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rsc.li/daltonOrganometallic chemistry in *aqua regia*: metal and ligand based oxidations of (NHC)AuCl complexes†‡Volodymyr Levchenko,^{ID} Cristiano Glessi,^{ID} Sigurd Øien-Ødegaard^{ID} and Mats Tilset^{ID}*

The synthesis and characterization of a series of N-heterocyclic carbene (NHC) complexes of Au(III), (NHC)AuCl₃, is described. High yields are obtained when the corresponding Au(I) species (NHC)AuCl are oxidized with inexpensive *aqua regia*. The oxidation is in some cases accompanied by substitution and/or anti addition of Cl₂ across the backbone C=C bond of unsaturated NHC ligands.

Introduction

Metallic gold has historically been regarded as one of the most inert of metals, arising from its low reactivity and high resistance to oxidation. The classic dissolution of metallic gold in *aqua regia*,¹ the 1 : 3 mixture of nitric acid and hydrochloric acid, remains important for chemists as the first step in the syntheses of gold complexes from the element. Its capacity to oxidize Au(0) to Au(III) is key to the successful use of aqua in this process (eqn (1)).²



In recent years, gold chemistry has gained a prominent position in the field of catalysis. In homogeneous catalysis, the carbophilic character of Au(I) and Au(III) alike allows the coordination of carbon–carbon π bonds with concomitant bond activation. This facilitates further reactions, including C–C and C–heteroatom bond forming reactions that are employed in the synthesis of complex organic molecules. Au(I) compounds, two-coordinate with linear geometry at Au, have dominated this chemistry. Complexes of the type L–Au–X are frequently used, with a plethora of σ -donating L ligands available, for example phosphines³ and N-heterocyclic carbenes (NHC's).^{4–7} This last class of organogold complexes, frequently in the form (NHC)AuCl, has proven to be an important precursor for the catalytically active (NHC)Au⁺ species with a weakly

coordinating counteranion. They have found applications in a large range of reactions, in particular involving creating and functionalizing C–C π bonds (alkenes, alkynes, arenes).^{4,7–9} Various Au(NHC) complexes have found uses in other applications, such as anticancer drugs¹⁰ and as photosensitizers.¹¹

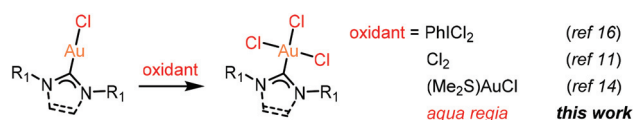
Recently, Au(III) chemistry has gained more attention, and robust synthetic methods to furnish such species are established. Preparative pathways include the decoration of Au(III) salts with appropriate ligands on one side, and oxidation of Au(I) precursors on the other. The oxidation of linear (NHC)Au(I) complexes to square planar (NHC)Au(III) congeners is usually carried out with a halide-containing oxidizing agent such as halogens^{12–15} (Cl₂, Br₂ and I₂), CsBr₃,¹⁶ N-halosuccinimides,¹⁷ (Me₂S)AuCl,¹⁸ and PhICl₂.^{12,19} The latter as well as gaseous Cl₂ are the most commonly used oxidizers for synthesis of (NHC)AuCl₃ complexes and usually lead to the formation of the desired products in high yields and purity (Scheme 1). Occasionally, the presence of side products or the difficult handling of these compounds represent a practical challenge, along with safety and environmental issues. Admittedly, *aqua regia* also raises such issues – and eventually the choice of oxidant (however unpleasant) will be made on the basis of a number of factors including selectivity, ease of use, costs, environmental issues, and more. In all circumstances, chemists need a well-equipped toolbox of synthesis methods.

The use of *aqua regia* as a solvent for preparative organometallic chemistry is very limited. It has been previously^{20–23}

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† Dedicated to Professor Robin Perutz's on the occasion of his 70th birthday.

‡ Electronic supplementary information (ESI) available: Experimental details, NMR spectra and other characterization data. Crystallographic data for **1j**, **2i–k**, **3b**, **4b**. CCDC 1960925–1960930. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9dt04472h



Scheme 1 Synthesis of Au(NHC)Cl₃: reported methods and this work.

