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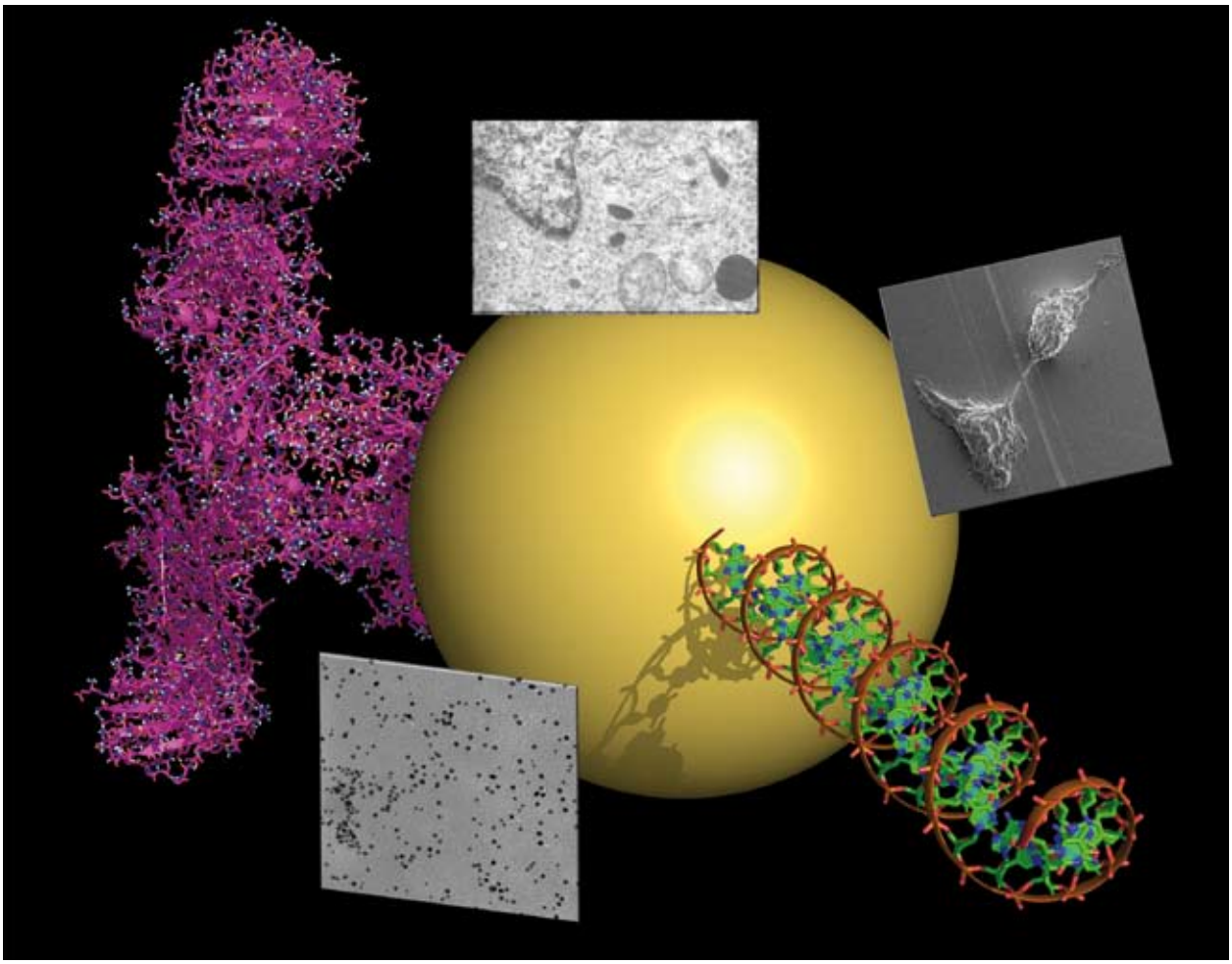

N-Heterocyclic carbenes in gold catalysis†

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The appealing properties of N-heterocyclic carbenes (NHC) as ancillary ligands and the high potential of gold as an organometallic catalyst have made their encounter inevitable. Still in its infancy, NHC–gold catalysis is nevertheless growing rapidly. In this *tutorial review*, catalytic transformations involving NHC-containing gold(I) and gold(III) complexes are presented. Particular attention is drawn to the versatility and selectivity of these catalysts.

