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In situ detection of an unstable *C,N*-Au(III) chelate by ^{15}N NMR methods

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ABSTRACT

Au(III)-NHC-oxazolyl complexes are prepared by oxidation and anion exchange of the corresponding Au(I)Cl-NHC-oxazolyl precursors, which are synthesized from appropriate imidazolium pre-ligands. As the Au(III) complexes are too unstable for proper isolation and spectroscopic characterization, selective ^{15}N NMR techniques provide valuable knowledge of *N*-coordination to gold by formation of *N*-ligated Au(III) complexes. The changes in ^{15}N-shift values ($\Delta\delta^{15}$N), observed by ^{1}H,^{15}N-HMBC 2D NMR studies, going from Au(I)Cl, via Au(III)Cl_3 to the *C,N*-Au(III) NHC-oxazolyl complexes, afford important information of the oxidation and the anion exchange processes. In particular, the huge up-field shift of the oxazoline-N by anion exchange ($\Delta\delta^{15}N_{AE}$: −71.3 ppm), represents significant evidence that oxazoline-*N*-coordination to Au(III) takes place by anion exchange, and, hence, that the target six-membered bidentate *C,N*-Au(III)-NHC-oxazoline chelated complex is formed.

Introduction

Homogeneous gold catalysis has emerged as a powerful tool in the last two decades to promote a great variety of organic scaffolds from unsaturated substrates. A broad review on the status of gold chemistry has lately been published as a thematic issue edited by Hashmi [1]. 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. However, the last years have witnessed a revival of gold (III) chemistry. The development of gold(III) complexes and the applications of gold(III) in synthesis and catalysis, including mechanistic aspects, have recently been summarized [2]. The interest toward the synthesis of chiral gold(III) complexes is also steadily growing. The progress achieved in the synthesis of well-defined chiral gold(III) complexes has lately been summarized [3].

We have previously reported studies on the Au(III) coordination ability of different polydentate nitrogen-based ligands, such as pyridines, oxazolines and amines, to give a variety of polydentate *N,N, N,O* [4–7], *P,N* [8], *N,N,O* [9] and *N,N,N,N* [10] Au(III) complexes (**I-VI,** Scheme 1). We prepared chiral Au(III) catalysts, based on bis-oxazoline (BOX) and 2-pyridyl-(–)menthol ligands [4]. and showed that the *N,N*-BOX-Au(III) **I** and N,O-Au(III)-pyr-alcohol **II** complexes represent an interesting group of Au(III) catalysts with specific and unique catalytic properties. Our experimental and theoretical studies on Au(III) bidentate coordination of a series of pyridine-oxazoline and quinoline-oxazoline based ligands, concluded that the superior activity of the *N,N*-Au(III)-pyridine-oxazolyl complexes **III** indicate that de-coordination of the pyridine-*N* ligand is a crucial step for efficient generation of catalytic activity [5]. Further mechanistic studies of Au(III)-bidentate pyridine-oxazoline mediated alkoxycyclization, based on combined NMR, X-ray and computational (DFT) investigations, demonstrated that substrate alkyne-coordination to the *N,N*-Au(III) active catalyst involves de-coordination of the pyridine nitrogen as the rate- limiting step [6]. In our recent endeavors to prepare *N,N,O*-chelating Au(III) complexes **IV** [9], we synthesized 2-pyridyl-6-alkylpyridine alcohol ligands. The Au (III) coordination ability depended on the pyridine 2,6-substituents, but successful coordination afforded novel chiral *N,N,O*-tridentate Au(III) complexes with the 2-pyridyl-6-neomenthol-1-yl-pyridine ligand. We also attempted to prepared chiral alcohol functionalised Au(III)-NHC complexes. However, several approaches failed to generate bidentate *C,O*-Au(III)-NHC-alcohol complexes [11] from the alcohol functionalized Au(III)-NHC structures. Inspired by our successful synthesis of *P,N*-Au(III)-phosphine-oxazoline complexes **V** [8], as well as the efficient coordination affinity of oxazoline-nitrogen to generate *N,N*-Au(III)-bis-heterocyclic structures, we therefore sought to synthesise oxazoline functionalized Au(III)-NHC complexes.