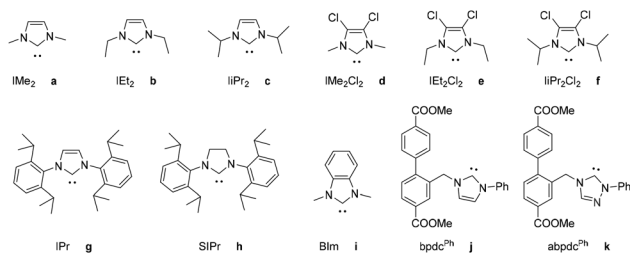


Fig. 1 NHC ligands used in this work and their abbreviations.

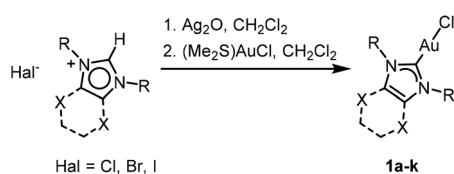
reported that Au(I) complexes with substituted pyrazolato (pz) ligands may be oxidized by *aqua regia* to Au(III) species without loss of the pz ligands, with or without concomitant chlorination of the pz ring. Except for our very recent report²⁴ that a rather electron poor dicobaltoceniumyltriazolylidene Au(I) complex can be favourably oxidized to Au(III) in *aqua regia* when other oxidants fail, there appears to be no other descriptions of the reactivity of Au complexes with gold–carbon bonds in this reaction medium. In this contribution, we describe the use of *aqua regia* as an oxidation agent for the oxidation of (NHC)AuCl complexes with more conventional NHC ligands to (NHC)AuCl₃ analogs. The range of NHC ligands explored is shown in Fig. 1. The reactions, which in most cases are high-yielding and involve simple work-up procedures, represent a surprising and attractive alternative to existing synthetic methods.

Results and discussion

Summary of main reactions

The (NHC)AuCl complexes **1a–k** were obtained according to modifications of the published procedures (see ESI† for details).^{25–28} The appropriate imidazolium salts were used as NHC-ligand precursors and were treated with Ag₂O to generate (NHC)Ag(I) species which were transmetalated *in situ* with (Me₂S)AuCl to furnish the (NHC)AuCl complexes (Scheme 2). The procedure of Nolan²⁸ usually works well, but in cases where the NHC precursors are imidazolium bromide or iodide salts, the (NHC)AuBr or (NHC)AuI complexes would be formed. For this reason we favoured the Ag₂O method, which leads to the desired (NHC)AuCl complex as the only or major product.

The *aqua regia* (reaction medium as well as oxidant for the reactions) was made by mixing 1 : 3 (v/v) concentrated solutions of nitric (65%) and hydrochloric (37%) acids. The (NHC)



Scheme 2 Synthesis of (NHC)AuCl complexes **1a–k**.

Table 1 Reactions of (NHC)AuCl (**1a–k**) to form (NHC)AuCl₃ (**2a–c**, **2g–k** and **3a–c**) in *aqua regia*

Entry	NHC	(NHC)AuCl	(NHC)AuCl ₃	Time, h	Yield, %
1	IMe	1a	2a	24	7 ^a
2	IEt	1b	2b	24	— ^a
3	IIPr	1c	2c	24	82 ^a
4	IMe ₂ Cl ₂	1d	3a	3	77
5	IEt ₂ Cl ₂	1e	3b	3	75
6	IIPr ₂ Cl ₂	1f	3c	5	84
7	IPr	1g	2g	5	72
8	SIPr	1h	2h	20	45
9	BIm	1i	2i	7	85
10	bpdC ^{Ph}	1j	2j	6	63
11	abpdc ^{Ph}	(1k)^b	2k	3	75 ^b

^a Reaction resulted in a mixture of NHC-backbone-chlorinated products, see text. The numbers given here are % of mixture by NMR, not actual yields. ^b Yield based on two steps from the imidazolium salt, without intermittent isolation of **1k**.

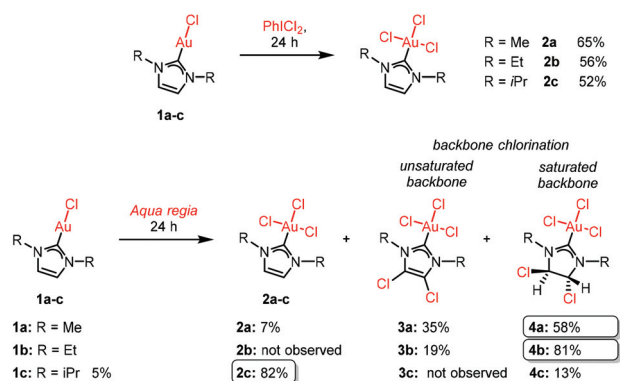
AuCl complexes were suspended in freshly prepared *aqua regia* (8 mL), stirred for a stated period at ambient temperature, filtered, and washed with water. In most cases (except **1a–c**), this procedure yielded the corresponding (NHC)AuCl₃ complexes as pure, yellow products in good to high yields. It is noteworthy that the rather harsh reaction conditions do not lead to cleavage of the Au–C(NHC) bonds. The details are given in Table 1. Any further optimizations or modifications for each case are described in ESI† for each substrate separately.

