_{Ar}), 131.9 (C_{Ar}), 128.8 (CH_{Ar}), 128.2 (CH_{Ar}), 127.0 (CH_{Ar}), 125.5 (CH_{Ar}), 124.5 (CH_{Ar}), 72.1 (CHOH), 57.2 (CHNH), 40.3 (CH_2), 20.9 (CH_3), 18.4 (CH_3). M.p

231 °C. HRMS (ESI) m/z [M + H^+]: calcd for $C_{20}H_{23}N_2O_3$ 339.1709, found 339.1713.

General procedure for synthesis of diamines

Oxalamide (1 eq.) and $AlCl_3$ (2 eq.) were placed in a predried Schlenck tube and placed under N_2-atmosphere. After dissolution in dry THF (10 mL), $LiAlH_4$ (5 eq., 1 M, THF) was added under vigorous stirring. Upon complete addition the solution was stirred at reflux for 16 hours. The solution was then cooled with an ice bath and quenched with NaOH (1 M). The resulting slurry was filtered and the washed thoroughly with DCM (150 mL). The organic phase was washed with NaOH (1 M, 2 × 50 mL) and brine (50 mL) before drying over Na_2SO_4. After concentration *in vacuo* the crude oils were purified by column chromatography (1 : 10/1 : 20 MeOH : DCM) to yield the pure diamines.

(*S*)-2-((2-(Mesitylamino)ethyl)amino)-3-methylbutan-1-ol (6a). Following the general procedure (*S*)-N^1-(1-hydroxy-3-methylbutan-2-yl)-N^2-mesityloxalamide (**5a**, 580 mg, 1.98 mmol) gave target product **6a** as a colourless oil in 77% yield (404 mg, 1.52 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.82 (s, 2H, CH_{Ar}), 3.66 (dd, J = 10.6, 4.0 Hz, 1H, CH_2), 3.41 (dd, J = 10.6, 7.3 Hz, 1H, CH_2), 3.00–3.11 (m, 2H, CH_2), 2.90–2.96 (m, 1H, CH_2), 2.80–2.85 (m, H, CH_2), 2.53 (broad s, 3H, 2 × NH + OH), 2.42–2.48 (m, 1H, CH), 2.27 (s, 6H, 2 × CH_3), 2.22 (s, 3H, CH_3), 1.81–1.90 (m, 1H, CH), 0.98 (d, J = 6.9 Hz, CH_3), 0.92 (d, J = 6.8 Hz, CH_3).

(*S*)-2-((2-(Mesitylamino)ethyl)amino)-2-phenylethan-1-ol (6b). Following the general procedure, (*S*)-N^1-(2-hydroxy-1-phenylethyl)-N^2-mesityloxalamide (**5b**, 422 mg, 1.29 mmol) gave target product **6b** as a colourless oil in 62% yield (239 mg, 0.80 mmol). ^{1}H NMR (400 MHz, ($CDCl_3$) δ (ppm) 7.31–7.36 (m, 2H, CH_{Ar}), 7.25–7.29 (m, 3H, CH_{Ar}), 6.80 (s, 2H, CH_{Ar}), 3.77 (dd, J = 8.7, 4.5 Hz, 1H, CH), 3.71 (dd, J = 10.7, 4.4 Hz, 1H, CH_2), 3.56 (dd, J = 10.7, 8.7 Hz, 1H, CH_2), 2.95–30.7 (m, 2H, CH_2), 2.72–2.78 (m, 1H, CH_2), 2.65–2.70 (m, 1H, CH_2), 2.24 (s, 6H, 2 × CH_3), 2.21 (s, 3H, CH_3).

(*S*)-2-((2-(Benzylamino)ethyl)amino)-3-methylbutan-1-ol (6c). Following the general procedure, (*S*)-N^1-benzyl-N^2-(1-hydroxy-3-methylbutan-2-yl)oxalamide (**5c**, 525 mg, 1.89 mmol) gave target product **6c** in 61% yield (287 mg, 1.15 mmol) as a colourless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.31–7.34 (m, 4H, Ar), 7.24–7.26 (m, 1H, Ar), 3.80 (s, 2H, CH_2Ph), 3.61 (dd, J = 10.8, 4.1 Hz, 1H, CH_2OH), 3.33 (dd, J = 10.8, 7.7 Hz, 1H, CH_2OH), 2.81–2.85 (m, 1H, CH_2), 2.69–2.80 (m, 3H, CH_2 + CH_2), 2.35–2.38 (m, 1H, CHNH), 1.73–1.78 (m, 1H, CH), 0.96 (d, J = 6.8 Hz, 3H, CH_3), 0.89 (d, J = 6.8 Hz, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 140.0 (C_{Ar}), 128.5 (CH_{Ar}), 128.2 (CH_{Ar}), 127.1 (CH_{Ar}), 64.5 (CHNH), 61.5 (CH_2OH), 53.8 (CH_2Ph), 49.2 (CH_2), 46.7 (CH_2), 29.5 (CH), 19.5 (CH_3), 18.8 (CH_3). IR $\tilde{\upsilon}$ (cm^{-1}) 3296, 3085, 3062, 2954, 2830, 1494, 1453, 1104, 735.