We have lately also continued our investigations on Au(III) bidentate complexes by synthesis of novel Au(III)-NHC-*N*-(2-naphthamide) complexes (**VII**, Scheme 1) [12], which represent an interesting group of gold catalysts. Complexes **VII** failed to give *C,N*-bidentate Au(III)-NHC-amide structures **VII'** by silver salt treatment ($AgSbF_6$). By replacing the *N*-naphtamide moiety in complex **VII** with an *N*-oxazolyl group, the

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corresponding *C,N*-bidentate gold-NHC-oxazolyl complexes (**7,** Scheme 1) could be formed. Similar NHC-oxazolyl ligands have been prepared for a) Ir [13] and b) Pt coordination studies [14]. The corresponding NHC-oxazoline ligands used for Ir coordination [13] were *N*-Me/iPr imidazolium derivatives, while the ligands in the Pt complexes [14] contained a more bulky CMe_2 one-carbon bridge between the heterocyclic imidazole and oxazoline units. Successful formation of both the respective six-membered *C,N*-bidentate Ir(II) and Pt(II) NHC-oxazoline complexes was reported.

The *N*-Bn modified imidazolium-*N*-oxazoline preligands (**4**, Scheme 2) are not previously reported. In the present study. we were aiming to utilize such structures to enable formation of bidentate *C,N*-gold complexes (**7**) with both NHC and oxazoline coordination sites. The preparation of Au(I)Cl-NHC-oxazolyl complexes (**5**) from pre-ligands (**4**) and Au(III)-NHC-oxazolyl complexes (**6**, **7**), by subsequent oxidation and anion exchange, is hereby described (Scheme 2).

Results and discussion

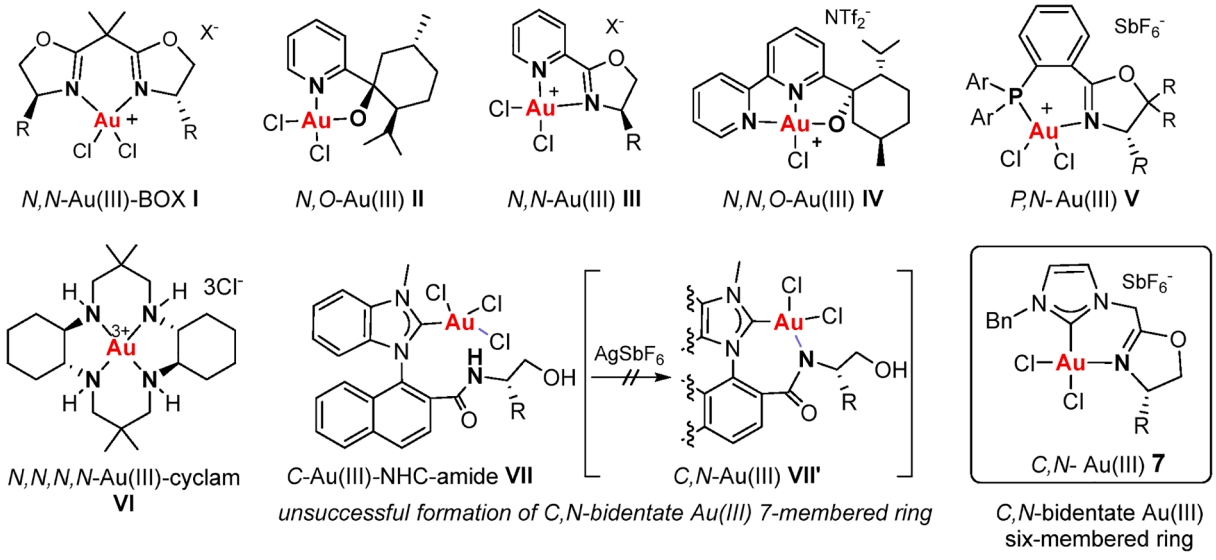
Preparation of gold-NHC-oxazolyl complexes (5–7)

The imidazolium pre-ligands (**4a,b**, Scheme 2), connected to an oxazole unit by a one-carbon CH_2 bridge, were readily synthesized in three steps (overall yields ≈ 20%). The chiral *N*-(2-hydroxyethyl)-2-chloroacetamide condensation products **2a,b** (37–52%, Scheme 2-i), prepared from the respective chiral amino alcohols (**1**, R = *i*Pr and *t*Bu) and 2-chloroacetyl chloride, were subjected to intramolecular cyclodehydration facilitated by Burgess reagent (1-methoxy-N-triethylammoniosulfonyl-methanimidate) [15,16], to give chloromethyl oxazole products **3a,b** (76–80%, Scheme 2-ii). Subsequent halogen (Cl/I) exchange, utilizing the Finkelstein protocol [17], and final *N*-alkylation with *N*-benzyl imidazole afforded target oxazolyl-imidazolium salts **4a,b** (50–77%, Scheme 2-iii).

