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Asymmetric Intramolecular Hydroamination of Allenes using Mononuclear Gold Catalysts

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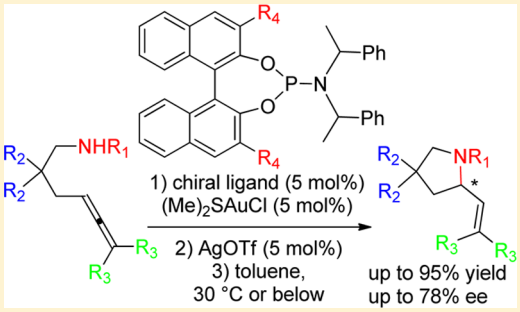
Supporting Information

ABSTRACT: The intramolecular gold-catalyzed asymmetric hydroamination of allenes was studied by screening a series of mononuclear gold(I) and -(III) complexes in combination with silver salts. Among the various chiral monophosphine 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 allenes at room temperature or below, with good conversions and enantioselectivities.



INTRODUCTION

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

In the past few years, the usefulness of gold[6] has been pointed out in various C−C multiple bond substrates such as 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, in that gold(I) can be considered as a challenging metal for asymmetric catalysis, as highlighted recently by Fürstner et al.[11] First, these authors stressed gold(I) favors a linear-dicoordination geometry[12] which positions the ligand and the activated substrate in a trans fashion, thus restricting 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,[14,15] gold(I)-catalyzed reactions are considered to be outer sphere in most cases, the metal coordinating the substrate π system and the nucleophile attacking from the back side which is far away from the chiral ligand. To overcome such drawbacks, three strategies have been developed in gold(I)-catalyzed asymmetric catalysis and to some extent for hydroamination reactions.

The first strategy implies the use of chiral phosphate anions such as 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 hydroaminations of allenes.[9u,v] The chiral phosphate counterion was shown to act as a ligand bonded to the gold species all along the hydroamination reaction.[16]

The second concept involves 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 hydroaminations 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. Moreover, a recent report from Widenhoefer et al.[9a] has shed light on difficulties arising from the use of dinuclear gold catalysts. Indeed, a decreasing enantioselectivity of the gold-catalyzed intermolecular hydroamination of allenes was observed, while in the meantime conversions increased. As assumed by the authors, whereas one gold center of the bis(gold) catalyst participates in the allene

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activation/C−N bond formation, the second center is apparently free to coordinate the N-allylic carbamate product, leading to a less selective catalyst species.

The third strategy developed in gold(I)-catalyzed asymmetric catalysis involves the use of a mononuclear gold(I) complex relying mainly on chiral phosphoramidite and diaminocarbene ligands. Though that approach has been efficient for various asymmetric organic reactions,[6b,17,18] it has until recently[11,19] not been applied to hydroamination reactions and remains promising. While the work reported herein was in progress in our laboratory, Fürstner et al. reported seminal examples of gold(I) phosphoramidite catalysts for asymmetric intramolecular hydroamination reactions of allenes.[11]

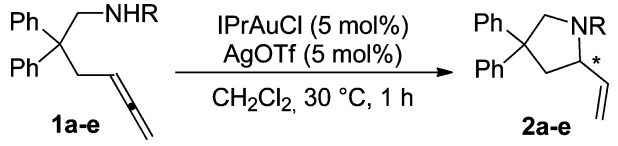
From a mechanistic point of view, gold(I)-catalyzed hydroamination reactions proved to be intriguing. Indeed, with poor nucleophiles, gold cationic complexes were shown to be the main catalysts, as no Brønsted acid was generated by coordination of the cationic gold species with weakly basic amine reagents.[14] However, stronger nucleophiles, including ammonia and hydrazine, proved to lead to two potent catalysts, a Brønsted acid and a gold amine complex. The latest was shown to catalyze exclusively the hydroamination reaction in several examples. In the case of enantiopure allene substrates, the reaction with amines proceeded smoothly with high chirality transfer, thus excluding the acid species as the main catalyst.[15] Though they suffer from a narrow reaction scope almost limited to disubstituted allenes, such chirality transfer and memory of chirality have emerged as useful tools in organic chemistry.[15j] Moreover, the nucleophilicity of the amine reagent seems to direct the nature of the catalyst species for the hydroamination reaction. Whereas an outer-sphere mechanism seems to be applied to weak amines which add in an anti fashion to the gold complex,[9f,t,x,14] an inner-sphere mechanism may be preferred for stronger nucleophiles.[9p,15h] However, some gold amide complexes were recently shown to be unreactive in the amination of alkynes, suggesting that the inner-sphere mechanism for addition to π bonds may not be preferred in some cases.[20] Interestingly, Ujaque et al. have compared by calculations the mechanisms of acid- and gold-catalyzed hydroaminations of alkenes and dienes.[21] Whereas the acid-catalyzed process was shown to be concerted, the gold-catalyzed 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 in lowering the energy barrier for the proton transfer step. Toste, Goddard, et al. studied through calculations and experiments the intramolecular aminoauration of unactivated alkenes, providing evidence of an anti addition mechanism for alkene aminoauration.[22] However, once prepared, such assumed catalytic intermediates did not 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.[22] The lattest was recently shown to be also the turnover-limiting step for gold(I)-catalyzed intramolecular allene hydroalkoxylation.[23a] The active mono(gold)vinyl complex proved to be in equilibrium with an inert off-cycle bis(gold) vinyl complex. In addition, the reversibility of C−Nuc bond formation was evidenced and might play an important role in the stereoselectivity of gold(I)-catalyzed hydrofunctionalization.[22,23] Furthermore, the nucleophile concentration proved to be critical for the stereochemical outcome of intermolecular hydroamination reactions of allenes.[9h] At high nucleophile concentrations, the amine addition was fast and favored a two-step, no intermediate pathway with a high level of chirality transfer. At low nucleophile concentration, a planar gold allene intermediate was formed and induced a loss of chirality. In addition, steric hindrance at the allylic positions was shown to determine the possible isomeric forms of the bent, cationic η^1-gold(I) transition species.[24]

On the whole, according to the previous statements, a deep understanding of gold catalyst activity and the achievement of highly selective gold-catalyzed hydroaminations of allenes and alkenes are still challenging areas. Hence, following our interest on hydroamination and aza-Michael reactions catalyzed by copper and gold complexes[25] and considering the inadequacy of applications of chiral mononuclear gold(I) species to asymmetric hydroamination,[11,19] we wish to report herein our own results on asymmetric intramolecular hydroaminations of allenes using mononuclear gold catalysts.

RESULTS AND DISCUSSION

In order to study the substituent effect on amine reactivity, we performed preliminary studies on the racemic intramolecular hydroamination of allene with amine substrates **1a−e** using IPrAuCl as precatalyst along with 5 mol % of AgOTf (Table 1). The catalysis proceeded well for electron-poor amine substrates (entries 1−4). Indeed, almost quantitative conversions were obtained in 1 h at 30 °C.

Table 1. Amine Substitution Effect on Reactivity



entry	reagent	R	product conversion (%)[a]
1	**1a**	CBz	>95 (**2a**)
2	**1b**	Ts	>95 (**2b**)
3	**1c**	Boc	>95 (**2c**)
4	**1d**	CONHPh	>95 (**2d**)
5	**1e**	Bn	>77 (**2e**)[b]

[a]Measured by NMR. [b]At 80 °C for 66 h in toluene.

