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Asymmetric Intramolecular Hydroamination of Alkenes in Mild and Wet Conditions—Structure and Reactivity of Cationic Binuclear Gold(I) Catalysts

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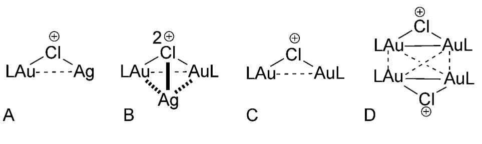
A selected diphosphine binuclear gold(I) chloride complex was combined with a silver salt to catalyze efficiently, for the first time, the asymmetric intramolecular hydroamination of alkenes with high conversions and enantioselectivities, in mild conditions and in presence of water. Both enantiomers of the products could be obtained by controlling the molecular ion-pairs through the solvent polarity. The gold(I) cationic active species was characterized unambiguously at the solid state by X-ray analysis and in solution by DOSY ^{1}H NMR experiments. No contribution of silver chloride was observed on the bonding mode of the catalyst.

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.[1c,2–6] Throughout recent years, the usefulness of gold has been applied to various C–C multiple bond substrates like alkynes, alkenes, allenes, and dienes for both intra- and intermolecular hydroamination reactions.[7] As high temperatures, long reaction times, and strict conditions are generally required, the gold catalyzed hydroamination of alkenes has been scarcely studied in its asymmetric version.[7,8] To the best of our knowledge, only four specific reports have been published so far. First, binuclear gold(I) catalysts were found to be active for intermolecular hydroamination of ethylene and 1-alkenes with cyclic ureas leading to high yields and enantioselectivities.[8d] Second, binuclear gold(I) species catalyzed intramolecular hydroamination of *N*-alkenyl ureas at room temperature with good yields and average enantioselectivities.[8c] A third work reported on the preparation and the use of several monodentate axially-chiral *N*-heterocyclic carbene and phosphine ligands for mononuclear gold(I) catalyzed intramolecular hydroamination of *N*-alkenyl tosylates. Moderate yields and enantioselectivities were obtained at quite high temperatures and reaction times.[8b] Finally, following our ongoing interest in hydroamination reactions,[9] we recently reported on mononuclear and binuclear gold(I) complexes and found phosphoramidite ligands could lead to valuable catalysts for the intramolecular hydroamination of several alkenes at mild temperatures, with good conversions and average enantioselectivities.[8a] Like many organometallics, most gold complexes require the combined use of silver salts to be activated. Indeed, reactive gold cationic species can be generated by abstraction of halides from neutral complexes. However, the existence of these so-called “naked gold complexes” [AuL] is still discussed for lack of structural evidence as isolable and well-defined species.[10,11c] Recent works have reported on the influence of silver salts on gold catalyzed reactions.[11] Impact on conversions and selectivities were observed and the interference of silver and chloride has been highlighted by several bonding modes for cationic monomeric and oligomeric phosphine gold chloride complexes (Scheme 1, A to D).[11d,12] Herein, we report on the combination of a binuclear gold(I) chloride complex and a silver salt to catalyze efficiently asymmetric intramolecular hydroamination of alkenes in mild and wet conditions, without any silver chloride effect on the bonding mode of the catalyst.



Scheme 1. Bonding modes of gold chloride complexes.

Our study started by screening several diphosphine ligands within earlier optimized reaction conditions.[8a] We found the best catalyst arose from DTBM-Segphos phosphine ligand ((*S*)-L7, see the Supporting Information). Though monocationic binuclear complexes were shown to be preferred in the case of the intramolecular hydroalkoxylation of allenes,[13] we found dicationic binuclear gold complexes were much more active and selective for the intramolecular hydroamination of alkenes (see Scheme 2 and the Supporting Information). Additional screenings confirmed toluene was the best non-polar solvent and perchlorate was the best anion (see the Supporting Informa-

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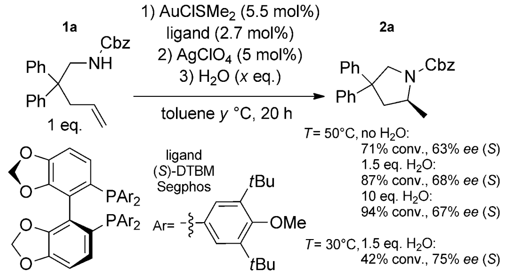
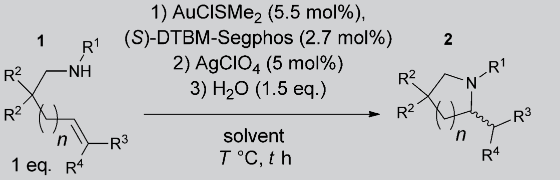


Scheme 2. First results.