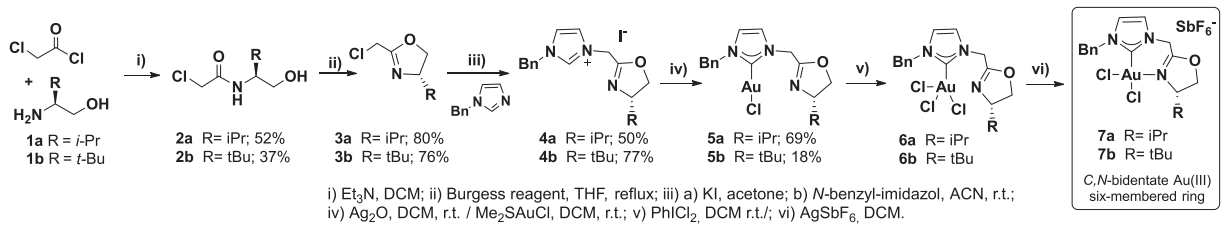
Coordination of the NHC-oxazolyl pre-ligands **4a,b** to gold(I) by transmetallation via a silver intermediate [18] (Ag_2O, $Me_2SAu(I)Cl$) yielded the novel Au(I)-NHC-oxazolyl complexes (**5a,b** Scheme 2-iv), which were characterized by NMR and HRMS. The low yield of the Au(I)-NHC-complex **5b** (*t*Bu, 18%) indicates that Au(I)-complex formation is more restricted by the bulky *t*Bu ligand [19] relative to the *i*Pr-substituted complex **5a** (69%), as also seen for Ir-NHC complexes [13]. The more sterically demanding effect of the *t*Bu substituent was also demonstrated by the observation of diastereotopic ^{1}H NMR CH_2-OH signals for *t*Bu-amide **2b** with restricted rotation, in contrast to the *i*Pr-amide **2a**.

Our previous attempts to generate potential *C,N*-bidentate seven-membered metallacycles **VII'** [12] by anion exchange ($AgSbF_6$) of Au(III) complexes **VII,** based on the NHC-*N*-1-(2-naphthamide) ligand framework, were unsuccessful (Scheme 1). In contrast, the Au(III) complexes **6a,b** could possibly allow formation of favored six-membered *C,N*-bidentate Au(III) chelate rings, similar to the analogous Ir [13] and Pt [14] metallacycles. Hence, the novel Au(I)-NHC-oxazolyl complexes (**5a,b**) were oxidized with dichloro-iodobenzene [20] and subsequently treated with $AgSbF_6$ for anion exchange of the Au(III)Cl_3-NHC complexes **6a,b**, in order to obtain the corresponding Au(III)-NHC-oxazolyl[SbF_6] complexes (**7a,b**, Scheme 2-v). A stepwise approach was most successful. The partly unstable Au(III) complexes (**6a,b**), formed by oxidation of Au(I) complexes (**5a,b**), were isolated by crystallization from a DCM/pentane solution and were pure enough for structural confirmation by ^{1}H and ^{1}H,^{15}N-HMBC NMR. Subsequent counter-ion exchange of Au(III)Cl_3-complex **6a** (R = *i*Pr) with a weakly coordinating anion, was performed by addition of $AgSbF_6$ to give the relative unstable Au(III)[SbF_6] complex **7a**. The decomposition of the complexes was immediately apparent upon oxidation, with full decomposition in < 4 h. The more bulky Au(III)Cl_3-complex **6b** (R = *t*Bu) failed to give the Au(III)[SbF_6] complexes **7b**, as only oxazoline decomposition products were observed.