Introduction

Gold catalysis, notably in its homogeneous catalysis incarnation, has emerged from a mere curiosity to a now very frequently publicized source of novel catalytic transformations of interest to the organic community.[1] Even though the use of simple gold(I) and gold(III) salts—such as AuCl, $AuCl_3$ and $NaAuCl_4$—has been reported, most studies employ gold(I) chloride complexes bearing a monodentate ancillary ligand, [(PPh_3)AuCl] certainly being the most frequently encountered catalyst.[1] These linear dicoordinated gold compounds, upon activation by a chloride "abstractor" such as a silver(I) salt, generate a mono-ligated cationic catalyst which requires strong electronic and steric stabilization from its ancillary ligand. Therefore, it comes as no surprise that N-heterocyclic carbenes (NHCs), commonly described as excellent σ-donors, are becoming increasingly employed in this field.

During the past 10 years, NHCs have impacted upon all fields of organometallic chemistry,[2] becoming serious alternatives to the ubiquitous tertiary phosphines. They usually impart high stability *and* enhanced reactivity to transition metals.[3] The first NHC–gold(I) complex was isolated in 1973,[4] but it is only recently that these compounds, mainly as Au^I species of formulae [(NHC)AuCl] **1** (Fig. 1), have gained popularity, taking advantage of straightforward synthetic routes developed recently.[5]

Notably, NHC–gold complexes have encountered successes as potential drugs,[6] as luminescent device,[7] and have permitted to uncover important general features regarding the nature of the NHC–metal bond.[8] In this review, we will focus on the applications of NHC–gold(I) and NHC–gold(III) compounds in homogeneous and heterogeneous catalysis. Their broad reactivity scope will notably be emphasized as well as selectivity issues when compared to other ligands bound to gold centers.

I. Enyne cycloisomerization and related reactions

The skeletal rearrangement of enynes is arguably the most popular reaction in gold catalysis.[9] Nevertheless, only a handful of reports have appeared that use NHC-based gold catalysts, clearly hinting at further studies in this field.

Recently, the efficient use of [(IMes)AuCl] **1a** (IMes = *N*,*N*′-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, see Fig. 1), in conjunction with $AgSbF_6$, was reported for the intermolecular bis-cyclopropanation of 1,6-enynes with alkenes (Scheme 1).[10]

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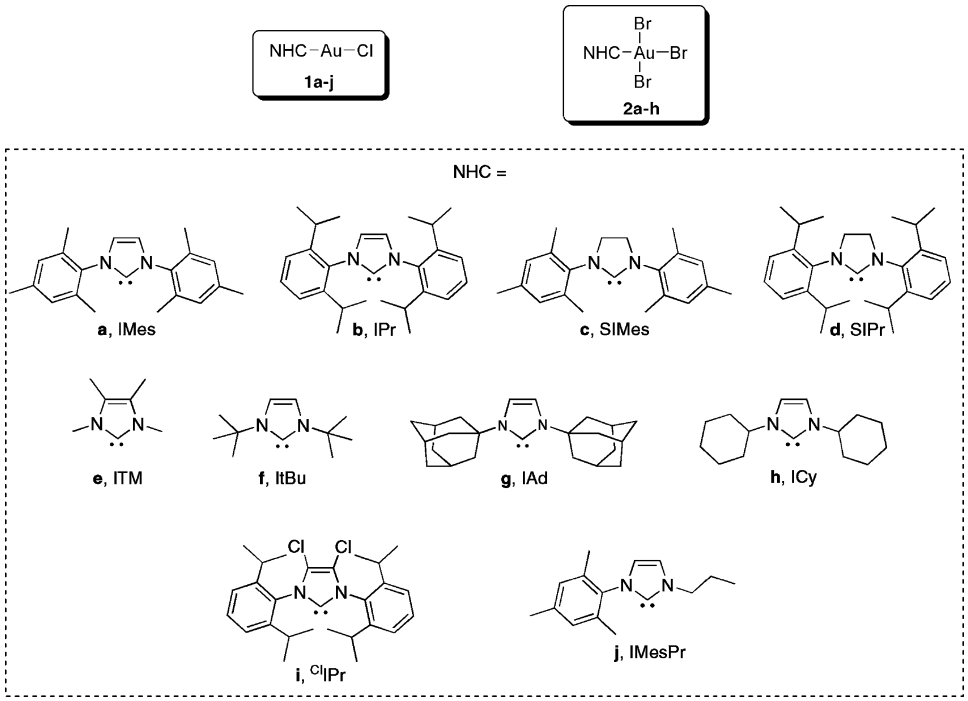
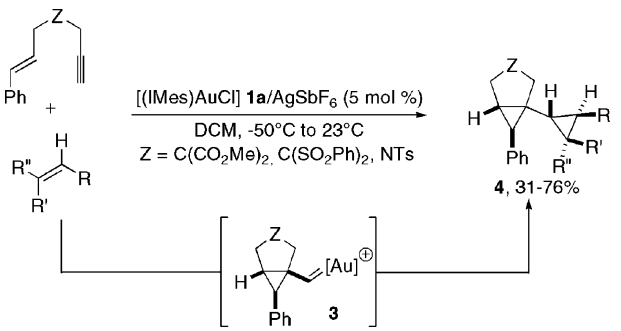