In order to aid product identifications, additional reactions with PhICl₂ were performed to furnish authentic samples of the respective (NHC)AuCl₃ species.¹² Their ¹H NMR spectra were used to confirm the identity of materials obtained following the *aqua regia* protocol. The ¹H NMR spectra of previously reported (NHC)AuCl₃ species **2d**,²⁹ **2g**,¹² and **2h**¹² were compared with literature data.

In general, we find that the most diagnostic indication of successful oxidation of (NHC)Au(I) to (NHC)Au(III) is a change of the chemical shift of the C(carbene) signal in the ¹³C NMR (CD₂Cl₂) spectra from the range δ 168.9–196.4 to 139.0–172.8. The average upfield change was 28.8 ppm.

The complex oxidations of the simple (NHC)Au(I) complexes **1a–c**

The compounds **1a–c** bear simple NHC ligands with an unsubstituted backbone and small aliphatic substituents (Me, Et, iPr) at the N atoms. It appears that oxidation of **1a** and **1b** complexes with the use of the chlorinating agents mentioned in the introduction have not yet been reported, and that the corresponding Au(III) trichloro derivatives remain completely undescribed so far. The oxidation of **1c** with PhICl₂ produces the corresponding Au(III) derivative **2c** in high yields (Scheme 3, top). We find that treatment of **1a** and **1b** with a slight excess of PhICl₂ also proceeds smoothly by selective oxidation at Au to furnish the respective (NHC)AuCl₃ complexes **2a** and **2b** in 65 and 56% unoptimized yields, respectively



Scheme 3 Oxidations of **1a**, **1b**, and **1c** with PhICl₂ (top) and *aqua regia* (bottom). Product distributions are given, based on ¹H NMR spectra of the crude reaction mixtures.

(Scheme 3, top). These products were characterized by ¹H NMR and HRMS.

On the other side, the reactions of **1a–c** in *aqua regia* proceeded to give mixtures of up to three (NHC)Au(III) species (Scheme 3, bottom). The products were isolated as mixtures which were not subjected to separation attempts. In all cases, NHC backbone-functionalized species – in which two Cl atoms had substituted the backbone H atoms or added to the backbone C=C bond – had formed at the expense of the simple Au-centered oxidation products **2a–c** although Au(I) to Au(III) oxidation had occurred in all cases. Thus, whereas **1a** furnished a low yield of **2a**, the two backbone-chlorinated species **3a** and **4a** dominated the reaction. Starting from **1b**, none was seen of the simple oxidation product **2b**; the addition product **4b** was the dominant species with substitution product **3b** as side product. For **1c**, the simple Au-centred oxidation product **2c** dominated whereas the addition to the backbone gave the minor product **4c**.

The oxidation products were identified by analysis of 1D and 2D ¹H and ¹³C NMR spectra, high resolution mass spectrometry, and elemental analysis (see ESI† for full details). Whereas the species **2a–c** were readily recognized through their =C–H signals (δ ca. 7.2) in addition to the matching N–R alkyl signals in the ¹H NMR spectra, **3a–b** exhibited only the N–R signals, whereas **4a–c** each displayed one additional >C(Cl)–H singlet arising from the backbone (δ ca. 5.8). Separate signals were seen for the diastereotopic NCH₂CH₃ protons in **2b** (ca. 1 ppm separated) and NCHMe₂ methyls in **2c** (ca. 0.1 ppm separated). The *trans* disposition of the two Cl atoms at the NHC backbone cannot be ascertained from the NMR data alone for **4a–c**, but was unambiguously established by a single-crystal X-ray structure determination for **4b** (*vide infra*). A ¹H-NOESY experiment was conducted on the mixture of compounds arising from **1b** and revealed a set of cross-peaks between the two diastereotopic methylene protons and the backbone protons for **4b**, confirming the backbone saturation (see ESI† for details). The *trans* geometry at the backbone of **4b** (and, by inference, **4a** and **4c**) strongly suggests that the

addition has involved an electrophilic chlorine reagent, by analogy with the commonly observed *anti* addition seen in addition of Cl₂ to alkenes. The electrophilic chlorine must arise from the chloride ions in the *aqua regia* medium.