The instability of the oxazolyl moiety in *C,N*-Au(III)Cl_2[SbF_6]NHC-oxazolyl complexes **7a,b** was unexpected, as our previous *P,N*-Au(III)Cl_2[SbF_6] phosphine-oxazolyl complexes [8] were stable and characterized by XRD. Also, the corresponding Au(I)Cl precursors (**5a,b**) were stable under ambient conditions, and no oxazoline decomposition was detected. The fact that NHC-metal complexes generally have greater electron density at the metal center than phosphine-metals, would not explain the instability of Au(III)NHC-oxazolyl products **7a,b**. The related stable *C,N*-Ir(cod)$_2$ [13] and $PtBr_2$ [14] NHC-oxazolyl complexes have been prepared in low to moderate yields and fully characterized, as well. However, it was proposed that the reason for unsuccessful formation of target *C,N*-Ir-NHC complexes from bulky *t*Bu-oxazoline-imidazolium pre-ligands, was that steric hindrance prevented complexation [13]. This strong observed effect of bulky oxazolyl groups also seems to explain the great difference (*i*Pr *vs* *t*Bu) in stability of our Au(III)Cl_3-complexes **6a,b**, as well as the challenging lack of stability of the *C,N*-Au(III)Cl_2[SbF_6]NHC-oxazolyl complexes **7a,b**. The non-coordinated oxazolyl groups appear to be unstable under the applied reaction



Scheme 1. Our previously reported polydentate Au(III) complexes **I-V** [4–10], studies on Au(III)-NHC- naphthamide **VII** complexes [12], and the target *C,N*-Au(III) products **7** in the present study.



Scheme 2. Synthesis of Au(I) and Au(III)-NHC-oxazolyl complexes **5**–**7**.

conditions.. Gold(III) complexes may occasionally suffer from low stability. In this study, we were hampered by the limited stability of the prepared Au(III) **6a,b** and **7a** complexes, being too unstable for handling, proper isolation, and complete spectroscopic characterization by NMR and HRMS. However, essential information to prove the Au(III) complex structures was provided by selective NMR techniques.

NMR studies of gold-NHC-oxazolyl complexes (5–7)

^{15}N NMR studies of impure heterocyclic mixtures may readily reveal crucial characteristics of the N-environments of a variety of *N*-heterocycles. In particular, ^{15}N NMR chemical shifts have been useful to give valuable information on metal *N*-coordination to prove the structure of *N*-ligated metal complexes. As we have experienced that *N*-coordination to Au(I) and Au(III) may be confirmed by ^{1}H, ^{15}N-HMBC 2D NMR studies for complexes with *N*-based ligands, such as pyridine and oxazolines [5,6], we carried out a similar study on gold complexes Au(I)Cl **5a,** Au(III)Cl$_3$ **6a** and *C,N*-Au(III) **7a**. Attempts to generate *C,N*-Au(III) complex **7b** (*t*Bu) failed, as ^{1}H,^{15}N-HMBC 2D NMR only showed decomposition products.

When metal complexes are not sufficiently stable for complete characterization by HRMS, NMR or X-ray, there is a need for selective careful methods to confirm the structure of the complex. The formed Au (III) products **6a** and **7a** were too unstable for HRMS characterization, and ^{1}H NMR showed additional decomposition products (Fig. 1b). However, by running reactions in deuterated solvent (d_2-DCM), immediate product analyses by ^{1}H,^{15}N-HMBC 2D NMR (Fig. 1c) were successful and gave appropriate selective information of Au(III) complexes **6a** and **7a**. Assignments of relevant δ^{1}H, δ^{13}C and δ^{15}N NMR shift values of complexes **4a** and **5a** were based on combination of 2D NMR, when possible, such as COSY, HSQC, as well as both ^{1}H,^{13}C HMBC and ^{1}H,^{15}N-HMBC**.** Values for δ^{1}H and δ^{15}N NMR (Fig. 1a-c) for complexes **5a, 6a** and **7a** are listed in Table 1.

