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Mononuclear gold catalysts for the asymmetric intramolecular hydroamination of alkenes

Christophe Michon[a,b,c,*], Marc-Antoine Abadie[a,c], Florian Medina[a,c], Francine Agbossou-Niedercorn[a,b,c,*]

[a] Université Lille Nord de France, 59000 Lille, France
[b] CNRS, UCCS UMR 8181, 59655 Villeneuve d'Ascq, France
[c] ENSCL, CCCF, (Chimie-C7) CS 90108, 59652 Villeneuve d'Ascq Cedex, France

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ABSTRACT

The intramolecular gold catalysed asymmetric hydroamination of alkenes was studied screening a series of mononuclear gold(I) and (III) complexes in combination with silver salts. Among the various chiral mono-phosphine and diaminocarbene ligands tried, the best catalysts arose from mononuclear gold(I) complexes synthesized from BINOL based phosphoramidite ligands. The latest were improved by addition of bulky substituents at specific positions of the BINOL scaffold. The resulting gold(I) complexes were combined with selected silver salts to afford efficient catalysts for intramolecular hydroamination of alkenes at mild temperatures, with good conversions and average enantioselectivities.

1. Introduction

The hydroamination of unactivated alkenes is the shortest synthetic route to secondary and tertiary amines [1]. For the enantioselective synthesis of optically pure amines, the most studied and privileged hydroamination method is metal-catalysis. Lanthanides and actinides (f-block) were widely screened and significant achievements were reported for intramolecular reactions [1b,c,g,2]. Group 4 metal (Zr, Ti) [1c,3] or main-group metal (Mg, Li) [1c,4] complexes led also to valuable results. By comparison, applications in asymmetric catalysis of transition metals from groups 3 to 11 (d-block) remain scarce but offer a broader functional group tolerance and substrate scope [1c,5,8l]. Moreover, the development of recoverable catalysts may favour groups 3–11 metals which can lead to stable and easy to handle organometallic catalysts.

Along the past years, the usefulness of gold [6] was pointed out on various C–C multiple bond substrates like alkynes [6,7], alkenes [6,8], allenes [6,9], and dienes [6,10] for both intra- and intermolecular hydroamination reactions as well as for diaminations. These results may be quite surprising because gold(I) can be considered as a challenging metal for asymmetric catalysis [11]. First, it is stressed gold(I) privileges a linear-dicoordination geometry [12] which positions the ligand and the activated substrate in a trans fashion restricting thus the asymmetric induction. Tri and tetracoordination of gold(I) proved to be less common [12,13]. Second, though the reaction mechanism appears to depend on the nature of the nucleophile, [9k,w,ah,14,15] gold(I) catalysed reactions are considered to be outer-sphere in most cases, the metal coordinating the substrate pi-system and the nucleophile attacking from the back side which is far away from the chiral ligand. However, some gold amide complexes were recently shown to be unreactive for the amination of alkynes suggesting that the inner sphere mechanism for addition to pi-bonds may not be preferred with some strong nucleophiles [16a]. In addition, it was also recently demonstrated that pi-bonds do not insert into the related gold–carbon bonds [16b]. Regarding the mechanisms of acid and gold catalysed hydroamination of alkenes and dienes, Ujaque et al. have performed interesting calculations [17]. Whereas the acid-catalysed process was shown as concerted, the gold catalysed reaction was found to be stepwise for the nucleophile-assisted and counterion-assisted pathways. Indeed, a proton-transfer agent, i.e. the nucleophile or the counterion, was crucial to lower the energy barrier for the proton-transfer step. LaLonde et al. studied through calculations and experiments the intramolecular aminoauration of unactivated alkenes providing

* Corresponding author at: ENSCL, CCCF, (Chimie-C7) CS 90108, 59652 Villeneuve d'Ascq Cedex, France. Tel.: +33 320434893/320434927; fax: +33 320436585.
E-mail addresses: christophe.michon@ensc-lille.fr (C. Michon), francine.agbossou@ensc-lille.fr (F. Agbossou-Niedercorn).

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evidence of an anti-addition mechanism for alkene aminoauration [18]. However, once prepared, such assumed catalytic intermediates didn't allow the hydroamination reaction to proceed leading only to the unreacted alkenes. The authors concluded that was due to the high energy barrier calculated for the protodeauration step [18]. Finally, the reversibility of C–Nuc bond formation was evidenced and may play an important role in the stereoselectivity of gold(I) catalysed hydrofunctionalization [18,19].

To date, three strategies have been developed in gold(I) catalysed asymmetric catalysis and to some extent to hydroamination reactions. The first one implies the use of chiral phosphate anions like TRIP in combination with a gold(I) complex to create a tight ion pair. The resulting chiral binding pocket proved to be highly efficient for some asymmetric intramolecular hydroamination of allenes [9ac,9ad]. The chiral phosphate counterion was shown to act as a ligand bonded to the gold species all along the hydroamination reaction [20].