The formation of the backbone-substituted products **3a** and **3b** is reminiscent of previous reports of Cl for H substitution reactions in free carbene NHC systems, as reported by the Arduengo^{30,31} group. Nolan and coworkers¹² reported on the undesired chlorination of the backbone-bonded methyl groups of the NHC ligand IPr^{Me} during the chlorination of the corresponding Au(I) complex (IPr^{Me})AuCl using Cl₂ as the chlorinating agent. We are unaware of previous cases where such chlorinations occur at the NHC backbone of metal-coordinated NHC complexes. Furthermore, to further investigate the backbone chlorination, the *aqua regia* oxidation procedure was performed on the uncoordinated ligand IET (of **1b**) in the form of its imidazolium bromide salt. No such reactivity was observed for the salt, although minor quantities of a series of unidentified species were seen: in order to obtain backbone chlorination of the NHC ring, coordination at Au is required. Further mechanistic details are not known; however we note that Au could have an influence on the backbone reactivity either indirectly (Au as a substituent on the ring; the reaction works only on the Au complex) or directly, through a gold-catalysed halogenation.

When the mixture of **3b** and **4b** was dissolved in CH₂Cl₂ followed by slow diffusion of pentane vapours into the solution, the two complexes crystallized nicely in separate crystals which could be hand-picked and subjected to independent structure determinations by X-ray diffraction analysis. ORTEP views of the molecular structures of **3b** and **4b** are shown in Fig. 2. The diffraction analysis of **4b** confirms that the two Cl atoms have been added to the backbone C=C bond in the NHC ligand in **2b** in an *anti* fashion. The Au–C(carbene) bond distances of 2.004(3) (**3b**) and 1.993(3) (**4b**) Å are typical for (NHC)Au(III)

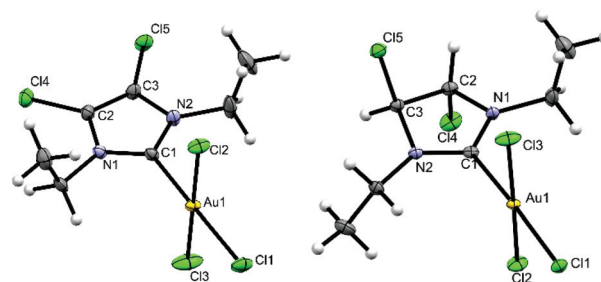


Fig. 2 ORTEP views of the solid-state molecular structures of **3b** (left) and **4b** (right) with 50% probability ellipsoids. Crystals were grown from the isolated mixture of **3b** and **4b** obtained in the reaction of **1b** in *aqua regia* for 24 h. Selected bond distances (Å) and angles (°): **3b**: C1–Au1 2.004(3), Au1–Cl1 2.304(1), Au1–Cl2 2.273(1), Au–Cl3 2.271(1), C2–C3 1.349(6), C2–Cl4 1.692(4), C3–Cl5 1.691(4), C1–Au–Cl1 178.4(1), C1–Au–Cl2 86.9(1), C1–Au–Cl3 90.7(1), Cl4–C2–C3 128.4(3), Cl5–C3–C2 129.3(3). For **4b**: C1–Au1 1.993(3), Au1–Cl1 2.3192(8), Au1–Cl3 2.2744(9), Au1–Cl2 2.2782(9), C2–C3 1.517(4), C3–Cl5 1.805(3), C2–Cl4 1.809(3), C1–Au–Cl1 177.14(9), C1–Au–Cl3 87.57(9), C1–Au–Cl2 87.63(9), Cl5–C3–C2 109.0(2), Cl4–C2–C3 109.4(2).

complexes, which spans the range 1.975–2.024 Å.^{12,13,32} The square planar geometry at Au(III) as well as the perpendicular orientation of the NHC ligand with respect coordination plane of Au(III) are as expected. The Cl–C–C angles (128.4° and 129.3°) at the backbone in **3b** deviate slightly from the ideal 120° angle of C(sp²). The structure of **4b** has a saturated backbone with Cl–C–C angles of 109.0° and 109.4°.