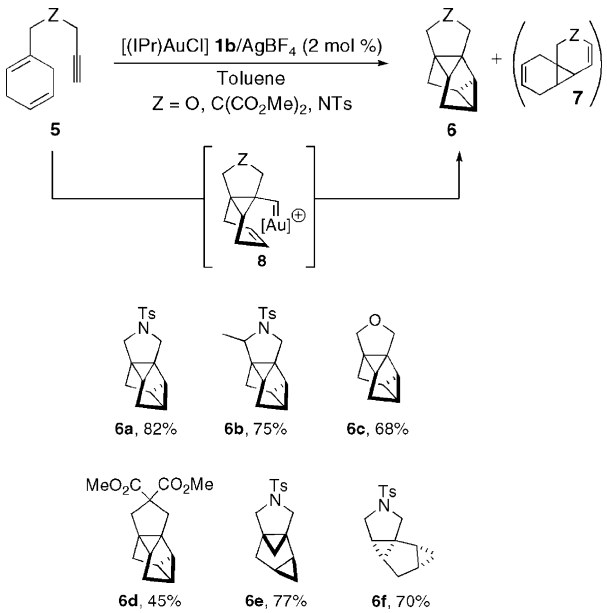
Fig. 1 Structures of NHC–gold complexes employed in catalysis.



Scheme 1 [(IMes)AuCl]-catalyzed intermolecular bis-cyclopropanation of enynes with alkenes.

In this transformation, the first cyclopropanation occurs intramolecularly, leading to cyclopropylcarbene intermediate **3**, which is trapped by an external alkene to afford bis-cyclopropyl compound **4**.

For this specific transformation, the NHC ligand on gold outperformed tertiary phosphine and phosphite ligands both in terms of yield and selectivity. The scope of the reaction was found to be broad, encompassing cyclic and acyclic alkenes. Interestingly, in the presence of an unsymmetrical diene, the second cyclopropanation occurred at the less hindered C=C bond. Subsequent developments by Chung *et al*. allowed for the synthesis of tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octanes **6** (Scheme 2) using [(IPr)AuCl] **1b** (IPr = *N*,*N*′-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene).[11] These highly strained compounds were obtained from a double intramolecular cyclopropanation of 1,6-enynes **5**, which possess a 1,4-cyclohexadiene core, *via* cyclopropylcarbene **8**. Optimization studies revealed the key importance of the solvent and the nature of the silver salt, notably allowing for a better control of the **6**/**7** selectivity; the

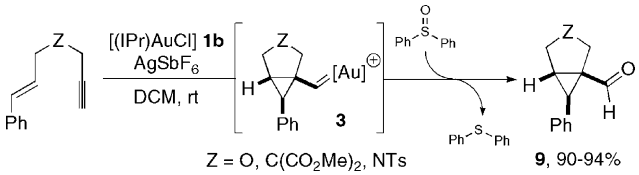


Scheme 2 [(IPr)AuCl]-catalyzed intramolecular bis-cyclopropanation.

architectural scope is shown in Scheme 2. Of note, the use of acyclic 1,4-dienes, instead of the rigid 1,4-cyclohexadiene framework, produced compounds **6e** and **6f**, other highly interesting entries into cyclopropyl-rich fused polycyclic structures.

Other evidence supporting the involvement of a cyclopropylcarbene species as an intermediate in the isomerization of 1,6-enynes was reported by Toste and co-workers.[12] Different types of Au-catalyzed enyne cycloisomerizations were carried out in the presence of diphenyl sulfoxide, which was found to

oxidize the carbenic intermediate **3** (eqn (1)). The IPr-containing catalyst **1b** exhibited superior activity in these oxidation reactions when compared to the PPh_3- or IMes-containing ones.



(1)

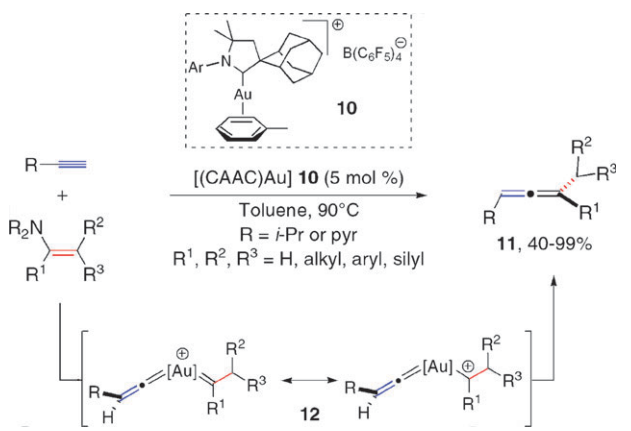
The authors further showed the generality of the oxidative trapping of a carbenoid intermediate in other gold-promoted reactions such as diazo insertion and acetylenic Schmidt rearrangement. Of note, a series of isolated [(NHC)Au(NTf_2)] complexes have been shown to catalyze a number of previously reported cycloisomerization reactions involving enynes,[13] clearly demonstrating that NHCs are highly efficient and polyvalent ligands for gold catalysis.