By comparison, a poor reactivity was observed for the electron-rich *N*-benzyl allene amine **1e**, which required a stronger and much longer heating (80 °C, 66 h) to reach 77% conversion (entry 5). The first study on asymmetric intramolecular hydroamination of allenes using mononuclear gold catalysts was achieved by screening various chiral ligands and complexes for the reaction of reagent **1a** (Table 2 and Chart 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*-allenyl carbamates proved to be privileged substrates when dinuclear gold(I) catalysts were used.[9t,x,z] In addition, as highlighted in the Introduction, the carbamate function was shown to participate in a low-barrier mechanistic hydroamination pathway through carbamate tautomerization assisted by a triflate anion acting as a proton shuttle.[21] Our screening started with mononuclear gold(I) complexes **3** and **5** based on diaminocarbene ligands,[26] but poor conversions and enantioselectivities were obtained (Chart 1 and Table 2 entries 1 and 3). The new gold(III) diaminocarbene complexes **4** and **6** were synthesized and

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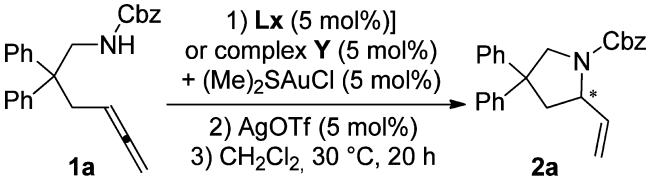
Table 2. Screening of Mononuclear Gold(I) and -(III) Catalysts

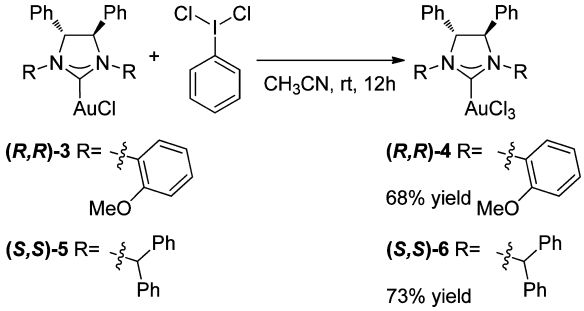


entry	ligand (L_x) or complex (Y)	conversion[a] (%)	ee (%)[b]	configuration[c]
1	(*R*,*R*)-**3**	7		
2	(*R*,*R*)-**4**	>95	14	*R*
3	(*R*,*R*)-**5**	24	3	*S*
4	(*S*,*S*)-**6**	0		
5[d]	(*S*,*R*,*R*)-L_1	>95	42	*S*
6	(*R*,*S*,*S*)-L_1	>95	41	*R*
7	(*S*,*R*)-L_2	50	13	*S*
8	(*S*,*R*,*R*)-L_3	10	6	*S*
9	(*R*,*R*,*R*)-L_4	>95	33	*R*
10	(*R*)-L_5	>95	16	*R*
11	(*S*)-L_6	70	17	*S*
12	(*S*)-L_7	>95	33	*S*
13	(*S*,*S*)-L_8	0		
14	(*R*,*R*,*R*)-L_9	>95	47	*S*
15	(*R*,*R*)-L_{10}	>95	15	*S*

[a]Measured by ^{1}H NMR. [b]Measured by HPLC at 220 nm. [c]Determined by HPLC by comparison with previous work (see the Supporting Information). [d]Same result for 1 h reaction.

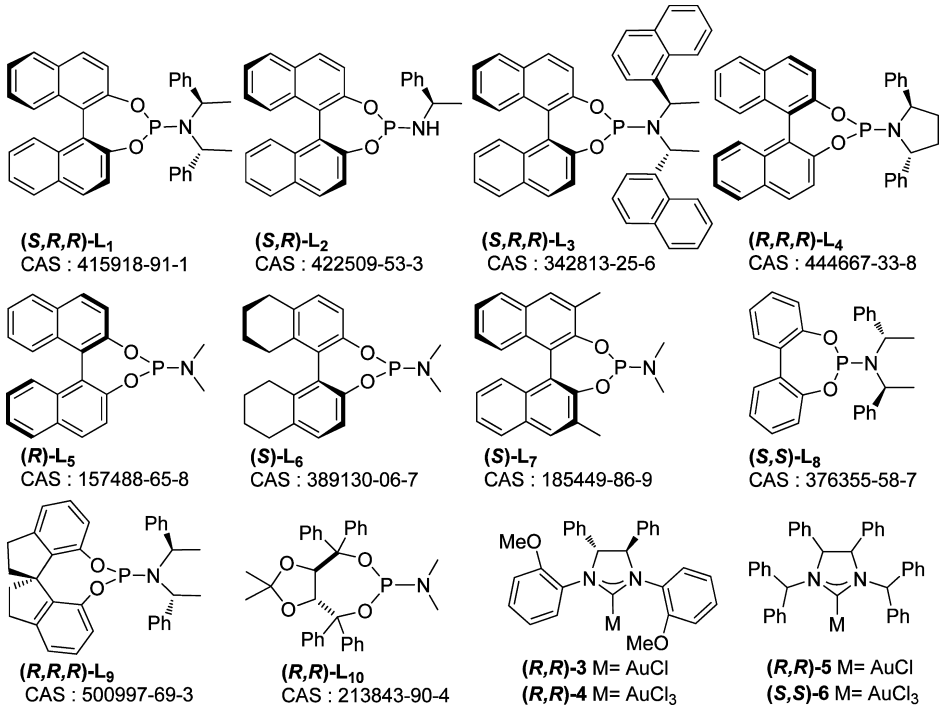
tested in the asymmetric intramolecular hydroamination of allene **1a** (Scheme 1 and Table 2, entries 2 and 4). Gold(III) precatalyst **4** displayed a high conversion and a poor enantioselectivity, whereas complex **6** was inactive. The result obtained using **4** can be explained by the coordination of one of the neighboring methoxy substituents to the gold(III) center;

Scheme 1. Mononuclear Diaminocarbene Gold(III) Catalyst Synthesis



such an effect has already been reported to significantly enhance the activity of gold-catalyzed hydrofunctionalization of allenes.[9p] We next switched to mononuclear gold(I) complexes containing phosphoramidite ligands (Chart 1 and Table 2). First, L_1 based on BINOL and the Whitesell amine was used, affording product **2a** with high conversion (95%) and average enantiomeric excess (ee) (42%) (Table 2, entries 5 and 6). The enantioselectivity of **2a** proved to be stable over time, the same ee value being measured at 1 and 20 h of reaction (entry 5). It is worth noting that the ee of the reaction product **2a** appeared to be proportional to the ee value of the chiral ligand L_1, suggesting the absence of nonlinear effects (see the Supporting Information, Table S1 and Figure S1).[27] Next, as shown by the use of phosphoramidite ligands L_2–L_5, any change in the chiral amine fragment proved to have a negative effect on the conversion and/or the enantioselectivity (Table 2, entries 7–10). Moreover, the switch from the Monophos ligand L_5 to L_6, that is to say a change from a BINOL scaffold to a partially hydrogenated one, led to a decrease in the conversion (entries 10 and 11) and demonstrated the negative effect of an increase in the ligand dihedral angle. The change to ligand L_8 based on a