(*S*)-2-((2-(Benzylamino)ethyl)amino)-2-phenylethan-1-ol (6d). Following the general procedure, (*S*)-N^1-benzyl-N^2-(2-hydroxy-1-phenylethyl)oxalamide (**5d**, 614 mg, 2.06 mmol) gave target product **6d** as a colourless oil in 62% yield (343 mg, 1.27 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.23–7.35 (m, 10H, CH_{Ar}), 3.73–3.75 (m, 2H, $PhCH_2$), 3.69 (dd, J = 10.5, 4.4 Hz, 1H, CH_2), 3.54 (dd, 10.5, 8.7 Hz, 1H, CH_2), 2.59–2.78 (m, 4H, 2 × CH_2). IR $\tilde{\upsilon}$ (cm^{-1}) 3292, 3084, 3060, 2904, 2831, 1493, 1452, 1359, 1124, 101, 746. HRMS (ESI) m/z [M + H^+]: calcd for $C_{17}H_{23}N_2O$ 271.1810, found 271.1815.

(1*S*,2*R*)-1-((2-(Mesitylamino)ethyl)amino)-2,3-dihydro-1*H*-inden-2-ol (6e). Following the general procedure, N^1-((1*S*,2*R*)-2-hydroxy-2,3-dihydro-1*H*-inden-1-yl)-N^2-mesityloxalamide (**5e**, 381 mg, 1.13 mmol) gave target product **6e** in 77% yield (271 mg, 0.87 mmol) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.21–7.27 (m, 4H, CH_{Ar}), 6.82 (s, 2H, CH_{Ar}), 4.66 (m, 1H, CH), 4.09 (d, J = 5.0 Hz, 1H, CH), 3.05–3.14 (m, 4H, 2 × CH_2), 2.95–3.01 (m, 2H, CH_2), 2.28 (s, 6H, 2 × CH_3), 2.22 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 143.1 (C_{Ar}), 142.2 (C_{Ar}), 140.9 (C_{Ar}), 131.6 (C_{Ar}), 129.8 (C_{Ar}), 129.5 (2 × CH_{Ar}), 128.1 (CH_{Ar}), 126.7 (CH_{Ar}), 125.6 (CH_{Ar}), 123.7 (CH_{Ar}), 71.0 (CH), 66.0 (CH), 49.1 (CH_2), 48.5 (CH_2), 39.6 (CH_2), 20.5 (CH_3), 18.3 (2 × CH_3). IR $\tilde{\upsilon}$ (cm^{-1}) 3236, 3068, 2912, 2851, 1483, 1457, 1112, 1077, 1016, 851. HRMS (ESI) m/z [M + H^+]: calcd for $C_{20}H_{27}N_2O$ 311.2123, found 311.2129.

General procedure for synthesis of imidazolium chlorides

To a solution of diamine **6** (1 eq.) in dry THF (2 mL) under N_2-atmosphere was added anhydrous HCl (1.25 M in MeOH, 1 eq.) which lead to immediate precipitation of a white solid. The solvent was evaporated off by N_2-stream. Toluene (1 mL) and trimethyl orthoformate (5 eq.) were added and the suspension was stirred at 90 °C for 16 hours. After cooling to room temperature and concentration *in vacuo* the crude salts were purified by column chromatography (1 : 10 MeOH : DCM) to yield the pure imidazolium chlorides as white solids.

(*S*)-3-(1-Hydroxy-3-methylbutan-2-yl)-1-mesityl-4,5-dihydro-1*H*-imidazol-3-ium chloride (7a). Following the general procedure, (*S*)-2-((2-(mesitylamino)ethyl)amino)-3-methylbutan-1-ol (**6a**, 60.0 mg, 0.227 mmol) gave target product **7a** as a white solid in 90% yield (63.2 mg, 0.203 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.79 (s, 1H, NCHN), 6.93 (s, 2H, CH_{Ar}), 5.82 (dd, J = 9.6, 3.7 Hz, 1H, OH), 4.41–4.49 (m, 1H, CH_2), 4.28–4.36 (m, 1H, CH_2), 4.09–4.16 (m, 1H, CH_2), 3.94–4.08 (m, 3H, CH + CH_2), 3.57–3.65 (m, 1H, CH_2), 2.39 (broad s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.25 (broad s, 3H, CH_3), 1.80–1.89 (m, 1H, CH), 1.05 (d, J = 6.6 Hz, 3H, CH_3), 1.01 (d, J = 6.7 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 160.1 (NCN), 140.3 (C_{Ar}), 130.3 (CH_{Ar}), 130.1 (broad, C_{Ar}), 129.6 (broad, C_{Ar}), 66.9 (CH), 58.6 (CH_2), 50.5 (CH_2), 44.9 (CH_2), 27.7 (CH), 20.9 (CH_3), 20.3 (CH_3), 18.9 (CH_3), 18.0 (broad, CH_3), 17.6 (broad, CH_3). IR $\tilde{\upsilon}$ (cm^{-1}) 3230, 2962, 2876, 1631, 1505, 1484, 1224, 1075, 1029, 640. m.p: 212 °C. HRMS (ESI) m/z [M+]: calcd for $C_{17}H_{27}N_2O$ 275.2123, found 275.2128.

