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Synthesis and Catalytic Activity of Gold Chiral Nitrogen Acyclic Carbenes and Gold Hydrogen Bonded Heterocyclic Carbenes in Cyclopropanation of Vinyl Arenes and in Intramolecular Hydroalkoxylation of Allenes

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Mononuclear and dinuclear chiral gold(I) carbene complexes with carbene ligands of the type HBHC (hydrogen bonded heterocyclic carbenes) and NAC (nitrogen acyclic carbenes) have been prepared by reaction of isocyanide gold(I) complexes and chiral amines or diamines. The reaction of [AuCl(CNPy-2)] (**1**) (Py = pyridyl) with the corresponding chiral primary amines afforded the chiral HBHC complexes (*R*)-[AuCl{C(NH(CHMePh))(NHPy-2)}] ((*R*)-**2**), and (*S*)-[AuCl{C(NH{CHMe(1-naphthyl)})(NHPy-2)}] ((*S*)-**3**), while the reaction of 2 equiv of **1** with diamines produced (*S*)-2,2′-bis[NH{C(AuCl)(NHPy-2)}]$_2$-binaphthyl ((*S*)-**4**), (1*R*,2*R*)-1,2-bis[NH{C(AuCl)(NHPy-2)}]-diphenylethane ((1*R*,2*R*)-**5**), and (1*R*,2*R*)-1,2-bis[NH{C(AuCl)(NHPy-2)}]-cyclohexane ((1*R*,2*R*)-**6**). On the other hand the addition of alkyl amines to (*S*)-2,2′-[NCAuCl]$_2$-binaphthyl ((*S*)-**8**) gave the chiral NAC complexes (*S*)-2,2′-bis[NH{C(AuCl)(NMe$_2$)}]$_2$-binaphthyl ((*S*)-**9**) and (*S*)-2,2′-bis[NH{C(AuCl)(N^{i}Pr$_2$)}]$_2$-binaphthyl ((*S*)-**10**), while the addition to (*S*)-2,2′-[NC-AuCl]$_2$-3,3′-Ph$_2$-binaphthyl ((*S*)-**12**) yielded (*S*)-2,2′-bis[NH{C(AuCl)(NMe$_2$)}]$_2$-3,3′-Ph$_2$-binaphthyl ((*S*)-**13**) and (*S*)-2,2′-bis[NH{C(AuCl)(NEt$_2$)}]$_2$-3,3′-Ph$_2$-binaphthyl ((*S*)-**14**). All the complexes are active catalysts in the cyclopropanation of vinyl arenes and in the intramolecular hydroalkoxylation of allenes, providing good yields and modest or poor enantioselectivity. The results show that all these ligands are compatible with different functions and reaction conditions and are worth considering as alternative systems to NHCs or phosphines in gold catalyzed reactions.

Introduction

The past 20 years have seen the development of gold(I) complexes as catalysts for organic transformations,[1] but applications of homogeneous gold catalysts in enantioselective processes have been reported only very recently.[2] The majority of the gold(I) catalytic systems used in enantioselective catalysis are dinuclear complexes of the type μ-(P−P)[(AuX)$_2$] (P−P = chiral bis(phosphine), X = anionic ligand or counterion), although chiral phosphoramidite ligands[3] and chiral counterions[4] have recently emerged as interesting alternatives in gold(I) catalysis.

The catalytic activity of NHC gold(I) complexes in many synthetic processes is well demonstrated.[5] We have recently reported that gold(I) complexes with other types of carbene ligands, that we have named HBHCs (hydrogen bonded heterocyclic carbenes, e.g., [AuCl{C(NRH)(NHPy-2)}]), or NAC (nitrogen acyclic carbenes, e.g., [AuCl{C(NHR)(NHR′)}] or [AuCl{C(NHR)(NR′$_2$)}]), are good catalysts in skeletal rearrangement and in methoxycyclization of enynes,[6−8] suggesting that this kind of carbene complexes should be incorporated