Chart 1. Ligands and Complexes Used for the Screening of Mononuclear Gold(I) and -(III) Catalysts



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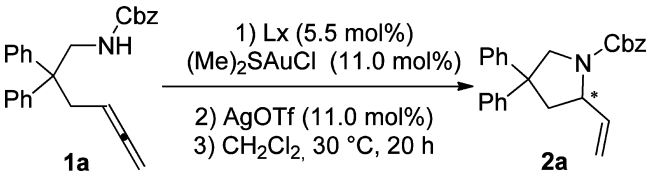
biphenyl scaffold had an even more dramatic effect, no conversion being observed (entry 13). It was worth noting that the 3,3′-substitution of the BINOL backbone by two methyl substituents ($\mathbf{L_7}$) led to a significant increase in the enantioselectivity (from 16 to 33% ee, entries 10 and 12). The spiro phosphoramidite ligand $\mathbf{L_9}$ afforded the best ee (47%), whereas the taddol-based ligand $\mathbf{L_{10}}$ gave a poor one (15%) (entries 14 and 15). Except for these last two ligands, which are based on different diol scaffolds, it appeared that the chirality of the BINOL fragment was the key factor controlling the stereochemistry of the product **2a**, both displaying the same configuration (entries 5−12).

In comparison to mononuclear gold(I) catalysts, dinuclear gold(I) catalysts did not afford better conversions and enantioselectivities under the same experimental conditions (Table 3 and Chart 2). A maximum of 90% conversion and

Table 3. Screening of Dinuclear Gold(I) Catalysts



entry	ligand ($\mathbf{L_x}$)	conversion[a] (%)	ee (%)[b]	configuration[c]
1	(*S*)-$\mathbf{L_{15}}$	90	42	*R*
2[d]	(*S*)-$\mathbf{L_{16}}$	0		
3	(*S*)-$\mathbf{L_{17}}$	90	21	*R*
4	(*R*,*R*)-$\mathbf{L_{18}}$	90	18	*S*
5	(*R*,*R*)-$\mathbf{L_{19}}$	90	7	*S*
6	(*R*,*R*)-$\mathbf{L_{20}}$	90	21	*R*
7[e]	(*S*,*S*)-$\mathbf{L_{21}}$	0		
8[e]	(*S*,*S*)-$\mathbf{L_{22}}$	0		

[a]Measured by ^{1}H NMR. [b]Measured by HPLC at 220 nm. [c]Determined from HPLC by comparison of previous work. [d]Performed with $AgClO_4$ in toluene. [e]The same results were obtained with a 1/1 gold/ligand ratio.

42% ee was reached with the biphep ligand $\mathbf{L_{15}}$ (entry 1). However, it was previously reported that a gold(I) catalyst based on $\mathbf{L_{15}}$ could lead to a much higher enantioselectivity for product **2a**, provided different anions, solvents, and reaction temperatures were used.[9x] Surprisingly, the change to $\mathbf{L_{16}}$ with a Segphos backbone led to complete loss of reactivity (entry 2). The use of trans ligands $\mathbf{L_{17}}$ and $\mathbf{L_{18}}$ (entries 3 and 4) or P-chiral phosphines $\mathbf{L_{19}}$ and $\mathbf{L_{20}}$ (entries 5 and 6) afforded **2a** in high conversions but moderate enantioselectivities. Finally, the use of chiral secondary phosphine oxides $\mathbf{L_{21}}$ and $\mathbf{L_{22}}$ did not allow any reaction (entries 7 and 8).

Regarding our screening of mononuclear gold(I) complexes issued from phosphoramidite ligands, we chose to focus on ligand $\mathbf{L_1}$, even though $\mathbf{L_9}$ was found to give the best results of our study. Indeed, BINOL-based phosphoramidite ligands[17] appeared to afford us broader possibilities of derivatization in comparison to the spiro-based ligands.[28]

In order to check the substituent effects on the selectivity of the reaction, we screened several substrates using ligand $\mathbf{L_1}$ (Table 4).

First, we reinvestigated the substituent effect on amine reactivity. All reactions afforded an almost quantitative conversion at 30 °C in 20 h, except for *N*-benzyl allenyl substrate **1e**, which required a 100 °C heating (Table 4, entry 5). Regarding the enantioselectivity, CBz and Boc substituents were by far the most appropriate with values of 42 and 41% ee, the *N*-urea allenyl substrate leading to a 28% ee (entries 1, 3, and 4). By offering a 32% ee, the tosyl group was less selective and induced a reversal of the stereoselectivity (entry 2). No enantioselectivity could be observed for *N*-benzyl allenyl reagent **1e** (entry 5). The mononuclear gold(I) catalyst based on the phosphoramidite ligand **L1** appeared to be sensitive to substituents on the allene moiety. For example, *N*-carbamate tris-substituted allene substrate **1f** afforded only a 22% ee (entry 6). The change of substituents at the C2 position of the 4,5-hexadienyl chain had an even more critical effect on the stereochemical outcome of the hydroamination reaction, enantioselectivities being very low for methyl and cyclohexyl substituents (entries 1, 7, and 8). A similar trend was observed when dinuclear gold(I) catalysts were used, though enantioselectivities were higher.[9x]

We next focused on the influence of the anion on the conversion and enantiomeric excess (Table 5). Among the various silver salts screened, triflate, tosylate, and perchlorate anions appeared to be the most appropriate (entries 1−10). Moreover, when no ligand or gold was used, silver triflate did not catalyze the hydroamination of **1a** (entry 6). When product **2a** was formed, the enantioselectivity and the nature of the ion pairing were found to be unrelated under our reaction conditions. A gold(I) catalyst based on **L1** proved to be unreactive when associated with chiral TRIP phosphate anion, even when stronger reaction conditions were used (entries 11 and 12).

To pursue our study on the influence of reaction parameters, various solvents were screened (Table 6). Except for acetonitrile (entry 13), the reaction ran quite well in polar or apolar solvents (entries 1−12). However, we noticed that the enantiomeric excesses were higher when reactions were performed in apolar aromatic solvents (entries 3−7) and concluded that tight ion pairs were critical to reach high levels of enantioselectivity. When the temperature was decreased to 0 °C and to −20 °C, the reaction did not proceed in dichloromethane and THF (entries 2 and 9) but did run smoothly in toluene, reaching respectively 62 and 67% ee (entries 4 and 5). That last enantioselectivity was obtained with a reduced conversion, suggesting a longer reaction time was needed. Moreover, the reaction outcome remained unchanged upon removal of AgCl by filtration through Celite of the phosphoramidite mononuclear gold(I) cationic species prepared prior to the catalysis (entry 1). Hence, no "silver effect" was observed in our gold-catalyzed hydroamination reactions.[29]

Considering our results and the general trends in gold(I)-catalyzed asymmetric reactions,[17] a series of phosphoramidite ligands related to $\mathbf{L_1}$ was foreseen. Based on the Whitesell amine and on BINOL, these ligands carry bulky substituents at the 3,3′-positions of the BINOL scaffold (see Chart 3, Table 7, and the Supporting Information).[30] As illustrated by some MM2 calculations, we were confident such phosphoramidite ligands would afford an enhanced steric hindrance around the gold(I) catalytic center and would lead to a better enantioselectivity (see the Supporting Information, Chart S1).