Finally, Bertrand *et al*. reported recently the use of a cyclic (alkyl)(amino)carbene ligand (CAAC) as a highly stabilizing ligand for the synthesis of the η^2-toluene gold(I) adduct **10** (Scheme 3).[14]

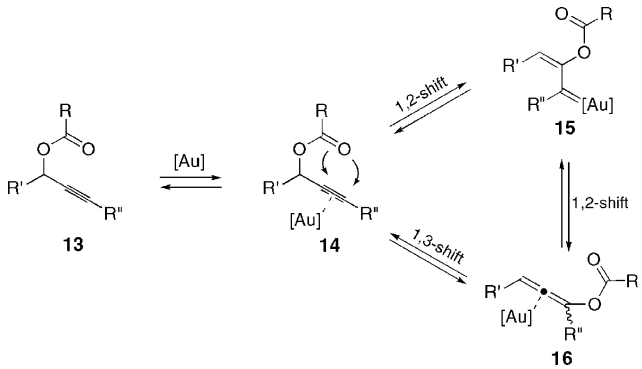
This stable cationic catalyst was found to selectively form allenes of type **11** from enamines and terminal alkynes (Scheme 3), a reaction that usually produces propargylic amines. The authors, based on thorough mechanistic studies, proposed that the reaction could proceed through a gold acetylide intermediate from which formal coupling between a carbene and a vinylidene, both attached to the gold center (intermediate **12**), would allow for the formation of the three-carbon allenic core. Importantly, the use of AuCl, [(PPh_3)AuCl]–K$B(C_6F_5)_4$ or the neutral counterpart of **10**, [(CAAC)AuCl], yielded only the previously reported propargyl amine product, stressing the requirement of both a cationic gold center and the presence of the CAAC ligand.

II. Propargylic esters

Propargylic esters, where the ester moiety usually performs a 1,2- or 1,3-shift upon electrophilic activation of the



Scheme 3 [(CAAC)Au]-catalyzed cross-coupling of alkynes and enamines.



Scheme 4 Gold-promoted activation of propargylic esters.

alkyne (Scheme 4), have recently emerged as a special class of substrates.[15] Interestingly, the intramolecular attack of the ester function, far from inhibiting their reactivity, triggers further carbene- and allene-based transformations.

A recent theoretical study by Cavallo and co-workers on the activation of propargylic acetates by gold(I) catalysts, demonstrated that, intermediates **14**, **15**, and **16** are in rapid equilibrium.[16] In their report, the authors considered both possibilities of an NHC or a phosphine ligand attached to a gold(I) cationic center. This allowed for a detailed comparison and led to the conclusion, based on the difference in energies, that the resting state was likely **16** in the case of the NHC, whereas, in the case of the phosphine, two intermediate species could be considered of lowest energy. This might explain why in specific cases, notably when an allene-based *versus* a carbene-based reactivity is necessary, NHC–gold compounds seem to be more selective. However, as highlighted in this report, it should be taken into account that, in addition to the nature of the ligand, the nature of the substrate, and notably the substitution at the propargylic and acetylenic positions, is of primary importance to the outcome of the reaction.

In this context, N-heterocyclic carbenes have encountered numerous successes and were notably shown to induce high selectivity in the oxidative rearrangement of propargylic pivalates.[12] In addition, NHC–gold complexes were also found to be selective for the cyclization of 1,5-enynes bearing a propargylic acetate.

As depicted in Scheme 5, the formation of bicyclo[3.1.0]-hexene **20** was observed only in the presence of gold catalysts and not in the presence of platinum compounds.[17] Ligand screening, involving pre-catalysts **1a–e**, **1g** and [(Ph_3P)AuCl], revealed that a complex set of steric and electronic parameters was at play in the formation of the unprecedented bicycle **20** over the "classical" products **18** and **19**. Of note, alkyl substitution at the acetylenic position induced total selectivity towards the new type of bicyclo[3.1.0]hexene whereas a phenyl substituent led to a complex mixture of unidentified products.