tion). Control experiments proved the reaction was not catalyzed by $AgClO_4$ itself. However, addition of the silver salt at last,[11c] when the gold chloride complex was premixed with the substrate, lowered significantly the conversion and slightly the enantioselectivity. The same trend was observed when catalyst was filtered through a PTFE filter (see the Supporting Information). Hence, at this stage, an effect of silver chloride on the hydroamination reaction and on the catalyst could not be excluded. Interestingly, the addition of water to the reaction mixture significantly improved yields and to a lesser extent enantioselectivities. To check if the dicationic gold(I)-perchlorate catalyst was likely to be hydrolyzed,[14] we followed by NMR spectroscopy the reaction of **1a** with a stoichiometric amount of pre-formed gold complex. The latter displayed unchanged ^{31}P NMR spectra along the reaction and no hydrate or hydroxide species could be observed through ^{1}H nucleus (see the Supporting Information). In addition, the presence of free protons in the reaction medium could be excluded because the use of a non-coordinative base like 2,6-di-*tert*-butyl-pyridine or a proton trap like $PhSi(Me)_3$ did not have any effect on the reaction (see the Supporting Information). Considering the significance of toluene as a solvent for the hydroamination reaction, the role of anion and cation π-interactions[15,16] between the catalyst and toluene may be invoked in the light of previous results in the field of gold catalysis.[8b,17] Moreover, regarding the increase of the conversions and enantioselectivities upon addition of water in the reaction medium, the propensity of perchlorate salts to increase the surface tension of water and, at the meantime, to act as salting-in agents might contribute to a better solvation of catalyst and organic molecules. Indeed, according the Hofmeister series, the perchlorate anion is a chaotrope acting through surface tension and direct ion binding.[18,19] Though well known in enzymatic catalysis,[19b,c] such anion effect has been less studied in homogeneous catalysis using transition metals.

Scope and limitations of the catalyst were investigated (Table 1). Regarding the enantiomeric excess (*ee*), *N*-alkenyl CBz substrate **1a** led to the best results (entries 1–3). Though highest conversions and *ee* were obtained at 30 °C, the reaction proved to be faster at 50 °C and remained quite selective. Surprisingly, by changing the solvent from toluene to methanol, we observed a reversal of enantioselectivity (entries 4, 5). As reported by Toste et al.,[20] the use of an alcohol along with a cationic binuclear gold complex can generate an acidic species, which catalyzes the hydroamination reaction of 4,6-heptadienyl sulfonamides through a Brønsted-acid catalyzed pathway. To check such a possibility, we performed a series of reactions by adding 1.5 equivalent of an alcohol to the reaction mixture in toluene (see the Supporting Information). Depending on the nature of the alcohol used, the conversions were improved, but no global trend could be observed. Only the use of (+)-phenylethanol, (−)-menthol, or methanol could increase slightly the *ee* values to 67 % *ee*, whereas conversions were respectively 88, 67, and 97 %. Finally, no hydroamination reaction of **1a** could be observed in the presence of a catalytic amount of HOTf (see the Supporting Information). On the basis of

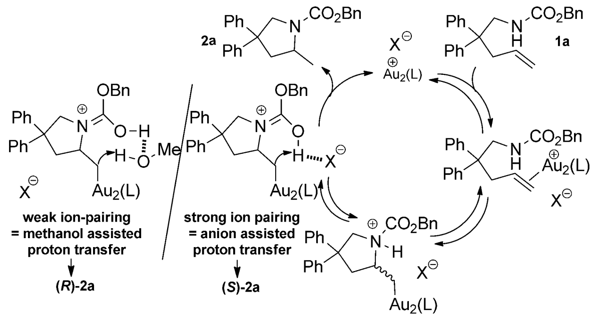
Table 1. Substrate scope study.