The new phosphoramidite ligand $\mathbf{L_{14}}$ was synthesized by reaction of the functionalized BINOL (*R*)- or (*S*)-**8d** with PCl_3 and the Whitesell amine **7** of defined configuration (Scheme 2). All of the other 3,3′-substituted ligands (Chart 3) were prepared according to the same synthetic pathway and previously reported procedures (see the Supporting Informa-

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Chart 2. Ligands Used for the Screening of Dinuclear Gold(I) Catalysts

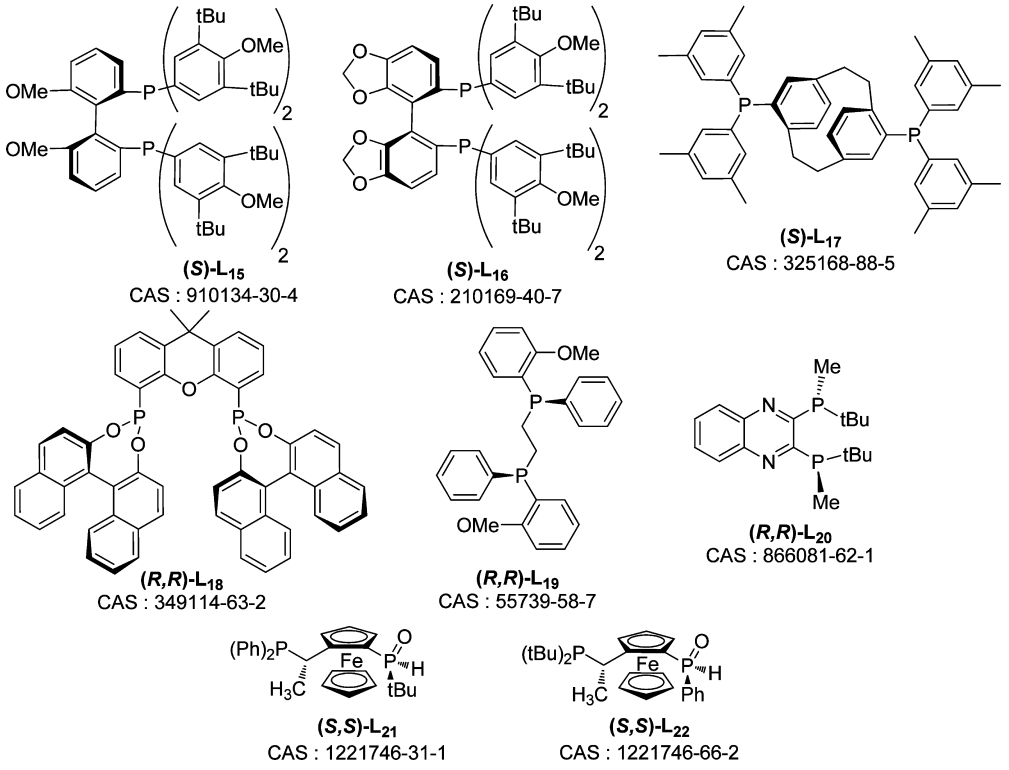
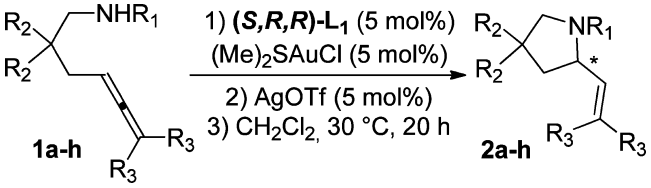


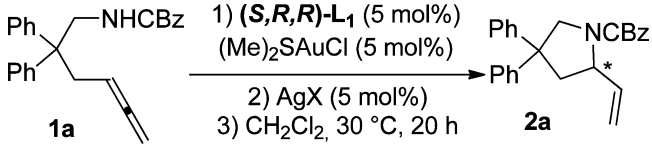
Table 4. Substituent Effects on Enantioselectivity



entry	R_1	R_2	R_3	conversion (%)[a]	ee (%)[b]
1	CBz	Ph	H	>95 (**2a**)	42
2	Ts	Ph	H	>95 (**2b**)	−32
3	Boc	Ph	H	>95 (**2c**)	41
4	CONHPh	Ph	H	>95 (**2d**)	28
5[c]	Bn	Ph	H	>95 (**2e**)	0
6	CBz	Ph	Me	93 (**2f**)	22
7	CBz	Me	H	>95 (**2g**)	9
8	CBz	$-(CH_2)_5-$	H	>95 (**2h**)	7

[a]Measured by ^{1}H NMR. [b]Measured by HPLC. [c]Performed at 100 °C for 20 h.

Table 5. Silver Salt Screening



entry	AgX	conversion (%)[a]	ee (%)[b]	configuration[c]
1	$AgSbF_6$	>95	24	*S*
2	$AgClO_4$	85	41	*S*
3	$AgBF_4$	>95	36	*S*
4	$AgNTf_2$	>95	26	*S*
5	AgOTf	>95	42	*S*
6[d]	AgOTf	0		
7[e]	AgOTs	>95	46	*R*
8	AgPNB	0		
9	$AgNO_3$	0		
10	AgBARF	>95	19	*S*
11[f,g]	(*R*)-AgTRIP	0		
12[g]	(*S*)-AgTRIP	0		

[a]Measured by ^{1}H NMR. [b]Measured by HPLC at 220 nm. [c]Determined by HPLC (see the Supporting Information). [d]Performed without $(Me)_2SAuCl$ and L_1. [e]Performed with (*R,S,S*)-L_1. [f]For 74 h. [g]Less than 10% conversion in toluene at 100 °C for 26 h.

tion). First, catalytic tests were performed on the most appropriate substrate, i.e. **1a**, performing the reactions under our best experimental conditions, in toluene at −20 °C for 20 h with AgOTf (Table 7, Chart 3). We started by studying L_9 again, but no significant increase of enantioselectivity was observed and conversion was reduced (entry 1). The use of phosphoramidite ligand L_1 confirmed the enhanced ee previously obtained and showed a close correlation between conversions and the ligand configurations (entries 2 and 3). We next studied the four stereoisomers of phosphoramidite ligand L_{11} bearing phenyl substituents. Again, conversions were highly dependent on the ligand configuration, values being quite disparate (entries 4−7). With an average 55% conversion and a good 78% ee, the ligand (*S,R,R*)-L_{11} afforded the best result (entry 7). A final attempt was run at −40 °C, but no reaction occurred (entry 8). Substrates **1b−d,g** were then tested using ligand (*S,R,R*)-L_{11} at −20 °C for 20 h. By offering a 44% ee, compound **1b**, bearing a tosyl group, was less selective and induced a reversal of the stereoselectivity, conversion being high (entry 9). Compound **1c** with a Boc substituent afforded a good enantioselectivity (66% ee), but conversion was moderate (entry 10). The *N*-urea allenyl substrate **1d** led to average enantiomeric excess and conversion (entry 11). Finally, the