(*S*)-3-(2-Hydroxy-1-phenylethyl)-1-mesityl-4,5-dihydro-1*H*-imidazol-3-ium chloride (7b). Following the general procedure, (*S*)-2-((2-(mesitylamino)ethyl)amino)-2-phenylethan-1-ol (**6b**, 239 mg, 0.801 mmol) gave target product **7b** as a white solid in 87% yield (241 mg, 0.697 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.27 (s, 1H, NCHN), 7.38–7.44 (m, 3H, CH_{Ar}),

7.35–7.36 (m, 2H, CH_{Ar}), 6.91 (s, 2H, CH_{Ar}), 6.19 (dd, J = 9.2, 3.9 Hz, 1H, OH), 5.54 (dd, J = 10.6, 4.2 Hz, 1H, CH), 4.28–4.34 (M, 1H, CH_2), 4.18–4.25 (m, 2H, 2 × CH_2), 4.07–4.11 (m, 1H, CH_2), 4.00–4.04 (m, 1H, CH_2), 3.90–3.95 (m, 1H, CH_2), 2.36 (broad s, 3H, CH_3), 2.30 (broad s, 3H, CH_3), 2.27 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.5 (NCN), 140.3 (C_{Ar}), 135.6 (broad C_{Ar}), 135.1 (broad C_{Ar}), 133.5 (C_{Ar}), 130.5 (C_{Ar}), 130.0 (broad 2 × CH_{Ar}), 129.4 (3 × CH_{Ar}) 127.7 (2 × CH_{Ar}), 63.8 (CH), 59.9 (CH_2), 50.6 (CH_2), 46.4 (CH_2), 21.0 (CH_3), 18.0 (broad 2 × CH_3). IR $\tilde{\upsilon}$ (cm^{-1}) 3221, 3032, 2920, 1628, 1483, 1379, 2276, 1138, 648. M.p: 239 °C HRMS (ESI) m/z [M+]: calcd for $C_{20}H_{25}N_2O$ 309.1967, found 309.1972.

(*S*)-1-Benzyl-3-(1-hydroxy-3-methylbutan-2-yl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (7c). Following the general procedure, (*S*)-2-((2-(benzylamino)ethyl)amino)-3-methylbutan-1-ol (**6c**, 98.0 mg, 0.415 mmol), gave target product **7c** in 71% yield (83.2 mg, 294 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.49 (s, 1H, NCHN), 7.33–7.40 (m, 5H, Ar), 5.81 (broad s, 1H, OH), 4.96 (d, J = 14.7 Hz, 1H, CH_2Ph), 4.72 (d, J = 14.7 Hz, 1H, CH_2Ph), 4.10–4.21 (m, 1H, CH_2), 3.94–4.01 (m, 1H, CH_2), 3.67–3.87 (m, 4H, CH_2 + CH_2OH), 3.56–3.62 (m, 1H, NCH), 1.78–1.90 (m, 1H, CH), 0.98 (d, J = 6.6 Hz, CH), 0.97 (d, J = 6.7 Hz, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.1 (NCN), 132.8 (C_{Ar}), 129.1 (CH_{Ar}), 128.7 (CH_{Ar}), 128.6 (CH_{Ar}), 67.3 (NCH), 58.6 ($PhCH_2$), 52.1 (CH_2OH), 47.4 (CH_2), 45.7 (CH_2), 27.5 (CH), 20.1 (CH_3), 19.1 (CH_3). IR $\tilde{\upsilon}$ (cm^{-1}) 3341, 3060, 2965, 1643, 1513, 1205, 635. M.p 125 °C.

(*S*)-1-Benzyl-3-(2-hydroxy-1-phenylethyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (7d). Following the general procedure, (*S*)-2-((2-(benzylamino)ethyl)amino)-2-phenylethan-1-ol (**6d**,) gave target product **7d** in 49% yield (143 mg, 0.450 mmol) as a pale yellow waxy solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.05 (s, 1H, NCHN), 7.30–7.42 (m, 10H, CH_{Ar}), 6.21 (broad s, 1H, OH), 5.06 (dd, J = 10.2, 3.7 Hz, 1H, PhCH), 5.00 (d, J = 14.8 Hz, 1H, $PhCH_2$), 4.75 (d, J = 14.8 Hz, 1H, $PhCH_2$), 4.33 (dd, J = 12.6, 10.3 Hz, 1H, CH_2OH), 3.93–4.01 (m, 2H, NCH_2 + CH_2OH), 3.82–3.90 (m, 1H, NCH_2), 3.58–3.75 (m, 2H, NCH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 158.3 (NCN), 133.7 (C_{Ar}), 132.5 (C_{Ar}), 129.2 (2 × CH_{Ar}), 129.1 (2 × CH_{Ar}), 128.9 (2 × CH_{Ar}), 128.8 (2 × CH_{Ar}), 127.5 (2 × CH_{Ar}), 64.5 (Ph*C*H), 60.7 (Ph*C*H_2), 52.4 (CH_2OH), 47.2 (CH_2), 46.5 (CH_2). IR $\tilde{\upsilon}$ (cm^{-1}) 3247, 3032, 2927, 1638, 1512, 1496, 1205, 702. HRMS (ESI) m/z [M+]: calcd for $C_{18}H_{21}N_2O$ 281.1654, found 281.1659.