The simple oxidation of the backbone-substituted (NHC)Au(I) complexes **1d–f**

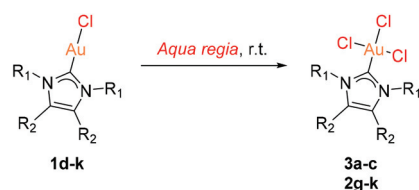
In order to better understand the nature of the various chlorination reactions of **1a–c**, we performed similar reactions starting with the already chlorinated **1d–f**. In all these cases, no reaction was seen at the backbone and only the products arising from selective oxidation of Au(I) to Au(III), *i.e.* **3a–c**, are obtained (Scheme 4). The *aqua regia* treatment of these compounds was relatively rapid, and extended reaction times led to gradual decomposition. Table 1 lists the optimum reaction times and yields.

The simple oxidation of the larger (NHC)Au(I) complexes **1g–k**

The applicability of the *aqua regia* oxidation protocol was next extended with attempts at synthesizing (NHC)AuCl₃ complexes that feature an unsubstituted backbone and bulky aromatic groups on the NHC nitrogens. Specifically, the IPr and SIPr carbenes (starting from **1g** and **1h**) were included, since these are among the most frequently used NHC ligands in Au(I) catalysis.³³ The oxidation of **1g–h** in *aqua regia* led to the smooth formation of the targeted Au(III) compounds **2g–h** in 72 and 45% yields, respectively, without any observable functionalization at the backbone (Table 1 lists the optimum reaction times and yields).

For **1h**, the evolution of the reaction over time was monitored in *aqua regia*. This revealed that the oxidation occurred rapidly during first 3 h, with less than 10% of starting material left at that time. However, the consumption of the rest of the starting material was considerably slower and eventually *ca.* 20 h were needed to effect the complete consumption of **1h** (see ESI†).

The *aqua regia* reaction protocol was also applied to the benzimidazole-based (NHC)AuCl complex **1i** and again, the reaction proceeded cleanly to furnish the desired Au(III) complex **2i** in 85% yield. This indicates that the scope of the protocol might include a broad range of (NHC)AuCl complexes, as long as reaction times are appropriately adjusted.



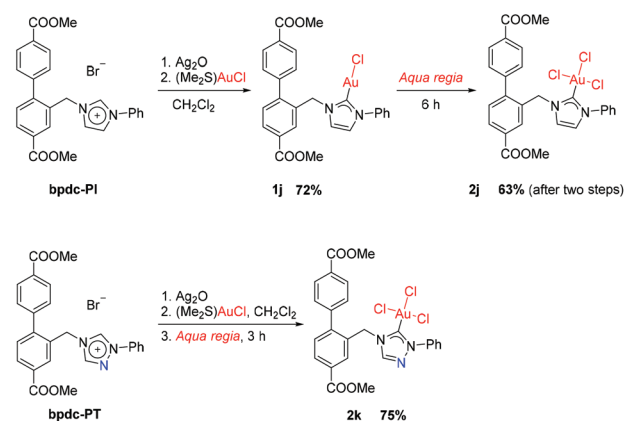
Scheme 4 Selective oxidations of **1d–k** in *aqua regia*.

Finally, the developed protocol was applied towards synthesis of (NHC)Au(III) systems with dicarboxylate functionalities that might allow them, after ester deprotection, to be incorporated into UiO-67³⁴ type metal–organic frameworks (MOFs). Although linkers with pendant imidazolium functionalities for incorporation into MOFs are well known,³⁵ their functionalization with Au(I) or Au(III) appears to be still unexplored. The imidazolium salt **bpdc-PI** (Scheme 5) was synthesized according to modified literature procedures,^{35–37} followed by metalation with Ag₂O and transmetalation to (Me₂S)AuCl to furnish the (NHC)AuCl complex **1j**. Oxidation in *aqua regia* furnished **2j** in 63% yield based on the imidazolium salt (Scheme 5). Importantly, no backbone functionalization nor degradation of the molecule, including the ester groups, occurred.

The same synthetic protocol was also applied to the preparation of the new triazolium-based NHC system in **2k**, synthesized in a fashion similar to **2j** (full synthesis of **bpdc-PT** is provided in ESI†). Also in this case high yields were obtained with no backbone side reactivity (Scheme 5).