^{1}H and ^{15}N NMR spectra of complexes **5a**, **6a** and **7a** revealed some significant effects, as shown by changes in chemical shifts ($\Delta\delta$) through the oxidation and anion exchange processes (Table 1). Essential selective information was revealed by measuring the changes in ^{15}N-shift values by oxidation ($\Delta\delta^{15}N_{ox} = \delta^{15}N_{\mathbf{6a}} - \delta^{15}N_{\mathbf{6a}}$) and by subsequent anion exchange (AE) ($\Delta\delta^{15}N_{AE} = \delta^{15}N_{\mathbf{7a}} - \delta^{15}N_{\mathbf{6a}}$). Also, the corresponding ^{1}H NMR values, $\Delta\delta^{1}H_{ox}$ and $\Delta\delta^{1}H_{AE}$, gave important

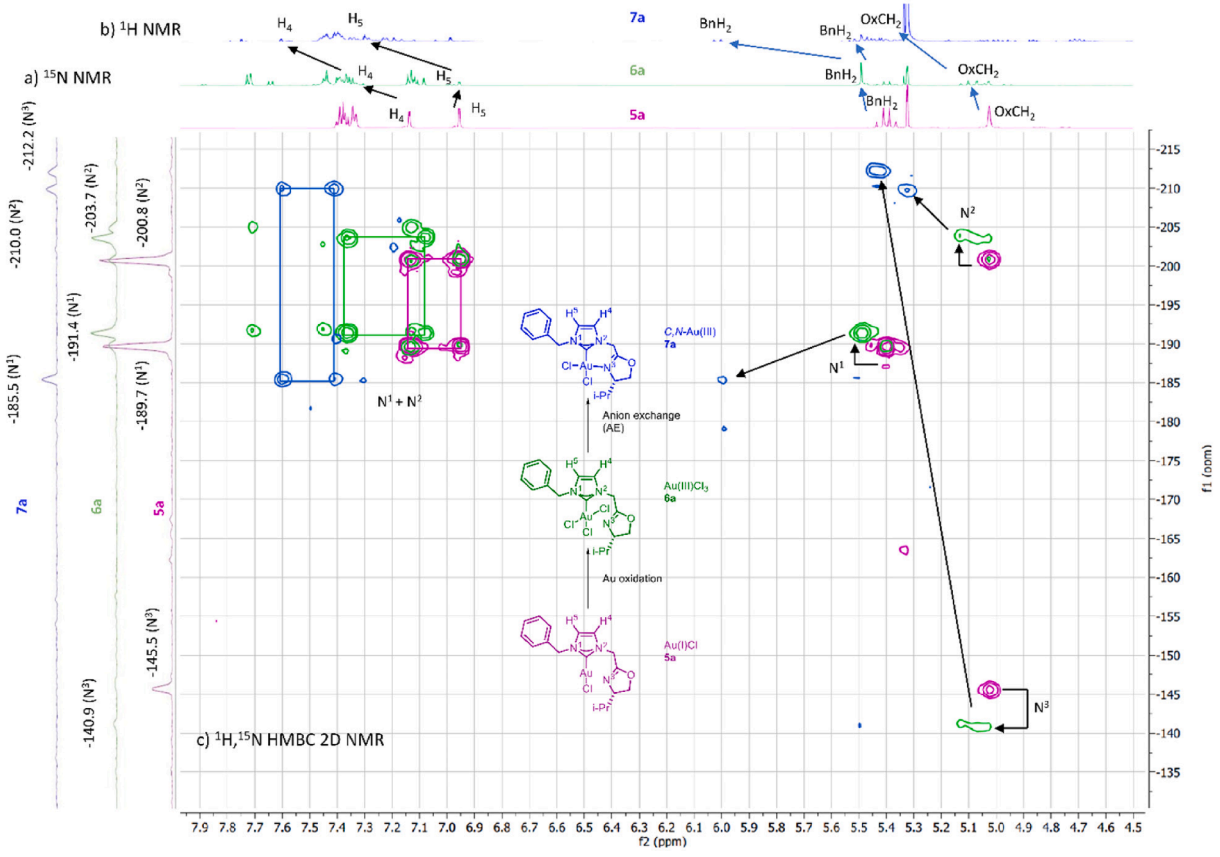


Fig. 1. 1D and 2D NMR (CD_2Cl_2) spectra of gold complexes Au(I)Cl **5a** (purple), Au(III)Cl$_3$ **6a** (green) and *C,N*-Au(III) **7a** (blue). a) ^{15}N NMR; b) ^{1}H NMR; and c) ^{1}H,^{15}N-HMBC 2D NMR. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Experimental $\delta^{15}N_{complex}$, $\Delta\delta^{15}N_{ox}$ and $\Delta\delta^{15}N_{AE}$, as well as $\delta^{1}H_{complex}$, $\Delta\delta^{1}H_{ox}$ and $\Delta\delta^{1}H_{AE}$ chemical shift values (ppm) of gold complexes Au(I)Cl **5a** (purple), Au(III)Cl_3 **6a** (green) and *C,N*-Au(III)**7a** (blue).