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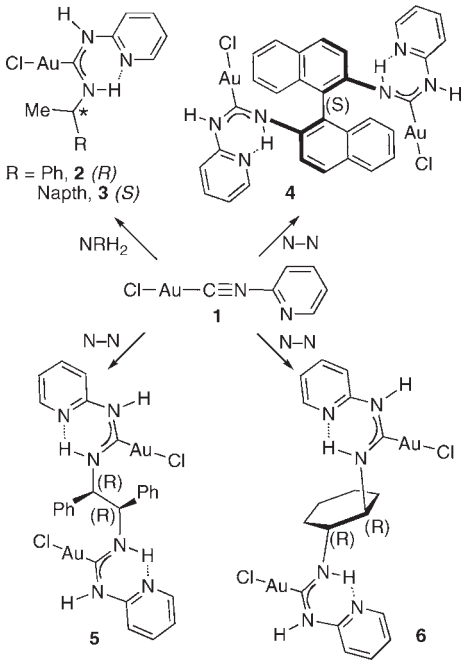
Scheme 1. Synthesis of the Chiral HBHC Gold Complexes **2**−**6**: NRH_2 = (*R*)-NH_2(Me)CH(Ph), **2**; (*S*)-NH_2(Me)CH(naph), **3**; N−N = (*S*)-(-)-1,1′-binapthyl-2,2′-diamine, **4**; (1*R*,2*R*)-(+)-1,2-diphenylethane-1,2-diamine, **5**; (1*R*,2*R*)-(-)-1,2-diaminecyclohexane, **6**



to the armory of metal-catalyzed reactions and further investigated. We are glad that our kind of NAC complexes have already been adopted by another group working in gold catalysis.[9] An advantage of these two kinds of complexes is that they are prepared by nucleophilic attack of amines to isocyanide gold complexes,[10−12] which provides an easy way to obtain systematic series of chiral carbene gold complexes by simply combining chiral amines or chiral isocyano-gold complexes. The isocyanide ligands are easy to obtain from chiral amines.[13]

Following this methodology we have carried out the synthesis of some chiral mononuclear or binuclear HBHC or NAC gold(I) complexes and studied their catalytic activity and enantioselectivity in two reactions that have been recently reported to be catalyzed by gold catalysts bearing chiral mono or-bidentate phosphane ligands, namely, the cyclopropanation of vinyl arenes[14] and the intramolecular hydroalkoxylation of allenes.[15] Chiral carbene gold(I) complexes have not been explored in gold enantioselective catalysis, except for one report of some monomeric NHC gold(I) complexes that appeared during the preparation of this paper, where the authors report good yields but low or moderate enantioselectivity for the asymmetric cyclization of 1,6-enynes.[16]

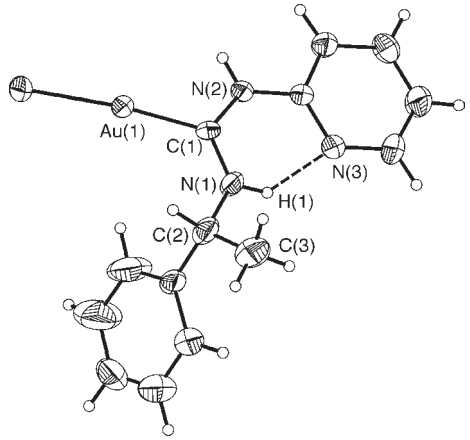


Figure 1. X-ray structure for (*R*)-**2** (only one of the two molecules of the asymmetric unit is shown). Selected bond lengths (Å): Au(1)−Cl(1) = 2.2884(19); Au(1)−C(1) = 1.994(8); C(1)−N(2) = 1.354(10); C(1)−N(1) = 1.297(11); N(3)−H(1A) = 1.898. Selected bond angles (deg): C(1)−Au(1)−Cl(1) = 173.8(2); N(2)−C(1)−N(1) = 118.3(8); N(3)−H(1)−N(1) = 133.70.

Results and Discussion

(a). Synthesis and Structural Characterization of Chiral Gold(I) Carbene Complexes. (a.1). Chiral HBHC Gold Complexes. The neutral chiral gold carbene complexes **2**−**6** (Scheme 1) were prepared by nucleophilic attack to the gold-coordinated isocyanide in [AuCl(CNPy-2)] (**1**)[6] with different chiral primary amines or diamines. All the gold complexes are air stable white solids.