Replacement of the alkene moiety by an arene in a formal 1,4-enyne structure led to the formation of substituted indenes **22** (eqn (2)).[18] Again, the presence and the nature of the NHC on the gold center was crucial to the outcome of the reaction,

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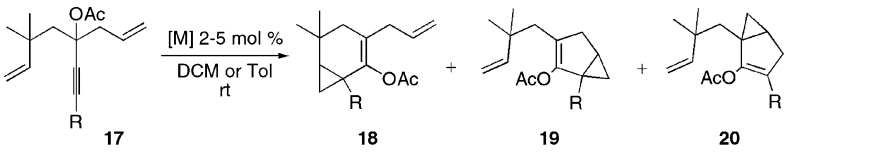
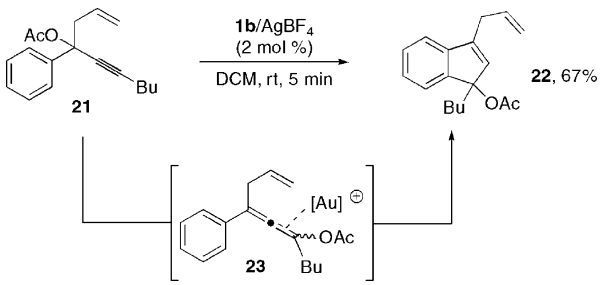


Scheme 5 Cycloisomerization of dienyne **17**.

pre-catalysts **1b** and **1g** were of comparable activity, being more selective than **1a**, **1d** and **1e**.

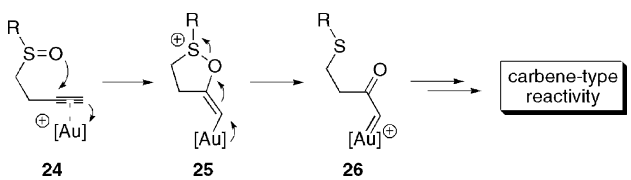


(2)

Interestingly, this transformation, described as a tandem [3,3] rearrangement–hydroarylation reaction, was shown to be selective over the cyclization of a 1,5-enyne framework (eqn (2)). The involvement of allene intermediates, such as **23**, prior to cyclization was supported by the successful formation of indenes from pre-isolated allenyl esters.

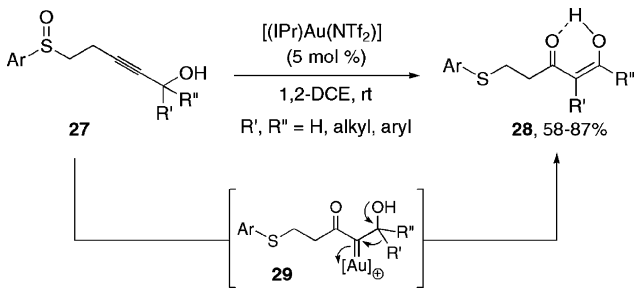
Soon after the report on the formation of indenes, Nolan, Maseras *et al*. reported the efficient formation of α,β-unsaturated ketones and aldehydes from similar propargylic acetates in the presence of water.[19] Capitalizing on the isolation in low yield of a by-product that was identified as a conjugated ketone, the authors consequently optimized an [(NHC)AuCl]-based catalytic system that proved highly efficient and broad in scope. This study highlighted the importance of reaction conditions and specifically the role of water in the reaction medium. Mechanistic investigations and computational studies supported [(NHC)Au(OH)], produced *in situ* from $[(NHC)Au]^+SbF_6^-$ and H_2O, instead of cationic $[(NHC)Au]^+SbF_6^-$ as the catalytically active species. Based on theoretical calculations, a full catalytic cycle featuring an unprecedented transfer of the OH fragment bound to the gold center to the C≡C bond was proposed.

Conceptually related to propargylic esters, homopropargylic sulfoxides exhibit an interesting reactivity that has been investigated recently. The sulfoxide moiety acts as a nucleophile through its oxygen atom (Scheme 6, **24** to **25**) and as a leaving group through its sulfur atom (Scheme 6, **25** to **26**).



Scheme 6 Au-promoted rearrangement of homopropargylic sulfoxides.