Entry	$\delta^{15}N_{5a}$ Au(I)Cl	$\delta^{15}N_{6a}$ Au(III)Cl_3	$\Delta\delta^{15}N_{ox}$	$\delta^{15}N_{7a}$ *C,N*-Au(III)	$\Delta\delta^{15}N_{AE}$
1 N^1-Bn	-189.7	-191.4	-1,7	-185.5	5.9
2 N^2-Ox	-200.8	-203.7	-2.9	-210.0	-6.3
3 N^3-cycl	-145.5	-140.9	4.6	-212.2	-71.3
	$\delta^{1}H_{5a}$ Au(I)Cl	$\delta^{1}H_{6a}$ Au(III)Cl_3	$\Delta\delta^{1}H_{ox}$	$\delta^{1}H_{7a}$ *C,N*-Au(III)	$\Delta\delta^{1}H_{AE}$
5 H^5	6.95	7.08	0.13	7.41[b]	0.33
4 H^4	7.13	7.36[b]	0.23	7.60	0.24
6 CH_2-Bn	5.37/5.42[diast]	5.49[c]	0.12/0.07	6.01/≈5.50[(b) diast]	0.52 / ≈-0.01[diast]
7 CH_2-Ox	5.02[c]	5.05, 5.11[diast]	0.03/0.09	5.43[b]	0.38/0.32

[a] negative and positive Δδ values represent down-field (<-) and up-field (->) change of NMR shift values (ppm).
[b] ^{1}H NMR signals are identified by 2D NMR correlation. [c] broad signals represent diastereotopic CH_2 groups.

knowledge. By combining the ^{1}H and ^{15}N NMR data of complexes **5a**, **6a** and **7a**, interesting results were obtained for the oxidation ($\Delta\delta_{ox}$; blue - purple) and anion exchange ($\Delta\delta_{ox}$; purple - green) steps, as demonstrated by the ^{1}H,^{15}N-HMBC 2D correlations (Fig. 1a-c). The respective Δδ values for ^{1}H and ^{15}N NMR are also given in Table 1.

The assignment of the δ^{15}N shift values of gold complexes **5a, 6a** and **7a** (Table 1, entries 1–3) was done by combining the total information shown by ^{1}H,^{15}N-HMBC 2D NMR correlations of all three complexes (Fig. 1c). Four distinct N/H correlation peaks for imidazole protons H^4 and H^5 and nitrogens N^1 and N^2 comprise each corner of three colored rectangles, which appear in the upper left part of the 2D NMR spectra. The imidazole N^1 and N^2 nitrogens also correlate with the benzylic CH_2-Bn and the oxazoline neighboring CH_2-Ox protons, respectively (upper right part of Fig. 1c). Additionally, the CH_2-Ox protons correlate with the oxazoline ring-nitrogen, N^3-cycl, in complexes **5a**, **6a** and **7a** (δ^{15}N −145.5, −140.9 and −212.2 ppm).

- *Au(I) to Au(III) Oxidation.* By oxidation of Au(I)Cl **5a** to Au(III)Cl_3 **6a**, the expected stronger electron-withdrawing effect of the more electrophilic Au^{3+} center compared to Au^+ was demonstrated by down-field ^{1}H NMR shifts observed for all relevant protons (H^4, H^5 CH_2-Bn, CH_2-Ox; Table 1, entries 4–7 and Fig. 1b). However, the oxidation caused, in general, small ^{1}H and ^{15}N NMR shift changes. Most obvious were the down-field shifts of the imidazole H^4 and H^5 protons ($\Delta\delta^{1}H_{ox}$ 0.13, 0.23 ppm, entries 4,5 and Fig. 1b). The H^4 and H^5 signals are not clearly seen in the ^{1}H NMR spectrum of the impure sample of Au(III)Cl_3 **6a**, but the respective $\delta^{1}H_{6a}$ shift values (7.08, and 7.36 ppm) are clearly identified by ^{1}H,^{15}N-HMBC 2D correlations (Fig. 1c).