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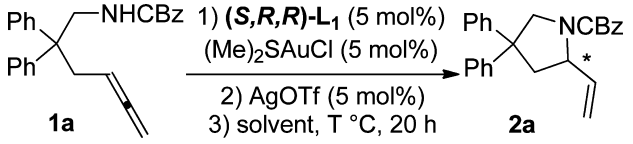
Table 6. Solvent Screening



entry	solvent	T (°C)	conversion (%)[a]	ee (%)[b]
1[c]	CH_2Cl_2	30	>95	42
2[d]	CH_2Cl_2	0	0	
3	toluene	30	>95	52
4	toluene	0	>95	62
5	toluene	−20	25	67
6	benzene	30	>95	57
7	*m*-xylene	30	>95	51
8	THF	30	>95	47
9[d]	THF	0	0	
10	1,4-dioxane	30	>95	51
11	CH_3NO_2	30	>95	31
12	CF_3CH_2OH	30	>95	29
13	CH_3CN	30	10	36

[a]Measured by ^{1}H NMR. [b]Measured by HPLC at 220 nm. [c]The same result was obtained using catalyst purified by filtration over Celite. [d]The same result was obtained at −20 °C for 20 h.

reaction of compound **1g** at 0 °C afforded a 68% conversion along with a moderate enantioselectivity of 15% in spite of the presence of a Cbz substituent (entry 12). This confirmed any change of substituent at the C2 position of the reagent 4,5-hexadienyl chain led to a critical decrease of the product enantiomeric excess. As previously observed for $\mathbf{L_1}$, the chirality of the $\mathbf{L_{11}}$ BINOL fragment was the key factor controlling the stereochemistry of the product **2a**; both were shown to display the same configuration. This same stereoselectivity was observed for two configurations of phosphoramidite ligand $\mathbf{L_{12}}$ bearing biphenyl substituents (entries 13 and 14). Product **2a** was afforded in high 95% conversions and good 78% ee for (*R,S,S*)-$\mathbf{L_{12}}$. The latter was allowed to react with reagent **1a** at −30 °C, but the enantioselectivity was not improved and a low conversion was obtained (entry 15). Phosphoramidite ligand $\mathbf{L_{13}}$ functionalized by anthracenyl substituents led also to high conversions (95%) but average to modest ee values (21−40%) were obtained (entries 16 and 17). Finally, phosphoramidite ligand $\mathbf{L_{14}}$ bearing benzhydryl substituents afforded **2a** in good to high conversions (75−90%) along with low to good ee values (4−66%), the configuration *R,S,S* being the best (entries 18−20). It was worth noting that the chirality of the $\mathbf{L_{14}}$ BINOL fragment no longer controlled the stereochemistry of the product **2a**, as both displayed opposite configurations (entries 18 and 20). Regarding all these synthesized phosphoramidite ligands, the best asymmetric induction was obtained by combining opposite stereochemical configurations on, respectively, the BINOL fragment and the Whitesell amine part, favored ligand configurations being *R,S,S* and *S,R,R*. The best conversions and ee values were obtained by running the reaction at −20 °C and using the phosphoramidite ligand (*R,S,S*)-$\mathbf{L_{12}}$.

CONCLUSIONS

The gold-catalyzed asymmetric intramolecular hydroamination of allenes was studied by screening a series of mononuclear gold(I) and -(III) complexes in combination with silver salts. Among the various chiral monophosphine and diaminocarbene ligands tried, the best catalysts arose from mononuclear gold(I)

Chart 3. Tuned Phosphoramidite Ligands Used for the Screening of Mononuclear Gold(I) Catalysts

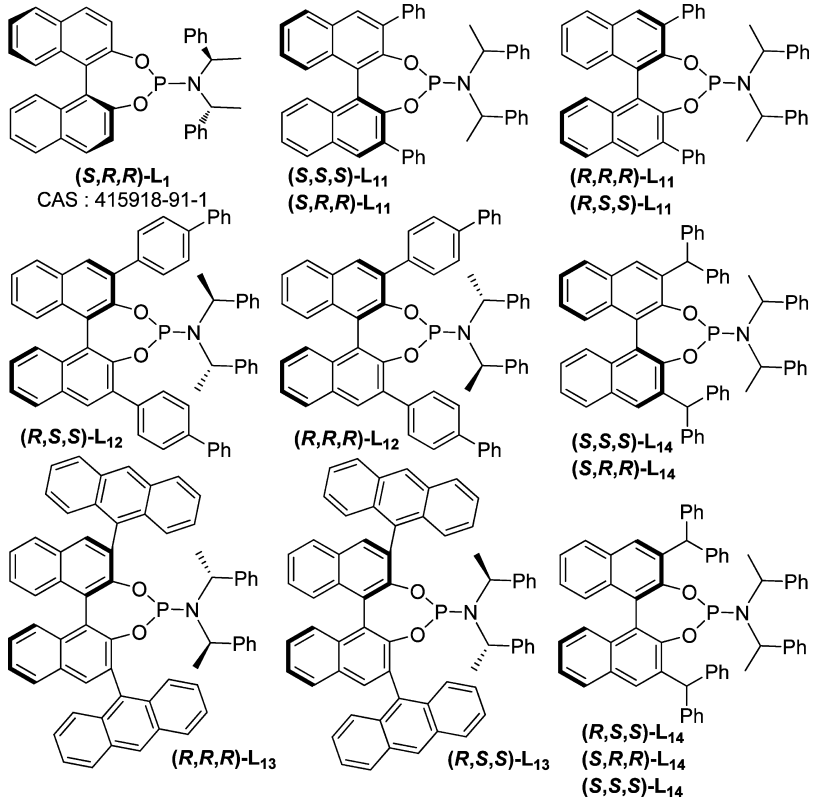


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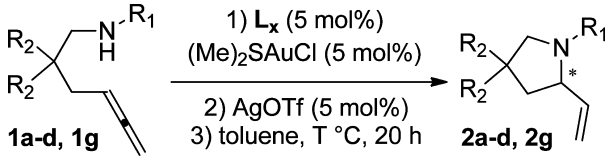
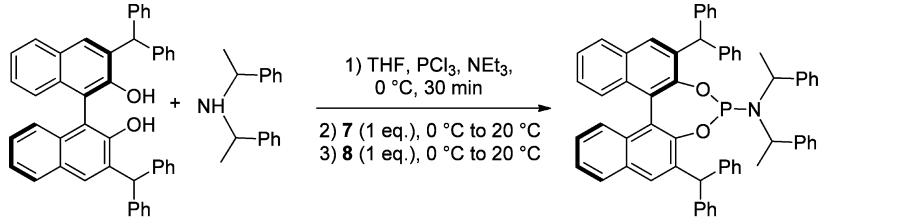
Table 7. Screening of Mononuclear Gold(I) Catalysts Based on Tuned Phosphoramidite Ligands