The second concept implies the use of chiral dinuclear gold(I)-phosphine complexes. Due to the broad choice of bisphosphine ligands, this approach has been versatile for some inter- and intramolecular asymmetric hydroamination of allenes and alkenes [6,8,9]. Surprisingly, little has been reported on the role of the second gold atom and the importance of gold–gold interactions in the catalytic course and therefore in the asymmetric induction [8e].

The third strategy developed in gold(I) catalysed asymmetric catalysis implies the use of mononuclear gold(I) complex relying mainly on chiral phosphoramidite and diaminocarbene ligands. Though that approach has been efficient for various asymmetric organic reactions [6b,21-23], it has until recently not been applied to hydroamination reactions and remains promising [8a,9i,11,24].

Though gold was shown to be active for intra- and intermolecular hydroamination of alkenes [6,8], high temperatures and long reaction times are generally required. Hence, asymmetric gold catalysed hydroamination of alkenes has been scarcely studied with, to the best of our knowledge, only three specific reports published so far. First, Zhang et al. reported on gold(I) catalysed intermolecular hydroamination of ethylene and 1-alkenes with cyclic ureas with good yields and enantioselectivities [8l]. Second, Kojima and Mikami published on gold(I) catalysed intramolecular hydroamination of *N*-alkenyl ureas at room temperature with good yields and average enantioselectivities [8e]. Strikingly, these two studies relied on chiral dinuclear gold(I)-phosphine based catalysts. Kojima and Mikami assumed such species highly accelerated intramolecular hydroamination of *N*-alkenyl ureas via proximal and bimetallic activation of alkene and urea. According to the authors, rigid dinuclear gold complexes having Au–Au interactions helped providing higher enantioselectivities. While the present work was nearing completion, a third report was published by Shi et al. about the preparation and the use of several monodentate axially-chiral *N*-heterocyclic carbene and phosphine ligands for mononuclear gold(I) catalysed intramolecular hydroamination of *N*-alkenyl tosylates. Moderate yields and enantioselectivities were obtained at quite high temperatures and reaction times [8a]. Interestingly, the authors studied their gold pre-catalysts by X-ray diffraction analyses and identified a weak gold–π interaction between the Au atom and one of the ligand aromatic ring. Presumably, such interaction might also occur with the gold cationic catalyst and influence the course of the reaction.

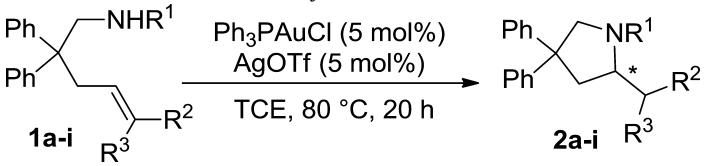
According to the previous statements, the achievement of efficient and highly selective gold catalysed hydroamination of alkenes is still a challenging field. Hence, following our interest on hydroamination and aza-Michael reactions [24,25] and considering the inadequacy of applications of chiral mononuclear gold(I) species to asymmetric hydroamination [8a,9f,11,24], we would like to report herein our own results on asymmetric intramolecular hydroamination of alkenes using mononuclear gold catalysts.

2. Results and discussion

First, we performed preliminary studies on the racemic intramolecular hydroamination of alkene with amine substrates **1a–i** using Ph_3PAuCl as pre-catalyst along with 5 mol% AgOTf (Table 1). Whereas electron rich amine substrates (entries 1–2) didn't afford any product, some electron poor substrates did. Indeed, *N*-alkenyl tosylate, benzylcarbamate and urea worked quite well (entries 3, 6, 10). The use of pre-catalyst IPrAuCl instead of Ph_3PAuCl increased significantly the product yield provided the alkene was not functionalized by any substituent (entries 7, 8, 9). Other *N*-alkenyl carboxamides proved to be non-reactive (entries 4, 5). Hence, a strong substituent effect appeared controlling the intramolecular hydroamination reaction.

A first study on asymmetric intramolecular hydroamination of alkenes using mononuclear gold catalysts was then achieved by screening various chiral ligands and complexes for the reaction of reagent **1f** (Table 2 and Fig. 1). A catalytic amount of AgOTf was used along with each gold complex in order to generate in situ the cationic active species. As already reported, *N*-alkenyl carbamates proved to be privileged substrates when gold(I) catalysts

Table 1
Amine substitution effect on reactivity.



Entry	Reagent 1a–i	R^1	R^2	R^3	Product 2a–i conversion (%)[a]
1[b]	**1a**	Bn	H	H	0 (2a)
2[b]	**1b**	CH_2Cy	H	H	0 (2b)
3	**1c**	Ts	H	H	>95 (2c)
4	**1d**	Ac	H	H	0 (2d)
5	**1e**	Bz	H	H	0 (2e)
6	**1f**	CBz	H	H	50 (2f)
7[c]	**1f**	CBz	H	H	90 (2f)
8[c]	**1g**	CBz	Me	H	0 (2g)
9[c]	**1h**	CBz	Me	Me	0 (2h)
10	**1i**	CONHPh	H	H	>95 (2i)

[a] Measured by ^1H NMR.
[b] Same result at 120 °C.
[c] With 5 mol% IPrAuCl instead of Ph_3PAuCl.