3-((1*S*,2*R*)-2-Hydroxy-2,3-dihydro-1*H*-inden-1-yl)-1-mesityl-4,5-dihydro-1*H*-imidazol-3-ium chloride (7e). Following the general procedure, (1*S*,2*R*)-1-((2-(mesitylamino)ethyl)amino)-2,3-dihydro-1*H*-inden-2-ol (**6e**, 136 mg, 0.438 mmol) gave target product **7e** in 87% yield (130 mg, 0.381 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.65 (s, 1H, NCHN), 7.28–7.39 (m, 4H, CH_{Ar}), 6.92 (broad s, 2H, CH_{Ar}), 6.57 (broad d, J = 4.2 Hz, 1H, OH), 5.41 (d, J = 6.2 Hz, 1H, NCH), 5.02–5.07 (broad m, 1H, CHOH), 4.28–4.41 (m, 2H, 2 × CH_2), 4.03–4.16 (m, 2H, 2 × CH_2), 3.32 (dd, J = 17.0, 7.2 Hz, 1H, $PhCH_2$), 3.04 (dd, J = 16.8, 5.9 Hz, 1H, $PhCH_2$), 2.36 (broad s, 6H, 2 × CH_3), 2.28 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.3 (NCN), 142.4 (C_{Ar}), 140.4 (C_{Ar}), 135.7 (C_{Ar}), 130.0 (CH_{Ar}), 129.9 (2 × CH_{Ar}), 127.6 (CH_{Ar}), 126.1 (CH_{Ar}), 125.1 (CH_{Ar}), 70.7 (CHOH), 65.5 (PhCH), 50.8 (CH_2), 49.0 (CH_2), 38.9 ($PhCH_2$), 20.9 (CH_3), 17.9 (2 × CH_3). IR $\tilde{\upsilon}$ (cm^{-1}) 3201, 2950, 2918, 1631, 1482, 1252, 1055, 664. M.p: 255 °C (decomp.). HRMS (ESI) m/z [M+]: calcd for $C_{21}H_{23}N_2O$ 321.1967 found 319.1973

General procedure for the synthesis of gold(I) NHC complexes

To a solution of imidazolium chloride **7** (1 eq.) in DCM (2 mL) was added Me_2SAuCl (1 eq.) and stirred for 10 minutes. K_2CO_3 (10 eq.) and water (2 mL) were then added. The mixture was then stirred vigorously for 2–7 hours. After completion of the reaction, DCM (15 mL) and water (15 mL) were added and the phases separated. The organic phase was then washed with brine (15 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The crude complexes were purified by filtering through a short silica plug (EtOAc) giving the gold(I) NHC complexes as white crystalline solids.

(*S*)-(1-(1-Hydroxy-3-methylbutan-2-yl)-3-mesitylimidazolidin-2-ylidene)gold(I) chloride (8a). Following the general procedure, (*S*)-3-(1-hydroxy-3-methylbutan-2-yl)-1-mesityl-4,5-dihydro-1*H*-imidazol-3-ium chloride (**7a**, 37.0 mg, 0.119 mmol), Me_2SAuCl (35.1 mg, 0.119 mmol) and K_2CO_3 (164 mg, 1.19 mmol) gave target gold(I) NHC complex **8a** as a white, crystalline solid in 92% yield (55.5 mg, 0.109 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.90(s, 2H, Ar), 4.28–4.33 (m, 1H, CH), 4.00 (dd, J = 11.8, 3.8 Hz, 1H, CH_2OH), 3.93–3.99 (m, 1H, CH_2), 3.69–3.84 (m, 4H, CH_2OH + CH_2), 2.28 (s, 3H, CH_3), 2.21 (s, 6H, 2 × CH_3), 1.99–2.08 (m, 1H, CH), 1.05 (d, J = 6.6 Hz, 3H, CH_3), 1.04 (d, J = 6.6 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 193.8 (CAu), 138.6 (C_{Ar}), 135.8 (C_{Ar}), 135.5 (C_{Ar}), 134.9 (C_{Ar}), 129.6 (CH_{Ar}), 129.6 (CH_{Ar}), 67.6 (CH), 61.7 (CH_2OH), 50.1 (CH_2), 45.2 (CH_2), 27.0 (CH), 21.0 (CH_3Ar), 21.0 (CH_3), 20.2 (CH_3), 17.9 (CH_3Ar), 17.9 (CH_3Ar). M.p. 209 °C (decomp). HRMS (ESI) m/z [M + $-Cl^-$ + CH_3CN] calcd for $C_{19}H_{29}AuN_3O$ 512.1976, found 512.1976.