In general, four stereoisomers can be formed for each gold center in gold(I) carbenes derived from primary amines, but only one was observed in the ^{1}H NMR spectra at room temperature in $CDCl_3$ for complexes **2**−**6** (also in Me_2CO-d_6 for **6**). As observed previously for non-chiral HBHCs,[6,7] this confirms the persistence in $CDCl_3$ (and also in Me_2CO-d_6) solution of the intramolecular hydrogen bond between the amide proton and the nitrogen of the 2-pyridyl group, forming a 6-member cycle. The ^{1}H NMR spectra show two N−H signals, one at about 13 ppm and the other at about 9.7 ppm. The chemical shift of the former corresponds to the hydrogen atom involved in the intramolecular hydrogen bonding. This hydrogen interaction is strong enough to stabilize exclusively the otherwise less favored *anti* isomer, as shown in Scheme 1.

X-ray quality crystals suitable for single crystal diffraction were obtained for (*R*)-**2**. There are two independent molecules of complex **2** in the asymmetric unit. The molecular structure of one of them (the other is very similar) is shown in Figure 1, with selected bond lengths and angles. The complex shows, as expected, a roughly linear geometry for gold (angle 173.8°). As observed for other HBHCs,[6,7] the Au−Cl distance in **2** is longer than that in $[AuCl_2]^-$ (2.257 Å),[17] reflecting the high *trans* influence of the carbene ligand.[18] The Au−C distance is within the range found for other HBHC gold(I) carbenes. The C(1)−N(2) and C(1)−N(1) distances are much shorter than the normal

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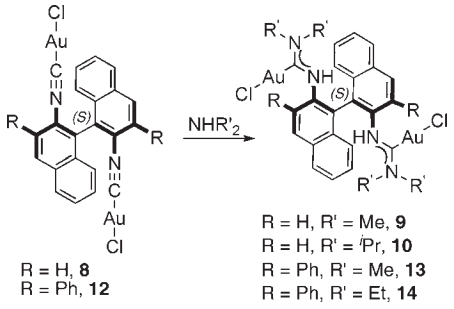
Scheme 2. Synthesis of the Chiral HBHC Gold Derivatives **9**−**10** and **13**−**14**



$C(sp^2)-N$ single bond distance of 1.45 Å,[19] which proves an important N→C π-bonding contribution to the bond. The H···N(3) distance and the corresponding N(1)−H···N(3) angle in the hydrogen bridge are in the range of moderate intramolecular N···H hydrogen bonds.[20]

(a.2). Chiral NAC Gold Complexes. In this case, the chiral binuclear NAC gold(I) complexes (*S*)-**9** and (*S*)-**10** have been prepared by using a chiral isocyanide gold complex (*S*)-2,2′-$[NCAuCl]_2$-binaphthyl ((*S*)-**8**), and non-chiral amines of different steric requirements meant to modify the steric hindrance at the gold(I) reaction site (Scheme 2). We have also used the bulkier isocyanide complex (*S*)-2,2′-$[NCAuCl]_2$-3,3′-Ph_2-binaphthyl ((*S*)-**12**), with a phenyl substituent in the 3,3′-position of the binaphthyl group, to synthesize (*S*)-**13** and (*S*)-**14**. The starting isocyanogold complexes were obtained from [AuCl(tht)] (tht = tetrahydrothiophene),[21] by substitution of tht with (*S*)-(+)-1,1′-Binaphthyl-2,2′-diisocyanide (**7**),[22] or with (*S*)-1,1′-Binaphthyl-(3,3′-diphenyl)-2,2′-diisocyanide (**11**), as reported for related gold compounds.[23] Ligand **11** was synthesized from (*S*)-2,2′-(3,3′-diphenyl)binapthylamine,[24] as reported in the experimental part. The chiral isocyanocomplexes were treated only with secondary amines to reduce the number of possible conformers in the products.

The ^1H NMR spectra of complexes **9**−**10** in $CDCl_3$ show the signals of only one isomer. In contrast, compounds **13**−**14** show a mixture of three isomers, and it is not easy to assign the preferred conformations from the spectroscopic data. X-ray quality crystals suitable for single crystal diffraction were obtained for **9**. A perspective view of the molecular structure is given in Figure 2, along with selected bond lengths and angles. The complex shows a nearly linear geometry for gold. The Au−C distance is in the range of distances found for other gold(I) carbenes. As observed for **2**, The C(1)−N(2) and C(1)−N(1) distances are similar to other Au(I) carbene complexes, and shorter than the $C(sp^2)-N$ single bond distance of 1.45 Å, indicating important N→C π-bonding contribution to the bond.