entry	R_1	R_2	ligand (L_x)	T (°C)	conversion[a] (%)	ee (%)[b]	configuration[c]
1	CBz	Ph	(*R,R,R*)-L_9	−20	30 (**2a**)	50	*R*
2	CBz	Ph	(*S,R,R*)-L_1	−20	5 (**2a**)	65	*S*
3	CBz	Ph	(*R,S,S*)-L_1	−20	25 (**2a**)	67	*R*
4	CBz	Ph	(*R,S,S*)-L_{11}	−20	5 (**2a**)	71	*R*
5	CBz	Ph	(*R,R,R*)-L_{11}	−20	>95 (**2a**)	31	*R*
6	CBz	Ph	(*S,S,S*)-L_{11}	−20	30 (**2a**)	31	*S*
7	CBz	Ph	(*S,R,R*)-L_{11}	−20	**2a** 55	78	*S*
8	CBz	Ph	(*S,R,R*)-L_{11}	−40	**2a** 0		
9	Ts	Ph	(*S,R,R*)-L_{11}	−20	>95 (**2b**)	−44	
10	Boc	Ph	(*S,R,R*)-L_{11}	−20	26 (**2c**)	66	
11	CONHPh	Ph	(*S,R,R*)-L_{11}	−20	62 (**2d**)	52	
12	CBz	Me	(*S,R,R*)-L_{11}	0	68 (**2g**)	15	
13	CBz	Ph	(*R,R,R*)-L_{12}	−20	>95 (**2a**)	24	*R*
14	CBz	Ph	(*R,S,S*)-L_{12}	−20	>95 (**2a**)	78	*R*
15	CBz	Ph	(*R,S,S*)-L_{12}	−30	17 (**2a**)	78	*R*
16	CBz	Ph	(*R,R,R*)-L_{13}	−20	>95 (**2a**)	40	*R*
17	CBz	Ph	(*R,S,S*)-L_{13}	−20	>95 (**2a**)	21	*R*
18	CBz	Ph	(*R,S,S*)-L_{14}	−20	75 (**2a**)	66	*R*
19	CBz	Ph	(*S,R,R*)-L_{14}	−20	86 (**2a**)	16	*R*
20	CBz	Ph	(*S,S,S*)-L_{14}	−20	90 (**2a**)	4	*R*

[a]Measured by ^{1}H NMR. [b]Measured by HPLC at 220 nm. [c]Determined from HPLC by comparison with previous work (see the Supporting Information).

Scheme 2. Synthesis of 3,3′-Dibenzhydryl-Substituted Phosphoramidite Ligand L_{14}



complexes built on BINOL-based phosphoramidite ligands. The latter were improved by addition of bulky substituents at the specific 3,3′-positions of the BINOL scaffold. The resulting gold(I) complexes were combined with selected silver salts to afford efficient catalysts for intramolecular hydroaminations of allenes at room temperature or below, with good conversions and enantioselectivities. In the future, such mononuclear gold(I) catalysts may be a good alternative solution to dinuclear gold(I) catalysts, when selectivity issues are encountered owing to the presence of two gold centers, the first being part of the most active and selective catalyst and the second leading to a competing nonselective catalyst species.[9a]

EXPERIMENTAL SECTION

General Remarks. All solvents were dried using standard methods and stored over molecular sieves (4 Å). All silver salts were weighted in a glovebox. All reactions were carried out under a dry nitrogen atmosphere and were at least repeated twice. Analytical thin-layer chromatography (TLC) was performed on Macherey precoated 0.20 mm silica gel Alugram Sil 60 G/UV254 plates. Flash chromatography was carried out with Macherey silica gel (Kielselgel 60). ^{1}H (300 MHz), ^{13}C (75 MHz), and ^{31}P (121 MHz) spectra were acquired on a Bruker Avance spectrometer. Chemical shifts (δ) are reported downfield of Me_4Si in ppm, and coupling constants are expressed in Hz. 1,3,5-Trimethoxybenzene and 1,2,4,5-tetrachlorobenzene were used as internal standards when needed. Infrared spectra were recorded on a ThermoScientific-Nicolet 6700 spectrometer; the samples were prepared with KBr powder. HPLC was performed on a Hitachi LaChromElite equipment with a micropump, a Peltier oven, and a DAD detector. HRMS-ESI analyses were performed at the CUMA Pharmacy Department, Université Lille Nord de France. Elemental analyses were performed at UCCS, Université Lille Nord de France. $AuS(Me)_2Cl$ was prepared following related procedures.[31,32] BARF and TRIP silver salts were prepared as reported.[33,34] Amino allene substrates were synthesized following reported procedures: **1a**,[9z] **1b**,[35] **1c**,[9z] **1d**,[9f] **1e**,[35] **1f**,[35] **1g**,[9x] **1h**.[11] Except for L_{14}, phosphoramidite ligands were prepared according to reported procedures: L_{11},[30e] L_{12},[30e] L_{13}.[17b] Gold(I) diaminocarbene complexes **3** and **5** were synthesized as reported.[26] See the Supporting Information for further details.

General Procedure for Ligand Screening. In a glovebox, $AuS(Me)_2Cl$ (2.9 mg, 0.01 mmol) and the corresponding ligand (0.01 mmol) were placed in a first Schlenk flask. Dry dichloromethane (1 mL) was added under a nitrogen atmosphere, and the resulting

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mixture was stirred at room temperature for 2 h. Afterward, the solvent was evaporated under vacuum and the resulting solid was dried 30 min before addition of AgOTf (2.3 mg, 0.009 mmol) in a glovebox. Dry dichloromethane (1 mL) was added under nitrogen, and the resulting solution was stirred for 30 min before being transferred to a second Schlenk flask containing amino allene substrate **1a** (68.9 mg, 0.18 mmol). After 20 h of stirring at 30 °C, the solution was filtered through a pad of silica gel using dichloromethane as solvent. After evaporation of solvent under vacuum, the resulting oil was analyzed by ^{1}H NMR and HPLC.

General Procedure for Silver Salt Screening. In a glovebox, 0.01 mmol of $AuS(Me)_2Cl$ (2.9 mg) and 0.01 mmol of (***S,R,R***)-L_1 (5.4 mg) were placed in a first Schlenk flask. Dry dichloromethane (1 mL) was then added under a nitrogen atmosphere, and the resulting mixture was stirred for 2 h at room temperature. Afterward, the solvent was evaporated under vacuum and the resulting solid was dried 30 min before addition of AgOTf (0.009 mmol) in a glovebox. Dry dichloromethane (1 mL) was added under a nitrogen atmosphere, and the resulting solution was stirred for 30 min before being transferred to a second Schlenk flask containing amino allene substrate **1a** (0.18 mmol, 68.9 mg). After 20 h of stirring at 30 °C, the solution was filtered through a pad of silica gel using dichloromethane as solvent. After evaporation of solvents under vacuum, the resulting oil was analyzed by ^{1}H NMR and HPLC.

General Procedure for Solvent Screening. In a glovebox, $AuS(Me)_2Cl$ (0.01 mmol, 2.9 mg) and (***R,S,S***)-L_1 (0.01 mmol, 5.4 mg) were added to a Schlenk flask. Dry solvent (1 mL) was then added under a nitrogen atmosphere, and the resulting mixture was stirred for 2 h at room temperature. Afterward, the solvent was evaporated under vacuum and the resulting solid was dried 30 min before addition of AgOTf (0.009 mmol, 2.3 mg) in a glovebox. The corresponding dry solvent (1 mL) was added under a nitrogen atmosphere, and the resulting solution was stirred for 30 min before being transferred in a second Schlenk flask containing amino allene substrate **1a** (0.18 mmol, 68.9 mg). After 20 h of stirring at 30 °C, the solution was filtered through a pad of silica gel using dichloromethane as solvent. After evaporation of solvents under vacuum, the resulting oil was analyzed by ^{1}H NMR and HPLC.