(1-((*S*)-2-Hydroxy-1-phenylethyl)-3-mesitylimidazolidin-2-yl) gold(I) chloride (8b). Following the general procedure, (*S*)-3-(2-hydroxy-1-phenylethyl)-1-mesityl-4,5-dihydro-1*H*-imidazol-3-ium chloride (**7b**, 33.1 mg, 0.096 mmol), Me_2SAuCl (28.3 mg, 0.096 mmol) and K_2CO_3 (133 mg, 0.96 mmol) gave target gold(I) NHC complex **8b** as a white, crystalline solid in 91% yield (47.2 mg, 0.087 mmol). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.40–7.42 (m, 4H, Ar), 7.37–7.39 (m, 1H, Ar), 6.91 (s, 1H, Ar), 6.90 (s, 1H, Ar), 5.94 (dd, J = 8.8, 5.4 Hz, 1H, CH), 4.25–4.33 (m, 2H, CH_2OH), 3.88–3.94 (m, 1H, CH_2), 3.78–3.83 (m, 1H, CH_2), 3.67–3.72 (m, 1H, CH_2), 3.50–3.55 (m, 1H, CH_2), 2.29 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.07–2.09 (broad m, 1H, OH). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 194.1 (CAu), 138.9 (C_{Ar}), 135.9 (C_{Ar}), 135.5 (C_{Ar}), 135.2 (C_{Ar}), 134.9 (C_{Ar}), 129.7 (CH_{Ar}), 129.7 (CH_{Ar}), 129.2 (CH_{Ar}), 128.7 (CH_{Ar}), 127.4 (CH_{Ar}), 64.0 (CH), 61.1 (CH_2OH), 50.5 (CH_2), 44.7 (CH_2), 21.0 (CH_3), 18.1 (CH_3), 18.0 (CH_3). IR (cm^{-1}) 3455, 3028, 2917, 2885, 1607, 1497, 1452, 1233, 1088, 1040, 854. M.p 175 °C (decomp.) HRMS (ESI) m/z [M + $-Cl^-$ + CH_3CN] calcd for $C_{22}H_{27}AuN_3O$ 546.1820, found 546.1826. CCDC ID: 2056825.†

(1-Benzyl-3-((*S*)-1-hydroxy-3-methylbutan-2-yl)imidazolidin-2-yl)gold(I) chloride (8c). Following the general procedure, (*S*)-1-benzyl-3-(1-hydroxy-3-methylbutan-2-yl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (**7c**, 39.3 mg, 0.139 mmol), Me_2SAuCl (40.9 mg, 0.139 mmol) and K_2CO_3 (192 mg, 1.39 mmol) gave target gold(I) NHC complex **8c** as a white, crystalline solid in 50% yield (33.5 mg, 0.0700 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31–7.38 (m, 5H, CH_{Ar}), 4.95 (d, J = 15.0 Hz, 1H, CH_2Ph), 4.79 (d, J = 15.0 Hz, 1H, CH_2Ph), 4.22–4.27 (m, 1H, CH), 3.95–3.98 (m, 1H, CH_2OH), 3.77–3.80 (m, 1H, CH_2OH), 3.71–3.77 (m, 1H, CH_2), 3.41–3.57 (m, 3H, CH_2), 1.91–2.00 (m, 1H, CH), 1.79 (broad s, 1H, OH), 1.01 (d, J = 6.7 Hz, 3H, CH_3), 0.99 (d, J = 6.7 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 193.0 (CAu), 134.9 (C_{Ar}), 129.0 (CH_{Ar}), 128.3 (CH_{Ar}), 127.9 (CH_{Ar}), 67.9 (CH), 61.8 (CH_2OH), 55.0 (CH_2Ph), 47.4 (CH_2), 45.3 (CH_2), 27.3 (CH), 20.3 (CH_3), 19.5 (CH_3). M.p 126 °C (Decomp.).

(1-Benzyl-3-((*S*)-2-hydroxy-1-phenylethyl)imidazolidin-2-yl)gold(I) chloride (8d). Following the general procedure, (*S*)-1-benzyl-3-(2-hydroxy-1-phenylethyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (**7d**, 29.0 mg, 0.092 mmol), Me_2SAuCl (27.1 mg, 0.092 mmol) and K_2CO_3 (130 mg, 0.92 mmol) gave target gold(I) NHC complex **8d** as a white, crystalline solid in 56% yield (26.4 mg, 0.052 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31–7.39 (m, 10H, Ar), 5.87 (dd, J = 8.9, 5.2 Hz, 1H, CH), 5.0 (d, J = 14.9 Hz, 1H, CH_2Ph), 4.74 (d, J = 14.8 Hz, 1H, CH_2Ph), 4.26–4.32 (m, 1H, CH_2OH), 4.17–4.22 (m, 1H, CH_2OH), 3.69–3.77 (m, 1H, CH_2), 3.53–3.60 (m, 1H, CH_2), 3.25–3.43 (m, 2H, CH_2), 2.58–2.61 (broad m, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 192.7 (CAu), 135.2 (C_{Ar}), 134.7 (C_{Ar}), 129.1 (CH_{Ar}), 128.9 (CH_{Ar}), 128.6 (CH_{Ar}), 128.3 (CH_{Ar}), 128.1 (CH_{Ar}), 127.5 (CH_{Ar}), 64.5 (CH), 61.2 (CH_2OH), 55.1 (CH_2Ph), 47.8 (CH_2), 44.7 (CH_2). IR (cm^{-1}) 3450, 3060, 3028, 2926, 2883, 1726, 1494, 1239, 1191, 700. HRMS (ESI) m/z [M + $-Cl^-$ + CH_3CN] calcd for $C_{20}H_{23}AuN_3O$: 518.1507, found 518.1514. M.p 145 °C (decomp). CCDC ID: 2056945.†