Also, a distinct down-field shift of the oxazoline nitrogen N^3 was observed ($\Delta\delta^{15}N_{ox}$ = 4.6 ppm; Table 1, entry 3 and Fig. 1a,c), while a marginal up-field shift was seen for the imidazole nitrogens N^1 and N^2 ($\Delta\delta^{15}N_{ox}$ −1.7, −2.9 ppm, respectively), showing a similar relative effect as for $H^5 < H^4$, by larger changes for elements closest to the oxazoline group. We have previously experienced that oxazole-based ligands are sensitive for hydrolysis and ring-opening [6]. In fact, oxidation of Au(I)Cl complex **5a** also afforded small amounts of corresponding oxazoline hydrolysis products (Fig. 1a,b), as seen by non-assigned δ^{15}N signals in the N^1 and N^2 region in the spectrum of Au(III)Cl_3 **6a**, (Fig. 1a,c). These signals have no visible N^3 counterparts, as amines (δ^{15}N ≈ 90 ppm) would be registered outside the range of this 2D NMR analysis.

The CH_2-Bn and CH_2-Ox protons were less affected by oxidation ($\Delta\delta^{1}H_{ox} < 0.1$ ppm, entries 6,7). However, ^{1}H NMR showed a change from two distinct diastereotopic CH_2-Bn protons (two doublets, J ≈ 15.0 Hz) for Au(I)Cl **5a**, which appeared as a broad singlet after oxidation to Au(III)Cl_3 **6a** (entry 6). The opposite effect was seen for CH_2-Ox, going from a broad singlet to diastereotopic signals (two doublets) upon oxidation to **6a** (entry 7). This change implies that geometrical reconfiguration takes place by oxidation of Au(I)Cl **5a** to Au(III)Cl_3 **6a** by enforcing a chiral environment for the CH_2-Ox protons instead of the CH_2-Bn protons. Both diastereotopic CH_2-Bn protons (2 × d) in Au(I)Cl **5a** correlated with N^2 nitrogen (broad spot at $\delta^{15}N_{5a}$ = −189.7 ppm), while the two CH_2-Ox diastereotopic protons in Au(III)Cl_3 **6a** correlated with both N^2 and N^3 nitrogens (broad spots at $\delta^{15}N_{6a}$ = −203.7 and −140.9 ppm).

- *Anion Exchange of Au(III) complex;* Elucidation of the ^{1}H,^{15}N-HMBC 2D NMR of the *C,N*-chelated Au(III)SbF_6 complex **7a**, generated by anion exchange of Au(III)Cl_3 **6a**, was more intricate than the previous 2D NMR spectra, due to unstable and impure products and diastereotopic CH_2 protons. Two of the three ^{15}N atoms displayed by ^{1}H,^{15}N-HMBC 2D NMR of complex **7a** represented correlations between imidazole protons H^4 and H^5 and $N^1$and N^2 (δ = −185.5, −210.0; upper left part Fig. 1c).

Thus, the CH_2-Ox protons correlate with the third N^3-cycl oxazoline-nitrogen at δ = −212.2 ppm, which demonstrates a huge N^3 up-field shift of $\Delta\delta^{15}N^{AE}$ = −71.3 ppm by anion exchange. This represents significant evidence that oxazoline-N^3-coordination to Au(III) takes place and that the six-membered chelate bidentate *C,N*-Au(III) complex **7a** is formed. The massive shift and decreased shielding of the N^3-nuclei is caused by increased N^3 electron donation by coordination to Au(III) by anion exchange. This large change in ^{15}N NMR shift value, $\Delta\delta^{15}N_{AE}$, is in accordance with our previous detailed studies of oxazoline-*N*-gold(III) coordination [8] for $\Delta\delta^{15}N_{coord}$ caused by coordination of oxazolines to Au(III). The smaller up-field shift for N^2 ($\Delta\delta^{15}N_{AE}$ = −6.3 ppm) may be explained by the six-membered metalacyclic structure of the bidentate *C,N*-Au(III) complex **7a**, which can dislocate electron density from the imidazole N^2 nitrogen. The opposite down-field shift of N^1 ($\Delta\delta^{15}N_{AE}$ = 5.9 ppm) might be explained by its position outside the metallacycle. The two diastereotopic CH_2-Bn protons in *C,N*-Au(III) **7a** showed two correlation spots with N^2 nitrogen ($\delta^{15}N_{7a}$ = −185.5 ppm), which allowed identification of one of the protons, "hidden" in a crowded part of the ^{1}H NMR spectrum. Thus, there is a large difference in shift value between the CH_2-Bn diastereomeric **7a** proton signals at $\delta^{1}H_{7a}$ 6.01 and ≈ 5.50 ppm.