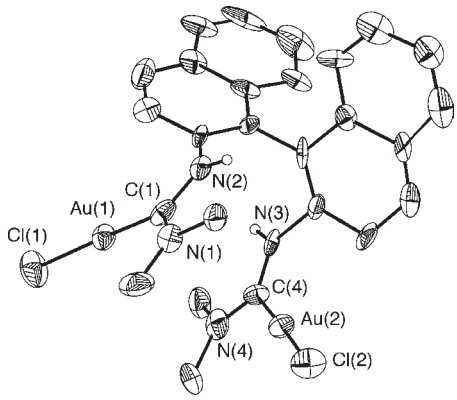
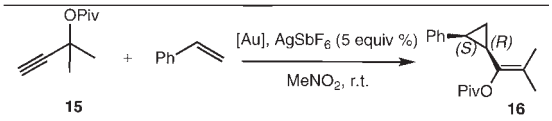


Figure 2. Molecular structure of **9**. Selected bond lengths (Å): Au(1)−Cl(1) = 2.268(7); Au(1)−C(1) 1.98(3); C(1)−N(2) = 1.40(3); C(1)−N(1) = 1.29(2); Au(2)−Cl(2); 2.256(7); Au(2)−C(4) = 2.02(2); C(4)−N(3) = 1.33(2); C(4)−N(4) = 1.36(2). Selected bond angles (deg): C(1)−Au(1)−Cl(1) = 176.8(7); N(2)−C(1)−N(1) = 118(2); C(4)−Au(2)−Cl(2) = 178.7(7); N(3)−C(4)−N(4) = 118.1(19).

Table 1. Gold-Catalyzed Enantioselective Cyclopropanation of Styrene with Propargyl Pivaloate

Entry	[Au]	Yield[a] [%]	*ee*[b] [%]
			
	15		**16**
1	**2**	53	<1
2	**3**	54	<1
3	**4**	75	20
4	**5**	78	11
5	**6**	71	5
6	**9**	72	24
7	**10**	70	10
8	**13**	61	8
9	**14**	65	<1
10	**μ-(P-P*)[AuCl]$_2$**[c]	70	81

[a] Isolated yields. [b] *ee* values determined by HPLC analysis on a chiral stationary phase. [c] P−P* = (*R*)-DTMB-SEGPHOS.[14]

The isomer observed in the X-ray structure displays a *syn* arrangement of the Au center and the N substituent bearing the naphthyl group, which possibly reduces the steric hindrance in the molecule. The same conformation has been observed in the recently reported structures of the gold(I) carbenes [AuCl{$C(NEt_2)$(NHPy-2)}] and [AuFmes{$C(NEt_2)$(NHPy-2)}].[6] In the binaphthyl group, the naphthalene rings make a dihedral angle of 75.68°. The absolute configuration of axially dissymmetric 1,1′-binaphthyl is *S*, the same as the precursor (*S*)-(+)-1,1′-Binaphthyldiisocyanide (**7**), confirming that, as expected, it is not modified during the reaction.

Catalytic Reactions

Two catalytic processes were studied: the cyclopropanation of vinyl arenes and the intramolecular hydroalkoxylation of allenes. The reactions were carried out under standard conditions (not optimized for the ligand), using 5 equiv% of cationic chiral HBHC and NAC catalysts obtained in situ by

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(20) Hydrogen bonding distance ranges proposed in the literature: strong, 1.2−1.5 Å; moderate, 1.5−2.2 Å; weak, 2.2−3.2 Å: Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997.
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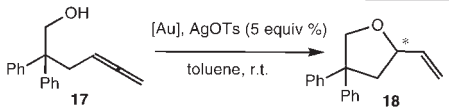
Table 2. Enantioselective Hydroalkoxylation of Allene **17** with the Chiral Catalysts **2**, **3**, **4**, **9**, and **10**

Entry	[Au]	Yield[a] [%]	*ee*[b] [%]
			
1	**2**	67	<1
2	**3**	61	2
3	**4**	95	22
4	**9**	42	20
5	**10**	55	8
6	**μ-(P-P*)[AuCl]$_2$**[c]	73	90

[a] Isolated yields. [b] *ee* values determined by HPLC analysis on a chiral stationary phase. [c] P−P* = (*S*)-DTMB-MeOBIPHEP.[15]

treating the corresponding neutral carbene complex with an equimolecular amount of silver salt ($AgSbF_6$ or AgOTs).