The net result is an intramolecular redox process where the sulfoxide function in **24** is converted into a sulfide function and the alkyne into an α-carbonyl gold carbenoid **26**. Hence, the parallel with propargylic esters appears clear with the formation of a carbenoid species from an alkyne, obtained *via* an intramolecular nucleophilic attack of an *O*-containing functional group onto the alkyne, followed by gold-assisted rearrangement. Further reactivity, as with propargylic esters, is a function of the pendant groups. Aryl sulfoxides have notably been employed and yielded benzothiepinones after insertion of the gold carbenoid into a C–H aryl bond.[20] Further studies demonstrated that this reaction could be equally performed with sulfimines, with final formation of enamines, and that 5-*exo*-dig *versus* 6-*endo*-dig attack occurred as a function of the substrate. Interestingly, in the case of a 6-*endo*-dig attack, the carbenoid was trapped by 1,2-migration of the sulfide, leading to α-thio conjugated enones. Alternatively, alkyl or aryl 1,2-migration can take place for substrates bearing a secondary or tertiary propargylic alcohol function such as **27**, leading to β-hydroxy enone **28** (eqn (3)).[21] Using unsymmetrical propargylic alcohols, the ability of 1,2-migration, in an intermediate such as **29**, was demonstrated to follow the order aryl > alkyl > H. In all cases, it appeared that NHC-based gold(I) catalysts, **1a** for the synthesis of benzothiepinones[20] and [(IPr)Au(NTf_2)] for β-hydroxy enone formation,[21] were best suited for these transformations involving alkynyl sulfoxide rearrangements.



(3)

III Alkene activation

Even though less studied—and less straightforward—than reactions involving alkynes, Au-catalysis can be extended to alkenes. The first report involving NHC–gold complexes in alkene activation only appeared in 2006, by Peris, Fernández *et al*. who disclosed a diboration of olefins. They demonstrated

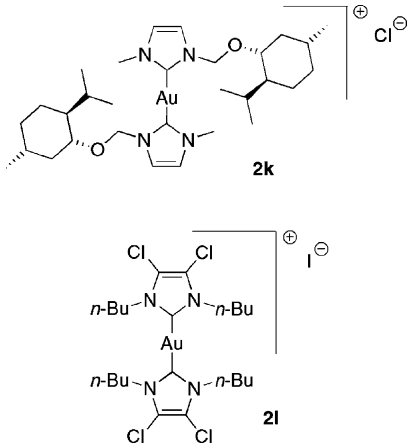


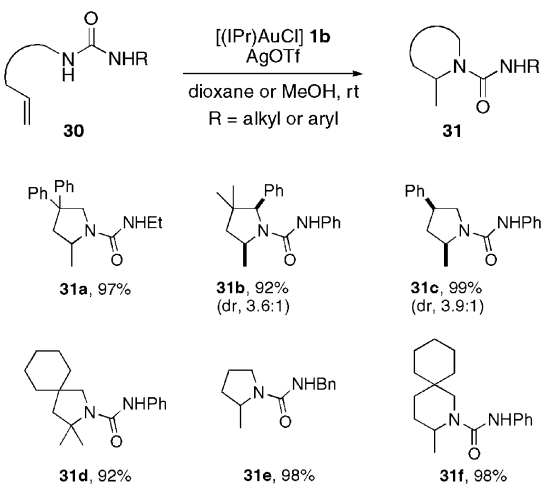
Fig. 2 Structures of bis-NHC gold(I) catalysts.

that bis-NHC complexes **2k** and **2l** (Fig. 2) efficiently catalyzed the diboration of styrene and vinylcyclohexane at room temperature.[22] It should be added that this is so far the only report of gold catalysis employing complexes with formulae $[(NHC)_2Au]^+X^-$.

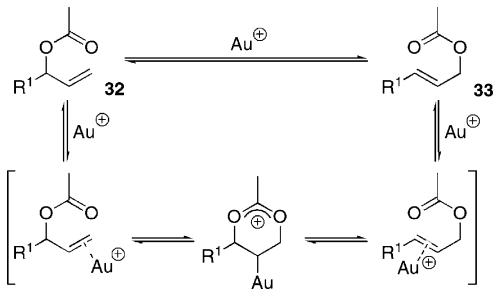
In seminal work, Widenhoefer and Bender showed that [(IPr)AuCl] **1b** was highly active in the hydroamination of unactivated alkenes (Scheme 7).[23] The authors found that **1b** displayed enhanced catalytic activity when compared to sterically hindered, electron-rich *o*-biphenylphosphine-containing gold species. Hence, the room temperature intramolecular hydroamination of a large array of *N*-alkenyl ureas **30** could be effectively carried out (Scheme 7).

The catalytic system displayed excellent *exo*-selectivity and good diastereoselectivity. The mechanism is believed to proceed *via* initial π-coordination of the alkene to the cationic gold center. The developing carbocation is then trapped intramolecularly by the nucleophilic amine and protodeauration completes the catalytic cycle.

Following the same principle, the isomerization reaction of allylic esters **32** to **33** was recently disclosed.[24] π-Activation of the C=C bond triggers an intramolecular attack by the carbonyl oxygen, leading to a 6-membered stabilized



Scheme 7 [(IPr)AuCl]-catalyzed hydroamination of alkenes.



Scheme 8 Proposed mechanism for the Au^I-catalyzed allylic rearrangement.