The present work on the preparation of gold(I) (**5**) and Au(III)-NHC-oxazolyl complexes (**6,7**) illustrate how 2D NMR techniques may provide essential information of unstable ligated metal complexes. The data obtained by ^{1}H,^{15}N-HMBC 2D NMR demonstrates how important knowledge, including *N*-Au(III) coordination, may be revealed to

confirm the stepwise structural changes which take place by oxidation and anion exchange for the formation of *C,N*-Au(III)-NHC-oxazolyl complexes (**7**).

Conclusion

(*S*)-*N*-Benzyl-*N*-oxazoline-imidazolium preligands (**4a,b**) were synthesized in three steps from the respective chiral *(S)*-2-alkyl-amino alcohols (alkyl = *i*Pr, *t*Bu), 2-chloroacetyl chloride and *N*-benzyl-imidazole (overall yields ≈ 20%). Novel Au(I)-NHC-oxazolyl complexes (**5a,b**) and Au(III)Cl_3-NHC complexes (**6a,b**) were prepared by initial gold(I) coordination (Ag_2O, $Me_2SAu(I)Cl$ of preligands **4a,b** and subsequent oxidation with dichloro-iodobenzene. The rather unstable Au(III)Cl_3-NHC complexes (**6a,b**) were directly treated with $AgSbF_6$, aiming at bidentate Au(III) complex formation by anion exchange. Only the corresponding *C,N*-Au(III)-NHC-oxazolyl[SbF_6] complex **7a** was formed. Due to the relatively unstable nature of Au(III) complexes (**6a,b** and **7a**), proper isolation and adequate NMR and HRMS characterization was challenging.

However, selective ^{15}N NMR techniques give valuable knowledge on *N*-ligated metal complexes by *N*-coordination to Au(I) and Au(III). Thus, $^{1}H,^{15}N$-HMBC 2D NMR studies of gold complexes Au(I)Cl **5a**, Au(III)Cl_3 (**6a**) and *C,N*-Au(III) (**7a)** afforded important information of the oxidation and the anion exchange processes. The changes in ^{15}N-shift values by oxidation ($\Delta\delta^{15}N_{ox}$) and by subsequent anion exchange ($\Delta\delta^{15}N^{AE}$) strongly indicated the formation of the initial Au(III)Cl_3-NHC-oxazoline complex (**6a**) and the target C,N-Au(III)-NHC-oxazolyl[SbF_6] complex (**7a)** by the two-step oxidation / anion exchange procedure from Au(I) NHC-oxazoline (**5a**). In particular, the huge up-field shift of the oxazoline-N^3 ($\Delta\delta^{15}N_{AE} = -71.3$ ppm) represented significant evidence that oxazoline-N^3-coordination to Au(III) took place by anion exchange, and, hence, that the six-membered chelate bidentate *C,N*-Au(III)-NHC-oxazoline complex (**7a**) was formed. The results demonstrate how $^{1}H,^{15}N$-HMBC 2D NMR of impure and unstable samples of gold complexes with *N*-based ligands may be used to confirm selective *N*-coordination to Au(III).

CRediT authorship contribution statement

Jostein Lund: Investigation, Formal analysis, Writing – original draft. **Helgi Freyr Jónsson:** Investigation, Formal analysis, Methodology, Writing – review & editing, Conceptualization. **Anne Fiksdahl:** Methodology, Writing – review & editing, Project administration, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.rechem.2022.100360.

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