The reaction of propargyl pivaloate **15** (Table 1) with styrene afforded only the *cis*-cyclopropane **16** in reasonable yields (53−78%), showing that both HBHC and NAC ligands can be applied in this reaction. The highest enantiomeric excesses in the reaction were obtained for **4** and **5** (Table 1, entries *3* and *4*) in the case of HBHC ligands, and for **9** and **10** (Table 1, entries *6* and *7*) in the case of NAC ligands. The enantioselectivity found in all the reactions is very poor compared with the values reported by Toste et al. using as catalyst the binuclear system (*R*)-DTBM-SEGPHOS-gold(I) (Table 1, entry *10*),[14] but it has to be considered that phosphine catalysts (and also NHC systems) are better understood and have been much more elaborated in the past years. In these initial studies of the new HBHC and NAC ligands we see that the best enantioselectivity results, even if modest (11−24% ee), have been obtained with catalysts **4**, **5**, **9**, and **10**, all based on the axially dissymmetric 1,1′-binaphthyl ligand. Obviously further elaboration of these ligands looks more promising than for mononuclear complexes. For this reason, we hoped that catalysts **13** and **14**, based on the bulkier (3,3′-diphenyl)-1,1′-binaphthyl chiral system might be more enantioselective than **9** and **10**, but surprisingly they are clearly worse. Since three conformers are present in solution for **13** and **14**, it might happen that they induced opposite enantioselectivity, in detriment of the overall enantiomeric excess.

Some chiral gold(I) HBHC and NAC complexes were also checked for the enantioselective hydroalkoxylation of the γ-hydroxyallene **17**, and the results are gathered in Table 2. Again, the best enantioselectivity results (22 and 20% ee, Table 2, entries *3* and *4*) are obtained with **4** and **9**. This result is similar to those obtained using binuclear complexes of the type μ-(P−P*)$[AuCl]_2$ with 2,2-bis(diarylphosphino)-biphenyl ligands such as binap or (3,5-xylyl)binap, but much lower that those obtained using the bulkier (*S*)-DTMB-MeOBIPHEP as the chiral ligand (Table 2, entry *6*).[15]

Conclusions

This study confirms the catalytic possibilities of the HBHC and NAC gold systems that we have recently introduced in gold catalysis as alternatives to phosphine and NHC ligands. In effect, the results show that the gold(I) complexes with these ligands are compatible with the conditions and reagents involved in the cyclopropanation of vinyl arenes and the intramolecular hydroalkoxylation of allenes. Moreover, it is demonstrated that enantioselectivity can be induced with these two kinds of ligands.

Certainly the enantiomeric excesses are still poor. This is due to the linear coordination of gold,[25] which places the reactive coordination site far away from the ancillary chiral ligand. However, this is the same problem encountered initially with phosphine and NHC ligands, which have been continuously improved in the past years after successive structural elaborations. Only a few ligand variations have been tested in our initial studies, where the purpose was not still to find optimized conditions for a specific synthesis, but to explore the applicability of these ligand types. The fact that introducing structural and electronic variations in the NAC ligands is easier (particularly for the NAC ligands) than in phosphines or NHCs offers many opportunities for a more flexible tuning of these ligand to the demands of specific reagents, and holds a promise for improved activity and enantioselectivity. Here we find that dinuclear gold complexes offer higher enantioselectivity and are, in principle, the structures of choice for further elaboration.

Experimental Section

General Conditions. In general the reactions were carried out under dry N_2, but the cyclopropanation of styrene was carried out in the air without problem. The solvents were purified according to standard procedures. [AuCl(tht)],[21] [AuCl(CNPy-2)] (**1**),[6] and (*S*)-2,2′-(3,3′-diphenyl)binapthylamine[24] were prepared according to literature procedures. The rest of the reactants are commercially available. Infrared spectra were recorded in Perkin-Elmer 883 or 1720X equipment. NMR spectra were recorded with Bruker AC300, ARX 300 and Bruker Avance 400 Ultrashield instruments. ^{1}H NMR spectra are referred to TMS. Elemental analyses were performed with a Perkin-Elmer 2400B microanalyzer.