Crystallographically determined molecular structures of **1j** and **2i–k** are depicted in Fig. 3 and selected bond lengths and angles are provided in Table 2. The X-ray-quality crystals were grown by slow diffusion of pentane vapors into dichloromethane (**2i**), chloroform (**2j**), and acetone (**2k**) solutions. Full crystallographic data are given in the ESI.†

In Au(I) complex **1j**, the Au–C(carbene) bond distance is 1.986(3) Å, quite typical of (NHC)AuCl complexes (1.958(7)–2.036(2) Å, based on a few reports^{38–40}). The Au–Cl distance is 2.3366(8) Å, and the Cl–Au–C(carbene) angle is 178.91(7)°, essentially linear as expected for a d¹⁰ Au(I) complex. In the Au(III) complexes, the Au–C(carbene) bond distances also fall in the range of previously reported ones,⁴¹ with values of 2.008(3) Å in **2i**, 2.003(3) Å in **2j**, and 2.003(4) and 2.009(4) Å for the two independent molecules in **2k**. Furthermore, in the Au(III) species the Au–Cl bond distances *trans* to C(carbene) were in the range 2.310(1) Å (**2k**) to 2.321(1) Å (**2i**), which agrees with typical distances in the range 2.298–2.325 Å seen in similar



Scheme 5 Synthesis of **2j** and **2k**, potentially amenable to MOF incorporation.

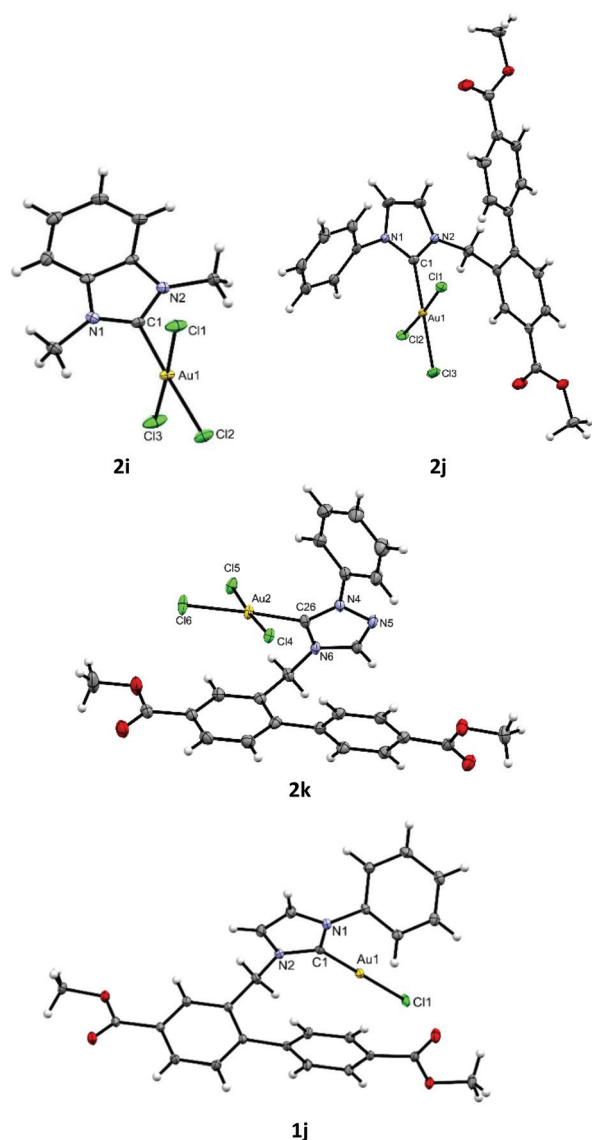
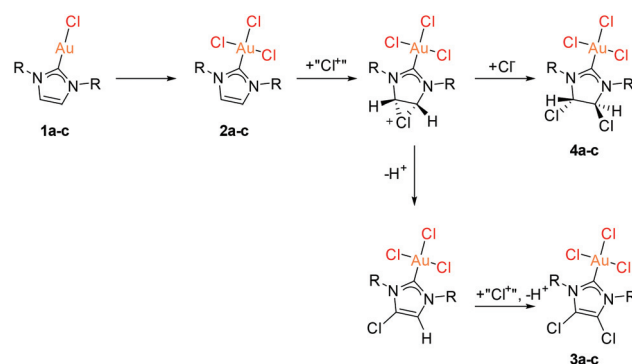