(1-((1*S*,2*R*)-2-Hydroxy-2,3-dihydro-1*H*-inden-1-yl)-3-mesitylimidazolidin-2-yl)gold(I) chloride (8e). Following the general procedure, (3-((1*S*,2*R*)-2-hydroxy-2,3-dihydro-1*H*-inden-1-yl)-1-mesityl-4,5-dihydro-1*H*-imidazol-3-ium chloride (**7e**, 21.6 mg, 0.061 mmol), Me_2SAuCl (17.8 mg, 0.061 mmol) and K_2CO_3 (84 mg, 0.605 mmol) gave target gold(I) NHC complex **8e** as a white, crystalline solid in 69% yield (23.2 mg, 0.042 mmol). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.30–7.38 (m, 4H, Ar), 6.92 (s, 1H, Ar), 6.91 (s, 1H, Ar), 6.10 (d, J = 6.9 Hz, 1H, NCH), 4.91–4.95 (m, 1H, CHOH), 3.67–3.85 (m, 3H, CH_2), 3.42–3.48 (m, 1H, CH_2), 3.37 (dd, J = 16.2, 7.8 Hz, 1H, CH_2), 2.96 (dd, J = 16.3, 6.2 Hz, 1H, CH_2), 2.29 (s, 3H, CH_3), 2.26 (s, 6H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 194.2 (CAu), 140.6 (C_{Ar}), 138.9 (C_{Ar}), 136.6 (C_{Ar}), 135.8 (C_{Ar}), 135.4 (C_{Ar}), 134.9 (C_{Ar}), 129.7 (CH_{Ar}), 129.7 (CH_{Ar}), 129.6 (CH_{Ar}), 127.7 (CH_{Ar}), 125.8 (CH_{Ar}), 125.6 (CH_{Ar}), 73.0 (CHOH), 66.2 (CHN), 50.7 (CH_2), 47.1 (CH_2), 40.1 (CH_2), 21.1 (CH_3), 18.0 (CH_3), 18.0 (CH_3). IR (cm^{-1}) 3440, 2919, 1659, 1499, 1456, 1271, 1151, 1088, 818. M.p 155 °C (decomp.) HRMS (ESI) m/z [M + Cl^-] calcd for $C_{21}H_{24}AuCl_2N_2O$ 587.0931, found 587.0937. CCDC ID: 2056827.†

General procedure for the synthesis of gold(III) NHC complexes

To a solution of gold(I) NHC complex **8** in DCM (2 mL) was added dichloro iodobenzene ($PhICl_2$, 1.1 eq.) and the solution stirred for 15–60 minutes after which the solvent was evaporated. The solid residue was washed with pentane (3 × 5 mL) and then further purified by column chromatography (EtOAc/pentane) to yield the pure gold(III) NHC complexes as yellow, crystalline solids.

(1-((*S*)-1-Hydroxy-3-methylbutan-2-yl)-3-mesitylimidazolidin-2-yl)gold(III) chloride (9a). Following the general procedure, (*S*)-(1-(1-hydroxy-3-methylbutan-2-yl)-3-mesitylimidazolidin-2-ylidene)gold(I) chloride (**8a**, 31.2 mg, 0.0616 mmol) and $PhICl_2$ (18.6 mg, 0.0677 mmol) gave target gold(III) NHC complex **9a** as a yellow crystalline solid in 91% yield (32.5 mg, 0.0560 mmol). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 6.95 (s, 1H, Ar), 6.94 (s, 1H, Ar), 4.25–4.29 (m, 1H, CH), 4.19–4.23 (m, 2H, CH_2 + CH_2OH), 4.06–4.11 (m, 2H, CH_2), 3.97–4.01 (m, 2H, CH_2), 3.73 (dd, J = 12.4, 8.6 Hz, 1H, CH_2OH), 2.39 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 1.99–2.04 (m, 1H, CH), 1.16 (d, J = 6.9 Hz, 3H, CH_3), 1.07 (d, J = 6.7 Hz, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 170.3 (CAu), 140.3 (C_{Ar}), 136.4 (C_{Ar}), 136.3 (C_{Ar}), 131.6 (C_{Ar}), 130.2 (CH_{Ar}), 67.0 (CH), 61.6 (CH_2OH), 51.8 (CH_2), 45.9 (CH_2), 28.2 (CH), 21.1 (CH_3Ar), 20.9 (CH_3), 19.1 (CH_3), 18.8 (CH_3Ar), 18.6 (CH_3Ar). IR (cm^{-1}) 3504, 2965, 2925, 1537, 1462, 1307, 1069, 855. HRMS (ESI) m/z [M + $-Cl^-$] calcd for $C_{17}H_{26}AuCl_2N_2O$ 541.1088, found 541.1093. M.p 210 °C (decomp). CCDC ID: 2056823.†