Entry	Reagent	R1	R2	R3	R4	*n*	Solvent	*T* [°C]	*t* [h]	Conv.[a] [%]	*ee*[b] [%]	Config.
1	**1a**	CBz	Ph	H	H	1	toluene	50	20	**2a** 87	68	(*S*)
2	**1a**	CBz	Ph	H	H	1	toluene	30	110	**2a** 90	75	(*S*)
3	**1a**	CBz	Ph	H	H	1	toluene	0	68	**2a** 19	68	(*S*)
4	**1a**	CBz	Ph	H	H	1	methanol	50	20	**2a** 61	−54	(*R*)
5	**1a**	CBz	Ph	H	H	1	methanol	30	110	**2a** 58	−59	(*R*)
6	**1b**	CBz	$-(CH_2)_5-$	H	H	1	toluene	50	20	**2b** 85	76	n.d.[c]
7	**1b**	CBz	$-(CH_2)_5-$	H	H	1	methanol	50	44	**2b** 56	−23	n.d.
8	**1c**	CBz	Me	H	H	1	toluene	50	86	**2c** 0	–	–
9[d]	**1d**	CBz	H	H	H	1	toluene	50	20	**2d** 19	6	n.d.
10	**1e**	CBz	Ph	Me	H	1	toluene	50	20	**2e** 0	–	–
11	**1f**	CBz	Ph	Me	Me	1	toluene	50	20	**2f** 18	11	n.d.
12[d,e]	**1g**	CBz	Ph	H	H	2	toluene	50	48	**2g** 0	–	–
13	**1h**	Fmoc	Ph	H	H	1	toluene	50	20	**2h** 64	63	n.d.
14[f]	**1h**	Fmoc	Ph	H	H	1	methanol	50	20	**2h** 0	–	–
15	**1i**	CO_2Me	Ph	H	H	1	toluene	50	20	**2i** 96	68	n.d.
16	**1i**	CO_2Me	Ph	H	H	1	methanol	50	20	**2i** 88	−61	n.d.
17	**1j**	Boc	Ph	H	H	1	toluene	50	20	**2l** 53	24	n.d.
18	**1j**	Boc	Ph	H	H	1	methanol	50	20	**2l** 47	−74	n.d.
19	**1k**	CONHPh	Ph	H	H	1	toluene	50	20	**2k** 95	6	n.d.
20	**1k**	CONHPh	Ph	H	H	1	methanol	50	20	**2k** 95	−46	n.d.

[a] From ^{1}H NMR. [b] From HPLC. [c] Not determined. [d] At 100 °C. [e] Same result in methanol. [f] Same result if no water added.

these additional results, we concluded that any Brønsted-acid catalysis[20] was unlikely. Beyond the simple solvent effect, the critical change in the reaction mechanism could arise from the weak molecular ion pairs induced by the use of methanol. The latter has already been shown to act as a proton-transfer agent,[21] similar in feature to that of anions[22] (Scheme 3).



Scheme 3. Mechanistic proposal.

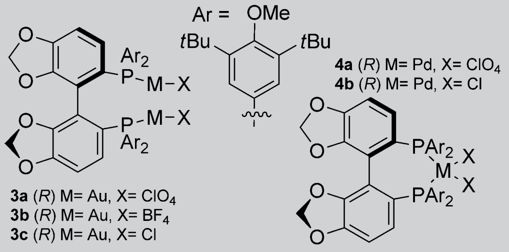
Therefore, the reaction started by the nucleophilic attack, which was previously found to be reversible.[23] Second, the tautomerization of the resulting intermediate was assisted by the perchlorate.[22] Finally, the stereochemical outcome of the hydroamination reaction appeared to be defined during the final protodeauration step[23] by differentiation of the two diastereomeric intermediates, depending on the solvent used (Scheme 3).

The change of substituents at the C2 position of the alkenyl chain had even a more critical effect on the reactivity and stereochemical outcome of the hydroamination reaction, previously attributed to some Thorpe–Ingold effects (entries 6–9).[24] Indeed, at the exception of substrate **1 b**, conversions and enantioselectivities were very low for reagents **1 c** and **1 d**, respectively, with methyl substituents and with a 5-hexenyl chain (entries 8, 9). In addition, amine reactivity proved to be sensitive to alkene substituents and ring size because substrates **1 e**–**g** did not react well, even within long reaction times (entries 10–12). Other substrates like *N*-alkenyl Fmoc, and methylester **1 h** and **1 i** afforded good conversions and *ee* (entries 13–16). The reactivity of *N*-alkenyl Boc, and urea substrates, **1 j** and **1 k**, was highly dependent of the solvent used. The best conversions and *ee* were obtained with methanol as a solvent (entries 17–20).

To define in solution the bonding mode of our cationic gold(I) species, DOSY ^{1}H NMR experiments were performed on gold complexes **3 a**–**c** and palladium references **4 a**–**b** (Table 2). We found a good agreement between diffusion coefficient *D* and hydrodynamic radius r_H of all species. This confirmed the presumed nuclearity and coordination of our catalysts and proved any chloride and/or silver bridged species[11c,d] was unlikely. Indeed, compounds with higher molecular volumes and weights would have displayed lower diffusion coefficient D and higher hydrodynamic radius r_H.