General Procedure for Temperature Screening. In a glovebox, $AuS(Me)_2Cl$ (0.01 mmol, 2.9 mg) and (***R,S,S***)-L_1 (0.01 mmol, 5.4 mg) were added to a Schlenk flask. Dry toluene (1 mL) was then added under a nitrogen atmosphere, and the resulting mixture was stirred for 2 h at room temperature. Afterward, the solvent was evaporated under vacuum and the resulting solid was dried 30 min before addition of AgOTf (0.009 mmol, 2.3 mg) in a glovebox. Dry toluene (1 mL) was then added under a nitrogen atmosphere, and the resulting solution was stirred for 30 min before being transferred to a second Schlenk flask containing amino allene substrate **1a** (0.18 mmol, 68.9 mg). After 20 h of stirring at the corresponding temperature, the solution was filtered through a pad of silica gel using dichloromethane as solvent. After evaporation of solvents under vacuum, the resulting oil was analyzed by ^{1}H NMR and HPLC.

(*R,S,S*)-(+)-(2,6-Dibenzhydryl-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalen-4-yl)bis(1-phenylethyl)amine ((*R,S,S*)-L_{14}). In the first flame-dried Schlenk flask, dry and degassed THF (1 mL) was placed under nitrogen and cooled to 0 °C. NEt_3 (1.02 mmol, 138 μL) followed by PCl_3 (0.17 mmol, 85 μL of a 2 M solution) were added under nitrogen, and the mixture was stirred at 0 °C for 30 min. Afterward, (*S*)-bis[1-phenylethyl]amine ((***S,S***)-**7**; 0.17 mmol, 39 μL) was added at 0 °C and the solution was stirred and warmed to room temperature for 4 h. In a second flame-dried Schlenk, compound (***R***)-**8d** (0.17 mmol, 106 mg) was placed and dried by dissolution in dry toluene (1 mL) and evaporation of the resulting solution under vacuum (two times). Then, the resulting dried (***R***)-**8d** was dissolved in dry and degassed THF (1 mL) and transferred by cannula to the first Schlenk flask at 0 °C. After it was stirred at room temperature overnight (12 h), the reaction mixture was quenched by adding dichloromethane (10 mL) followed by brine (20 mL). After extraction, the organic phase was dried over Na_2SO_4 and evaporated under vacuum. The solid residue was purified by flash chromatography on silica gel using a 1/1 mixture of petroleum ether and toluene (R_f = 0.6). After evaporation of solvents under vacuum and further washes with acetone and petroleum ether, compound (***R,S,S***)-L_{14} was obtained as a white solid (0.12 mmol, 105 mg, 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.56 (br s, 3H), 2.15 (br s, 3H), 4.47 (br s, 1H), 4.83 (br s, 1H), 5.90 (s, 1H), 6.27 (s, 1H), 6.75−7.20 (m, 20H), 7.20−7.60 (m, 18H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 1H). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 142.5. ^{13}C NMR (75 MHz, $CDCl_3$): δ 50.3 (CH_3), 50.3 (CH_3), 52.8 (CH), 122.8 (C), 122.8 (C), 124.6 (CH), 124.7 (CH), 125.8 (CH), 125.9 (CH), 126.3 (CH), 126.4 (CH), 126.7 (CH), 126.9 (CH), 127.2 (CH), 127.9 (CH), 128.3 (CH), 128.3 (CH), 128.4 (CH), 128.5 (CH), 128.5 (CH), 128.8 (CH), 129.4 (CH), 129.7 (C), 130.0 (CH), 130.3 (CH), 131.0 (C), 131.4 (CH), 132.0 (C), 132.5 (C), 135.5 (C), 135.6 (C), 142.6 (C), 143.2 (C), 144.3 (C), 144.4 (C), 148.2 (C), 148.5 (C), 148.6 (C). HMRS (ESI): *m/z* calcd for $C_{62}H_{51}NO_2P$ 872.3652 [MH^+], found 872.3644. $[\alpha]_D^{20}$ = +62° (CH_2Cl_2, *c* = 0.1 g/100 mL).

(*S,S,S*)-(−)-(2,6-Dibenzhydryl-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalen-4-yl)bis(1-phenylethyl)amine ((*S,S,S*)-L_{14}). This compound was prepared from (*S*)-**8d** and amine (***S,S***)-**7** using the same procedure as for (***R,S,S***)-L_{14}. $[\alpha]_D^{20}$ = −187° (CH_2Cl_2, *c* = 0.1 g/100 mL).

(*S,R,R*)-(−)-(2,6-Dibenzhydryl-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalen-4-yl)bis(1-phenylethyl)amine ((*S,R,R*)-L_{14}). This compound was prepared from (*R*)-**8d** and amine (***R,R***)-**7** using the same procedure as for (***R,S,S***)-L_{14}. $[\alpha]_D^{20}$ = −39° (CH_2Cl_2, *c* = 0.1 g/100 mL).

Benzyl-2,2-dimethyl-4,5-hexadienylcarbamate (1g). Following a related procedure,[9x] dry diisopropylamine (1.7 mL, 10 mmol) and dry THF (5 mL) were placed in an oven-dried Schlenk flask. The solution was then cooled to 0 °C and *n*BuLi (1.2 equiv, 12 mmol, 7.5 mL, 1.6 M solution) was added under nitrogen. After 1 h of stirring at room temperature, dry isobutyronitrile (0.9 mL, 10 mmol) diluted in dry THF (3 mL) was added under nitrogen. After another 1 h of stirring at room temperature, propargyl bromide (1.2 equiv, 12 mmol, 1.5 mL, 80 wt % solution in toluene) was added under nitrogen and the solution was stirred overnight at room temperature. Then, 10 mL of distilled water was added, the layers were separated, and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under vacuum to afford 2,2-dimethyl-4-pentynenitrile as a slightly yellow oil, which was used for the next step without any further purification due to its volatility. In an oven-dried Schlenk flask, paraformaldehyde (2 equiv, 20 mmol, 0.63 g) and CuBr (0.4 equiv, 4.2 mmol, 0.6 g) were diluted in dry 1,4-dioxane (10 mL). Then, dry diisopropylamine (2 equiv, 20 mmol, 3 mL) and the oil obtained previously were added under nitrogen. After it was stirred at reflux overnight, the solution was filtered through a pad of silica gel with dichloromethane/petroleum ether (1/1). Evaporation of solvents afforded 2,2-dimethylhexa-4,5-dienenitrile as a slightly yellow oil which was used without any further purification step due to its volatility. In an oven-dried Schlenk flask, dry Et_2O (20 mL) and $LiAlH_4$ (26 mmol, 0.5 g) were added to the oil obtained previously. After it was stirred at room temperature overnight, the solution was neutralized at 0 °C with H_2O and $NaOH_{aq}$ (6 M). After filtration through a pad of Celite, the organic layer was dried over $MgSO_4$ and concentrated under vacuum to afford 2,2-dimethylhexa-4,5-dien-1-amine as a slightly yellow oil which was used without any further purification step due to its volatility. The resulting product was placed in a flask with benzyl chloroformate (1.2 equiv, 12 mmol, 1.6 mL), ethanol (40 mL), distilled water (16 mL), and $NaHCO_{3aq}$ (1 M, 24 mL). After 45 min of stirring at room temperature, saturated $NaCl_{aq}$ (50 mL) was added, the layers were separated, and the resulting aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under vacuum to afford a colorless oil which was purified by by flash chromatography using a 9/1 petroleum ether/EtOAc solvent mixture (R_f = 0.4). After evaporation of solvents under vacuum, compound **1g** was obtained as a colorless oil (1.3 mmol, 0.34 g, 13% overall yield over four steps). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (s, 6H), 1.93 (m, 2H), 3.06 (d, 2H, *J* = 6.9), 4.64 (m, 2H), 4.82