(1-((*S*)-2-Hydroxy-1-phenylethyl)-3-mesitylimidazolidin-2-yl)gold(III) chloride (9b). Following the general procedure, (1-((*S*)-2-hydroxy-1-phenylethyl)-3-mesitylimidazolidin-2-yl)gold(I) chloride (**8b**, 31.4 mg, 0.0581 mmol) and $PhICl_2$ (17.6 mg, 0.0639 mmol) gave target gold(III) NHC complex **9b** as a yellow crystalline solid in 53% yield (18.9 mg, 0.0309 mmol). ^{1}H NMR (400 MHz, CD_3CN) δ (ppm) 7.57–7.60 (m, 2H, Ar), 7.39–7.49 (m, 3H, Ar), 7.03 (s, 1H, Ar), 7.02 (s, 1H, Ar), 5.69 (t, J = 6.4 Hz, 1H, CH), 4.18–4.25 (m, 3H, CH_2 + CH_2OH), 3.99–4.14 (m, 2H, CH_2), 3.79–3.87 (m, 1H, CH_2), 3.29 (t, J = 6.0 Hz, 1H, OH), 2.41 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.31 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CD_3CN) δ (ppm) 169.3 (CAu), 141.1 (C_{Ar}), 138.1 (C_{Ar}), 137.8 (C_{Ar}), 135.5 (C_{Ar}), 133.4 (C_{Ar}), 130.7 (CH_{Ar}), 130.7 (CH_{Ar}), 129.9 (CH_{Ar}), 129.7 (CH_{Ar}), 129.4 (CH_{Ar}), 65.0 (CH), 61.9 (CH_2OH), 52.8 (CH_2), 48.1 (CH_2), 21.1 (CH_3), 19.1 (CH_3), 19.0 (CH_3). IR (cm^{-1}) 3512, 2947, 1537, 1496, 1461, 1314, 1173, 1139, 1081, 1068, 854, 691. M.p 184 °C (decomp). CCDC ID: 2056946.†

(1-Benzyl-3-((*S*)-1-hydroxy-3-methylbutan-2-yl)imidazolidin-2-yl)gold(III) chloride (9c). Following the general procedure, ((1-benzyl-3-((*S*)-1-hydroxy-3-methylbutan-2-yl)imidazolidin-2-yl) gold(I) chloride (**8c**, 17.1 mg, 0.0357 mmol) and $PhICl_2$ (10.8 mg, 0.0393 mmol) gave target gold(III) NHC complex **9c** as a yellow crystalline solid in 89% yield (17.5 mg, 0.0318 mmol). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.38–7.41 (m, 5H, Ar), 5.05 (d, J = 14.8 Hz, 1H, CH_2Ph), 4.83 (d, J = 14.8 Hz, 1H, CH_2Ph), 4.11–4.15 (m, 2H, NCH + CH_2OH), 4.00–4.05 (m, 1H, CH_2), 3.79–3.81 (m, 1H, CH_2), 3.66–3.73 (m, 3H, CH_2OH + CH_2), 2.09 (broad s, 1H, OH), 1.94–2.00 (m, 1H, CH),

1.09 (d, J = 6.8 Hz, 3H, CH_3), 1.04 (d, J = 6.7 Hz, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 168.9 (CAu), 132.2 (C_{Ar}), 129.3 (C_{Ar}), 129.2 (C_{Ar}), 128.7 (C_{Ar}), 67.2 (CH), 61.7 (CH_2OH), 54.4 (CH_2), 48.5 (CH_2), 46.0 (CH_2), 27.9 (CH), 20.8 (CH_3), 19.1 (CH_3). IR (cm^{-1}) 3530, 2962, 2931, 1560, 1497, 1454, 1360, 1286, 1077, 928. HRMS (ESI) m/z [M + $-Cl^-$ + CH_3CN] $C_{17}H_{25}N_3OCl_2Au$ 554.1040, found 554.1041. m.p (185 °C (decomp.).

(1-Benzyl-3-((*S*)-2-hydroxy-1-phenylethyl)imidazolidin-2-yl) gold(III) chloride (9d). Following the general procedure (1-benzyl-3-((*S*)-2-hydroxy-1-phenylethyl)imidazolidin-2-yl)gold(I) chloride (**8d**, 35.9 mg, 0.070 mmol) and $PhICl_2$ (21.2 mg, 0.077 mmol) gave target gold(III) NHC complex **9d** as a yellow crystalline solid in 96% yield (39.3 mg, 0.067 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.48–750 (m, 2H, Ar), 7.40–7.44 (m, 8H, Ar), 5.72 (dd, J = 8.0, 5.4 Hz, 1H, NCH), 4.96 (d, J = 15.0 Hz, 1H, CH_2Ph), 4.91 (d, J = 15.0 Hz, 1H, CH_2Ph), 4.21–4.33 (m, 2H, CH_2OH), 3.98–4.07 (m, 1H, CH_2), 3.71–3.77 (m, 1H, CH_2), 3.51–3.64 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.5 (CAu), 132.9 (C_{Ar}), 132.1 (C_{Ar}), 129.4 (CH_{Ar}), 129.3 (CH_{Ar}), 129.2 (CH_{Ar}), 129.2 (CH_{Ar}), 128.8 (CH_{Ar}), 128.0 (CH_{Ar}), 63.7 (CH), 61.1 (CH_2), 54.5 (CH_2), 48.6 (CH_2), 45.9 (CH_2). IR (cm^{-1}) 3507, 3061, 3031, 2945, 2890, 1585, 1555, 1356, 648. M.p 183 °C (decomp.).