1,3-acetoxonium. Regeneration of the carbonyl bond affords the isomerized olefin **33** (Scheme 8).

A series of [(NHC)AuCl] pre-catalysts, comprising **1a**, **1b**, **1d–h**, were tested along with AuCl and [(Ph_3P)AuCl] and it was observed that, in this particular transformation, the steric hindrance of the ligand, more than its electronic properties, was a key parameter. Hence, bulky ligands, such as ItBu and IAd performed better than smaller ones like ITM, ICy or PPh_3 (Table 1). The authors proposed that a bulky ligand, rather than having an effect on the catalytic reaction itself, would shield the cationic gold center more efficiently than a smaller ligand and prevent catalyst decomposition. Interestingly, the reaction could be carried out under microwave heating without alteration of the yield or the purity of the products. This highlights the robustness of the NHC–Au^I bond and the interest in employing this type of catalyst when somewhat harsh conditions are required for a given transformation. The scope of this allylic rearrangement was found to be quite broad, notably including trisubstituted olefins, with the exception of nitrile-containing substrates, which probably hinder catalysis by *N*-coordination to gold.

Very recently, an example of gold-induced olefin polymerization was reported with NHC–gold(III) compounds.[25] Different styrene-type monomers could be polymerized at room temperature in the presence of [(NHC)$AuBr_3$] **2a–h** (Fig. 1) and $NaBAr'_4$ (BAr'_4 = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate). The study showed that, contrary to NHC–gold(III), NHC–gold(I) compounds were not effective pre-catalysts. The influence of the NHC ligand was further investigated as well as the possibility of an acid catalyzed polymerization. The authors finally concluded that a cationic, rather than radical, polymerization was at play since both the metal center and the ligand influenced the physical properties of the polymeric material produced. This mechanistic hypothesis is in accordance with the generation, *via* π-alkene activation, of a gold-stabilized carbocation. Even though mechanistically diverse, it should be noted that the polymerization of L-lactide in the presence of an [(NHC)AuCl] initiator has also been studied.[26]

IV. Alkyne hydration and related reactions

In 2003, Herrmann reported the very first application of an NHC–gold species in catalysis.[27] The authors studied the addition of water to alkynes, a known reaction in the presence of phosphine–gold compounds, leading to ketones. Hence, the conversion of 3-hexyne to 3-hexanone was achieved with

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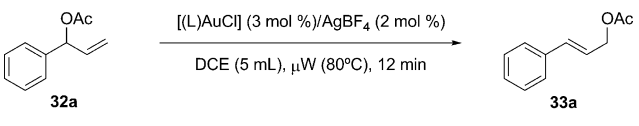
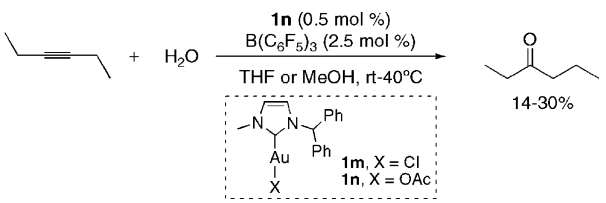
Table 1 Ligand effect in Au-catalyzed allylic rearrangement



Entry	L	33a[a]
1[b]	none	< 5%
2	IPr	99%
3	SIPr	98%
4	IMes	95%
5	IAd	97%
6	ItBu	98%
7[b]	ICy	61%
8[b]	ITM	56%
9[b]	P(C6H5)3	53%

[a] ^{1}H NMR conversions. [b] Substantial amount of oligomerization.

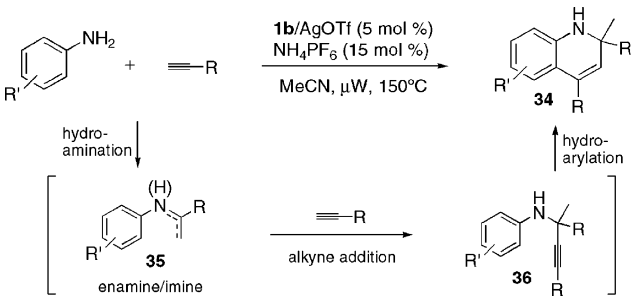
0.5 mol% of [(NHC)Au(OAc)] **1n** (eqn (4)). It was notably observed that **1m** was inactive but that *in situ* formation of **1n**, from a mixture of **1m** and AgOAc, provided similar results to reactions performed with well-defined **1n**, highlighting the key role of the coordination of the counteranion in gold(I) chemistry. Even though results were modest, it certainly validated the utilization of NHCs as supporting ligands in gold catalysis.