(*R*)-[AuCl{C(NH(CHMePh))(NHPy-2)}] ((*R*)-2). (*R*)-(+)-α-Methylbenzylamine (154 μL, 1.19 mmol) was added to a solution of **1** (0.200 g, 0.59 mmol) in CH_2Cl_2 (20 mL) and the resultant solution is stirred at room temperature. After 45 min, the solution did not show ν(C≡N) IR absorption. The volatiles were removed, the white residue was recrystallized in CH_2Cl_2/*n*-hexane. The white solid obtained was washed with *n*-hexane (3 × 10 mL) and vacuum-dried, yielding 0.210 g (78%). ^{1}H NMR (300 MHz, $CDCl_3$, 295 K), δ: 12.87 (d, J = 8.1 Hz, 1H, N*H*(CH$_3$)CH(C_6H_5)), 9.53 (br, 1H, N*H*C_5H_4N), 8.25 (d, 1H, J = 1.2 Hz, NHC_5H_4N), 7.73 (m, 1H, NHC_5H_4N), 7.50−7.20 (m, 5H, NH(CH$_3$)CH(C_6H_5)), 7.17 (m, 1H, NHC_5H_4N), 7.08 (m, 1H, NHC_5H_4N), 5.44 (dq, J = 8.3, 6.8 Hz, 1H, C*H*), 1.71 (d, J = 6.8 Hz, 3H, CHCH_3). $[\alpha]_D^{25}$ −94.0 (*c* 1, $CHCl_3$). Anal. Calcd for $C_{14}H_{15}N_3ClAu$: C, 36.74; H, 3.30; N, 9.18. Found: C, 37.09; H, 3.15; N, 9.17.

(*S*)-[AuCl{C(NH(CHMe(1-Naphthyl)))(NHPy-2)}] ((*S*)-3). (*S*)-(-)-1-(1-naphthyl)ethylamine (60 μL, 0.37 mmol) was added to a solution of **1** (0.118 g, 0.35 mmol) in CH_2Cl_2 (20 mL), and the resultant solution was stirred at room temperature. Work up as for **2** yielded 0.153 g of a white solid (86%). ^{1}H NMR (300 MHz, $CDCl_3$, 295 K), δ: 12.98 (d, J = 8.3 Hz, 1H, N*H*(CH$_3$)CH($C_{10}H_7$), 9.86 (br, 1H, N*H*C_5H_4N), 8.24 (m, 1H, NHC_5H_4N), 8.17 (m, 1H, $C_{10}H_7$), 7.75 (m, 1H, NHC_5H_4N), 7.70 (m, 2H, $C_{10}H_7$), 7.35 (m, 3H, $C_{10}H_7$), 7.30 (m, 1H, NHC_5H_4N), 7.17 (m, 1H, NHC_5H_4N), 7.03 (m, 1H, NHC_5H_4N), 6.13 (dq, J = 7.7, 6.8 Hz,

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1H, C*H*), 1.84 (d, J = 6.8 Hz, 3H, CHCH_3). $[\alpha]_D^{25}$ +147.0 (c 0.5, $CHCl_3$). Anal. Calcd for $C_{18}H_{17}AuClN_3$: C, 42.58; H, 3.37; N, 8.28. Found: C, 42.91; H, 3.46; N, 7.77.

(*S*)-2,2′-bis[NH{C(AuCl)(NHPy-2)}]$_2$-binaphthyl ((*S*)-4). (*S*)-(−)-1,1′-binapthyl-2,2′-diamine (15 mg, 0.053 mmol) was added to a solution of **1** (0.034 g, 0.1 mmol) in THF (10 mL). Work up as for **2** yielded 0.030 g of a white solid (61%). ^{1}H NMR (400 MHz, $CDCl_3$, 295 K), δ: 14.22 (s, 2H, N*H*-Binaphthyl), 10.25 (s, 2H, N*H*C_5H_4N), 8.22 (d, J = 8.0 Hz, 2H, binaphthyl), 7.95 (dd, J = 8.8, 8.0 Hz, 2H, binaphthyl), 7.60 (t, J = 9.0 Hz, binaphthyl), 7.58 (m, 2H, NH-C_5H_4N), 7.43 (m, 6H, binaphthyl), 7.01 (m, d, J = 8.0 Hz, NH-C_5H_4N, 2H), 6.70 (m, 2H, NHC$_5H_4$N), 6.56 (m, 2H, binaphthyl). $[\alpha]_D^{25}$ +192.0 (c 1, $CHCl_3$). Anal. Calcd for $C_{32}H_{24}Au_2Cl_2N_6$: C, 40.14; H, 2.53; N, 8.78. Found: C, 40.25; H, 2.80; N, 9.08.