(1-((1*S*,2*R*)-2-Hydroxy-2,3-dihydro-1*H*-inden-1-yl)-3-mesityl-imidazolidin-2-yl)gold(III) chloride (9e). Following the general procedure, (1-((1*S*,2*R*)-2-hydroxy-2,3-dihydro-1*H*-inden-1-yl)-3-mesitylimidazolidin-2-yl)gold(I) chloride (**8e**, 33.6 mg, 0.061 mmol) and $PhICl_2$ (18.4 mg, 0.067 mmol) gave target gold(III) NHC complex **9e** as a yellow crystalline solid in 69% yield (26.1 mg, 0.042 mmol). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.51 (d, J = 7.5 Hz, 1H, Ar), 7.40 (t, J = 7.4 Hz, 1H, Ar), 7.36 (t, J = 7.4 Hz, 1H, Ar), 7.32 (d, J = 7.5 Hz, 1H, Ar), 6.95 (s, 2H, Ar), 6.08 (d, J = 7.5 Hz, 1H, NCH), 5.02 (qd, J = 7.9, 2.8 Hz, 1H, CHOH), 3.92–4.06 (m, 3H, CH_2), 3.52–3.59 (m, 1H, CH_2), 3.49 (dd, J = 16.7, 8.2 Hz, 1H, CH_2), 3.15 (d, J = 3.0 Hz, 1H, OH), 3.00 (dd, J = 16.7, 7.6 Hz, 1H, CH_2), 2.40 (s, 6H, CH_3), 2.31 (s, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 169.7 (CAu), 141.0 (C_{Ar}), 140.5 (C_{Ar}), 136.5 (C_{Ar}), 136.4 (C_{Ar}), 134.9 (C_{Ar}), 131.5 (CH_{Ar}), 130.7 (CH_{Ar}), 130.4 (CH_{Ar}), 130.4 (CH_{Ar}), 128.4 (CH_{Ar}), 126.8 (CH_{Ar}), 125.7 (CH_{Ar}), 71.6 (CHOH), 66.0 (CHN), 52.2 (CH_2), 47.9 (CH_2), 39.8 (CH_2), 21.2 (CH_3), 18.9 (CH_3), 18.8 (CH_3). IR (cm^{-1}) 3509, 2922, 1607, 1536, 1494, 1217, 1189, 735. HRMS (ESI) m/z [M + $-Cl^-$] calcd for $C_{21}H_{24}AuCl_2N_2O$ 587.0931, found 587.0937. M.p 189 °C (decomp). CCDC ID: 2056822.†

General procedure for gold catalyzed alkoxycyclisation reactions

Dimethyl(*E*)-2-(prop-2-yn-1-yl)-2-styrylmalonate (28.6 mg, 0.1 mmol) and gold catalyst (**8**, **9**; 5 mol%) were dissolved in 2 mL MeOH. $AgSbF_6$ (5–15 mol%) was added and the solution stirred for 15 min. The formed precipitate was filtered off on Celite and the reaction mixture stirred until completion of the reaction. The solvent was removed *in vacuo* and the crude mixture was purified by column chromatography (20 : 1 pentane : EtOAc) to give products **13** and **14**. Results are summarized in Table 2.

Dimethyl 3-(methoxy(phenyl)methyl)-4-methylenecyclopentane-1,1-dicarboxylate (13). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.23–7.33 (m, 5H, CH_{Ar}), 4.91 (q, J = 1.6 Hz, =CH_2), 4.50 (m, 1H, =CH_2), 4.14 (d, J = 5.9 Hz, 1H, CH), 3.71 (s, 3H, CH_3), 3.65 (s, 3H, CH_3), 3.18 (s, 3H, CH_3), 2.93–3.00 (m, 1H, CH), 2.85–2.90 (m, 2H, CH_2), 2.41 (ddd, J = 13.3, 8.1, 1.4 Hz, 1H, CH), 2.31 (dd, J = 13.4, 9.0 Hz, 1H, CH_2). ^{1}H NMR corresponds to previously reported data.[59]

Dimethyl 4-(methoxy(phenyl)methyl)-3-methylcyclopent-2-ene-1,1-dicarboxylate (14). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.27–7.37 (m, 5H, CH_{Ar}), 5.58–5.59 (m, 1H, =CH), 4.31 (d, J = 4.4 Hz, 1H, CH), 3.75 (s, 3H, CH_3), 3.66 (s, 3H, CH_3), 3.23 (s, 3H, CH_3), 2.92–2.96 (m, 1H, CH), 2.55 (dd, J = 13.6, 7.1 Hz, 1H, CH_2), 2.32 (dd, J = 13.7, 8.3 Hz, 1H, CH_2), 1.67 (m, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.0 (C=O), 146.2 (C=C), 140.7 (C_{Ar}), 128.4 (CH_{Ar}), 127.5 (CH_{Ar}), 126.8 (CH_{Ar}), 124.9 (C=CH), 82.4 (CH), 57.0 (CH_3), 54.7 (CH), 52.6 (CH_3), 52.5 (CH_3), 33.2 (CH_2), 15.3 (CH_3). IR (cm^{-1}) 2952, 2824, 1731, 1492, 1166, 1025. HRMS (ESI) m/z [M + $-Cl^-$] calcd for $C_{18}H_{22}O_5Na$ 341.1365, found 341.1370.

Conflicts of interest

There are no conflicts to declare.

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