(4)

The hydration of alkynes was also a reaction chosen by Nolan *et al.* as a benchmark test for the evaluation of the catalytic activity of a series of NHC–gold(III) complexes of formulae [(NHC)AuBr$_3$], **2a–h** (Fig. 1).[28] These compounds, easily obtained by oxidative addition of elemental bromine to [(NHC)AuBr], were the first NHC–gold(III) species shown to display a catalytic behavior. They showed good activity in refluxing methanol, following the Markovnikov addition rule, and yielded a number of methyl ketones. The main drawbacks of this catalytic system are the high catalyst loading required (*e.g.* 10 mol%) and the lack of activity with internal alkynes.

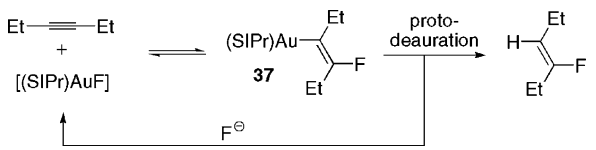
The use of amines instead of water as the nucleophile in this reaction leads to the formation of imines or enamines as a function of the degree of substitution of the amino group. The newly formed functional group can, in turn, be activated for further reactivity. Following this precept, Che *et al.* recently



Scheme 9 [(IPr)AuCl]-catalyzed tandem hydroamination–hydroarylation.

reported the formation of 1,2-dihydroquinolines and quinolines from anilines and alkynes catalyzed by [(IPr)AuCl] **1b**.[29] As shown in Scheme 9, a number of 1,2-dihydroquinolines **34** could be obtained from simple starting materials in a tandem process. Experimental evidences were gathered leading to the proposal that enamine **35** and propargylic amine **36** were intermediates. It is worth noting that, during catalyst screening, [(IPr)AuCl] **1b** was found to be more efficient than its IMes counterpart **1a** and as active as [{(*o*-biphenyl)di-*tert*-butylphosphine}AuCl] which possesses a bulky and electron-rich phosphine ligand.

Closely related to the hydration of alkynes, which is formally a hydrohydroxylation reaction, a catalytic hydrofluorination of alkynes was disclosed recently by Sadighi *et al.*[30] In a key experiment, the authors observed the formation of vinylgold **37**, a likely hydrofluorination intermediate, resulting from the addition of the Au–F bond across 3-hexyne (eqn (5)).



(5)

Subsequent fine-tuning of the reaction conditions, notably of the fluoride source and the acidic media, permitted the development of a catalytic transformation using [(NHC)AuCl]–$AgBF_4$ mixtures. Additionally, it should be noted that only *trans*-hydrofluorination was observed and that ^{Cl}IPr (4,5-dichloro-1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) **i** (see Fig. 1), a less electron-rich ligand than IPr, was found to be more efficient in this reaction than IPr or SIPr.

Enlarging the scope of [(NHC)Au]-catalyzed H–X addition across π-bonds, Corma and co-workers recently reported the hydrosilylation of styrene and benzaldehyde by **1j** (see Fig. 1).[31] As acknowledged by the authors, results were modest but promising and further developments are needed—only one NHC was tested—to fully exploit the possibilities offered by Au-catalyzed hydrosilylation. Nevertheless, it ultimately demonstrates the high versatility of NHC ligands in gold catalysis.

Concluding remarks

Less than half a decade has passed since the first report on gold catalysis involving N-heterocyclic carbene ligands

appeared in 2003.[27] Since then, the handful of contributions that have appeared have impressively spanned a wide spectrum of organic transformations. This range encompasses enyne cycloisomerization, in a broad sense, hydroarylation, diboration, [3,3] rearrangement, hydroamination, hydration and polymerization. Additionally, new areas of research with promising potential are now being investigated. These include alkane C–H activation,[32] olefin hydrogenation[33] and cross-coupling reactions;[34] remarkably, the latter being catalyzed by a *heterogeneous* NHC-containing gold(I) system. Hence, over a short period of time, it has already been demonstrated that NHC-based gold(I) and gold(III) catalysts can activate alkynes, allenes and alkenes as well as carbonyl and aryl halide compounds. This clearly highlights the important versatility of NHC ligands in the context of Au-catalysis.

In addition to this flexibility, the ease of synthesis of NHC–gold complexes combined with their inherent stability render the NHCs quite appealing. They have become more than ''alternatives'' to tertiary phosphines. The recent discoveries of outstanding activity and unexpected selectivity, in certain transformations, will clearly draw more attention to this class of ligand. Furthermore, the recent demonstration that a chiral counteranion strategy might be more valuable than a classical chiral ligand approach in cationic gold-promoted transformation[35] has opened new avenues for N-heterocyclic carbene-based asymmetric catalysis.

Finally, we believe that the broad availability of NHC-containing gold compounds will undoubtedly fuel more research activity in this fascinating field.[36]

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