At the solid state, the structure of gold catalyst **3 b** was confirmed by X-ray diffraction analysis (Figure 1). The data were refined using a rigid body approach because *tert*-butyl substituents were disordered. Tetrafluoroborate anions proved to be coordinated to the gold atoms which were not bond to each other. Hence, by using weakly coordinative anions like perchlorate and tetrafluoroborate, complexes **3 a**–**b** could be considered as neutral species like it was previously observed for other complexes with NTf_2 anion.[25] We measured for **3 b** a molecular radius of 8.989(19) Å (see the Supporting Information), which was close to its r_H value, calculated from the DOSY ^{1}H NMR experiments. On the whole, we concluded no contri-

Table 2. Results of DOSY ^{1}H NMR experiments.



3a (*R*) M= Au, X= ClO_4
3b (*R*) M= Au, X= BF_4
3c (*R*) M= Au, X= Cl
4a (*R*) M= Pd, X= ClO_4
4b (*R*) M= Pd, X= Cl

Compound	D(^{1}H) [10^{-9} m^2 s^{-1}]	r_H [Å]
(*S*)-DTBM-Segphos	5.03	8.1
(*R*)-**3 a**	4.98	8.2
(*R*)-**3 b**	4.85	8.4
(*R*)-**3 c**	4.96	8.2
(*R*)-**4 a**	4.91	8.3
(*R*)-**4 b**	4.96	8.2

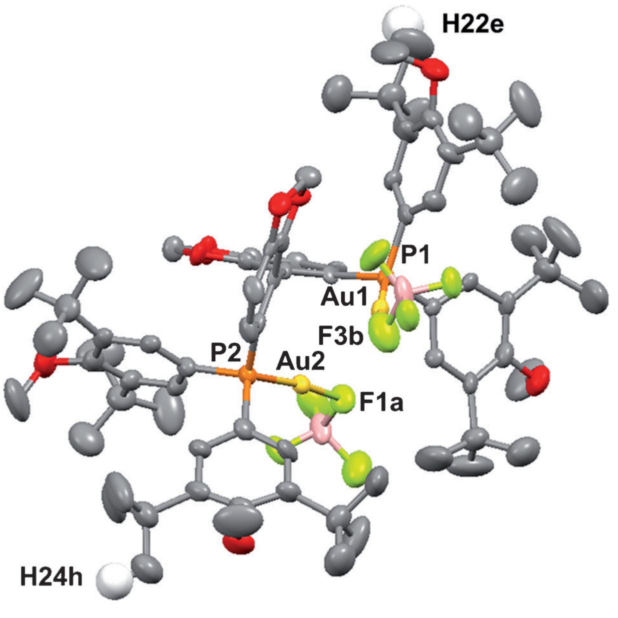


Figure 1. Molecular structure of catalyst **3 b** at the solid state. Thermal ellipsoids are shown at the 50 % probability level. Hydrogens atoms and 2 molecules of toluene were omitted for clarity. Selected bond lengths (Å): Au1–Au2 4.390(19), P1–Au1 2.213(2), P2–Au2 2.205(2), Au1–F3b 2.101(15), Au2–F1a 2.095(15), H22e–H24h 17.9778(6). CCDC 995301.

bution of silver chloride was observed on the bonding mode of complexes **3 a**–**b**.

To summarize, when combined with silver perchlorate, a selected binuclear gold(I) chloride complex based on DTBM-Segphos ligand catalyzed efficiently for the first time the asymmetric intramolecular hydroamination of alkenes at mild temperatures in presence of water with high conversions and enantioselectivities. Both enantiomers of the products could be obtained by controlling the molecular ion-pairs through the solvent polarity. The involved binuclear gold(I) cationic catalyst which has been previously discussed for lack of structural proofs, was characterized unambiguously at the solid state by X-ray analysis and in solution by DOSY ^{1}H NMR experiments.

Experimental Section

Typical procedure for the substrate screening: In a glovebox, $AuS(Me)_2Cl$ (0.01 mmol, 2.95 mg) and (*S*)-DTBM-Segphos (0.005 mmol, 5.90 mg) are prepared in a first Schlenk flask. Under a nitrogen atmosphere, dry dichloromethane (1 mL) is then added and the resulting mixture is stirred for 1 hour at room temperature. Afterwards, the solvent is evaporated under vacuum and the resulting solid is dried 30 min before addition of $AgClO_4$ (0.009 mmol, 1.87 mg) in a glovebox. Under a nitrogen atmosphere, dry toluene (1 mL) is added and the resulting solution is stirred for 30 min before being transferred to a second Schlenk flask containing the corresponding substrate (0.18 mmol). Finally, H_2O (0.28 mmol, 5 μL) is added under nitrogen to the reaction mixture. After 20 h under stirring at 50 °C, the solution is filtered through a pad of silica gel using dichloromethane as solvent. After evaporation of solvents under vacuum, the resulting oil is studied by ^{1}H NMR spectroscopy and HPLC analysis.

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Keywords: alkene · asymmetric catalysis · gold · hydroamination · phosphine ligands · silver

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