Fig. 3 ORTEP views of the molecular structures of **1j** and **2i–k** with 50% probability ellipsoids. Selected bond distances and angles are given in Table 2. Only one of the crystallographically independent molecules in the unit cell for **2k** is shown. Full crystallographic data are provided in ESI.†



Scheme 6 Formation of **3a–c** and **4a–c** through backbone activation.

complexes.^{12,41} The high *trans* influence of the NHC ligand elongates the Au–Cl bond *trans* to NHC compared to the Au–Cl bonds *cis* to NHC, ranging from 2.276(2) (**2i**) to 2.303(1) Å (**2k**). The C(carbene)–Au–Cl(*trans*) angles are essentially linear in all complexes, from 176.68° to 178.31°.

Discussion

The fact that none of the reactions in *aqua regia* leads to complexes that are backbone-functionalized, yet not oxidized to Au(III), leads us to hypothesize that the oxidation of Au(I) to Au(III) is the first step of all reactions (Scheme 6). The reactivity of the C=C bond of the NHC ligands in the resulting **2a–c** then is a secondary process which occurs for **2a–c** only. The lack of backbone-functionalization reactivity of **2d–k** under the reaction conditions employed may be a result of contributions from steric effects, and perhaps of poorer solubility of these species (thence, shorter residence times) in *aqua regia*.

It seems likely that the rapid oxidation to Au(III) helps protect the Au(III)–C(carbene) bond with respect to protolytic cleavage, when compared to the Au(I)–C(carbene) bond. Once formed, the Au(III) species **2a–c** undergoes reactions with an electrophilic source of chlorine, forming a putative chloronium intermediate which ultimately produces the *trans* addition product **4a–c** after nucleophilic attack by chloride, alternatively the substitution products **3a–c** after proton loss and one more round of approach by electrophilic chlorine (Scheme 6). In an independent experiment, complex **2b** was

Table 2 Selected bond distances (Å) and angles (°) for complexes **1j** and **2i–k**

	1j	2i	2j	2k ^a	
Au–C(carbene)	1.986(3)	2.008(3)	2.003(3)	2.009(4)	2.003(4)
Au–Cl(<i>trans</i>)	2.3366(8)	2.321(1)	2.3144(7)	2.314(1)	2.310(1)
Au–Cl(<i>cis</i>)	n.a.	2.281(2)	2.2952(7)	2.294(1)	2.295(1)
C(carbene)–Au–Cl(<i>trans</i>)	178.91(7)	176.68(8)	178.31(8)	177.1(1)	177.4(1)
C(carbene)–Au–Cl(<i>cis</i>)	n.a.	86.76(8)	90.00(8)	88.5(1)	88.2(1)
		90.19(8)	87.12(8)	89.3(1)	89.2(1)

^a Data for two independent molecules in the unit cell.

subjected to *aqua regia* treatment and indeed, a mixture of **3b** and **4b** (24% : 76%) was formed (see ESI, Fig. S22†). The reaction medium is an obvious possible source of this electrophilic chlorine, although the involvement of gold chloro species should not be discounted. More detailed mechanistic studies are obviously warranted but severely hampered by the poor solubility of reactants in *aqua regia* as well as intractability of *aqua regia* as an NMR solvent in modern NMR spectrometers.

Concluding remarks

In summary, a new protocol for oxidation of (NHC)AuCl complexes to (NHC)AuCl₃ has been described. The reaction workup involves only filtration and washing with water. The described protocol is practical, easy to perform and suitable for various types of NHC ligand systems. Furthermore, the reaction itself involves only the use of aqueous acid solutions, without involvement of organic solvents. Interestingly, sterically unhindered NHC complexes can undergo backbone functionalization, which consists of either chlorine addition or chlorine substitution at the C=C double bond of the unsaturated NHC heterocycle. With improved control of selectivity and yields, this otherwise complicating and undesired side reaction may also be synthetically useful. The reactivity seen in *aqua regia* offers new possibilities and may serve as inspiration for the use of *aqua regia* as a chlorinating agent in preparative organometallic chemistry.

Experimental

General procedure for oxidation in *aqua regia*

To the selected (NHC)AuCl complex, 8 mL of freshly made *aqua regia* were added. The suspension was vigorously stirred in a closed vial at room temperature. Afterwards, the suspension was filtered, washed with two portions of water, and dried under a stream of air.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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