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(bs, 1H), 5.06 (m, 3H), 7.35 (m, 5H).^{13}C NMR (75 MHz, $CDCl_3$): δ 24.7, 35.4, 39.1, 50.5, 66.8, 73.9, 85.8, 128.2, 128.3, 128.6, 136.7, 156.8, 209.8 (CO). HMRS (ESI): m/z calcd for $C_{16}H_{22}NO_2$ 260.16451 [MH^+], found 260.16308.

Benzyl 4,4-Dimethyl-2-vinylpyrrolidine-1-carboxylate (2g). This compound was isolated after flash chromatography with petroleum ether/ethyl acetate (8/2), R_f = 0.7, as a colorless oil (quantitative). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.02 (s, 3H), 1.09 (s, 3H), 1.53 (m, 1H), 1.91 (dd, 1H, J = 8.1 Hz), 3.11 (d, 1H, J = 11.1 Hz), 3.45 (dd, 1H, J = 12.3 Hz), 4.35 (m, 1H), 5.12 (m, 4H), 5.81 (m, 1H), 7.35 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) as a mixture of 2 rotamers: δ [26.3, 26.5], [37.2, 37.7], [46.4, 47.3], [59.5, 59.6], 60.1, 66.7, [114.2, 114.7], 127.8 ($4C_{Ar}$), 128.5 ($1C_{Ar}$), 137.0, [139.3, 140.0], [155.2, 155.6] (CO). HRMS (ESI): m/z calcd for $C_{16}H_{22}NO_2$ 260.16451 [MH^+], found 260.16298. The enantiomeric excess (ee) was measured by HPLC using Regis (*S,S*)-Whelk 01 CSP, at 25 °C, with (90/10) *n*-hexane/*i*PrOH, 1 mL/min, λ 220 nm, t_R(minor) = 17.0 min and t_R(major) = 25.6 min. The ee was too low to measure a $[\alpha]_D^{20}$ value.

((4*R*,5*R*)-1,3-Bis(2-methoxyphenyl)-4,5-diphenylimidazolin-2-ylidene)gold Trichloride (4). This new compound was prepared by following a related procedure.[31] In a flame-dried Schlenk tube were placed and dried a stirring bar, Au(I) complex **3** (67 mg, 0.1 mmol), and iodobenzene dichloride (55 mg, 0.15 mmol). Under nitrogen, acetonitrile (3 mL) was added and the reaction mixture was stirred overnight (ca. 12 h) at room temperature. Diethyl ether was then added to precipitate a solid which was further washed with petroleum ether. After recrystallization (dichloromethane/petroleum ether) and drying under vacuum, compound **4** was obtained as a yellow solid (50 mg, 0.07 mmol, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.00 (s, 6H), 5.49 (s, 2H), 6.95 (m, 4H), 7.35 (m, 4H), 7.47 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.5 ($2CH_3$), 76.2 (2CH), 112.6 (CH_{Ar}), 113.7 (CH_{Ar}), 121.3 (CH_{Ar}), 124.8 (C), 125.7 (C), 127.4 (CH_{Ar}), 129.6 (CH_{Ar}), 130.1 (CH_{Ar}), 130.7 (CH_{Ar}), 131.7 (CH_{Ar}), 136.9 (C), 154.3 (C), 170.0 (C_{Au}). $[\alpha]_D^{20}$ = +179° (CH_2Cl_2, c = 0.2 g/100 mL). HRMS (ESI+): m/z calcd for $C_{29}H_{27}N_2O_2AuCl_3$ [MH^+] 737.0798, found 737.0600. Anal. Calcd for ($C_{29}H_{26}AuCl_3N_2O_2$ + CH_2Cl_2): C, 43.79; H, 3.43; N, 3.40. Found: C, 43.26; H, 3.28; N, 3.44.

((4*S*,5*S*)-1,3-Dibenzhydryl-4,5-diphenylimidazolin-2-ylidene)gold(III) Trichloride (6). This compound was prepared by following a related procedure.[31] In a flame-dried Schlenk tube were placed and dried a stirring bar, Au(I) complex **5** (100 mg, 0.13 mmol), and iodobenzene dichloride (70 mg, 0.19 mmol). Under nitrogen, acetonitrile (3 mL) was added and the reaction mixture was stirred overnight (ca. 12 h) at room temperature. Diethyl ether was then added to precipitate a solid which was further washed with petroleum ether. After recrystallization (dichloromethane/petroleum ether) and drying under vacuum, compound **6** was obtained as a yellow solid (79 mg, 0.09 mmol, 73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.76 (s, 2H), 6.65 (s, 2H), 7.05 (m, H_{Ar}), 7.36 (m, H_{Ar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 68.5 (2CH), 74.5 (2CH), 129.9 ($4CH_{Ar}$), 129.6 ($4CH_{Ar}$), 129.3 ($4CH_{Ar}$), 129.2 ($5CH_{Ar}$), 129.1 ($3CH_{Ar}$), 128.5 ($2CH_{Ar}$), 128.3 ($4CH_{Ar}$), 126.0 ($4CH_{Ar}$), 135.1 (2C), 137.6, 138.2 (4C), 171.6 (C_{Au}). $[\alpha]_D^{20}$ = −14 (CH_2Cl_2, 0.2 g/100 mL). HRMS (ESI+): m/z calcd for $C_{41}H_{35}AuCl_3N_2$ [MH^+] 857.1526, found 857.1995. Anal. Calcd for ($C_{41}H_{34}AuCl_3N_2$ + $^1/_2$ CH_2Cl_2): C, 55.35; H, 3.92; N, 3,11. Found: C, 54.94; H, 3.90; N, 3.14.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, and tables giving additional data, experimental procedures, and characterizations for other compounds, ^{1}H and ^{13}C NMR spectra of all final products (new or reported), HRMS spectra of new compounds, and HPLC analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

TLC, thin-layer chromatography; GC, gas chromatography; HPLC, high-pressure chromatography; CSP, chiral stationary phase; NMR, nuclear magnetic resonance; HRMS, high-resolution mass spectroscopy; ESI, electrospray ionization; THF, tetrahydrofuran; TRIP, 3,3′-bis(2,4,6-triisopropylphenyl)-1,1′-binaphthyl-2,2′-diyl hydrogenphosphate; BARF, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate; PNB, *p*-nitrobenzoate; CBz, benzylcarbamate; Ts, tosyl; Bn, benzyl; Boc, *tert*-butyl carboxylate; NTf, trifluoromethaneimidate; IPr, 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene

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