(1*R*,2*R*)-1,2-bis[NH{C(AuCl)(NHPy-2)}]-diphenylethane ((1*R*,2*R*)-5). (1*R*, 2*R*)-(+)-1,2-diphenylethane-1,2-diamine (0.035 g, 0.165 mmol) was added to a solution of **1** (0.101 g, 0.33 mmol) in CH_2Cl_2 (30 mL). Work up as for **2** yielded 0.115 g of a white solid (85%). ^{1}H NMR (400 MHz, Me_2CO-d_6, 295 K), δ: 13.82 (s, 2H, N*H*), 10.33 (s, 2H, N*H*C_5H_4N), 8.56 (d, J = 4.0 Hz, 2H, C_5H_4N), 7.90 (m, 2H, C_5H_4N), 7.40−7.15 (m, 14H, C_6H_5 and NHC$_5H_4$N), 6.00 (m, 2H, C_6H_5C*H*,). Anal. Calcd for $C_{26}H_{24}Au_2Cl_2N_6$: C, 35.27; H, 2.73; N, 9.49. Found: C, 36.14; H, 2.85; N, 8.99. $[\alpha]_D^{25}$ +6.0 (c 1, Me_2CO).

(1*R*,2*R*)-1,2-bis[NH{C(AuCl)(NHPy-2)}]-cyclohexane ((1*R*,2*R*)-6). (1*R*, 2*R*)-(−)-1,2-diaminecyclohexane (0.020 g, 0.165 mmol) was added to a solution of **1** (0.101 g, 0.33 mmol) in CH_2Cl_2 (30 mL). Work up as for **2** yielded 0.071 g of a white solid (58%). ^{1}H NMR (400 MHz, Me_2CO-d_6, 295 K), δ: 12.93 (s, 2H, N*H*), 10.13 (s, 2H, N*H*C_5H_4N), 8.53 (d, J = 4.0 Hz, 2H, C_5H_4N), 7.86 (m, 2H, C_5H_4N), 7.20 (m, 4H, NHC$_5H_4$N), 4.41 (m, 2H, NC*H*(CH$_2$)$_4$C*H*N), 2.28 (m, 2H, NCH(C*H*$_2$)$_4$CHN), 1.80 (m, 2H, NCH(C*H*$_2$)$_4$CHN), 1.70 (m, 2H, NCH(C*H*$_2$)$_4$CHN), 1.50 (m, 2H, NCH(C*H*$_2$)$_4$CHN). Anal. Calcd for $C_{18}H_{22}Au_2Cl_2N_6$: C, 27.46; H, 2.82; N, 10.68. Found: C, 27.52; H, 2.94; N, 10.34. $[\alpha]_D^{25}$ −153.4 (c 1, Me_2CO).

(*S*)-(+)-1,1′-Binaphthyl-2,2′-diisocyanide (7). Formic acid (64 μL, 1,69 mmol) was added to a 0 °C acetic anhidride (129 μL, 1.37 mmol). After the addition, the solution was stirred at 50 °C for 2 h and then cooled to room temperature. THF (1.5 mL) was added, the solution was cooled down to 0 °C, and (*S*)-(−)-1,1′-binapthyl-2,2′-diamine (150 mg, 0.528 mmol) was added and after 20 min the mixture was allowed to warm to ambient temperature and be stirred for 4 h. Then, the volatiles were pumped off, and the crude formamide was purified by dissolving it in *n*-hexane:ethyl acetate (1:1) and passing the solution through silicagel. The volatiles were pumped off, and the solid was crystallized in dichloromethane/pentane. The white solid obtained was washed with pentane (3 × 10 mL) and vacuum-dried, yielding 0.164 g (91%) of 2,2′-binaphthyldiformamide that was used in the subsequent transformation.[26] To a solution of (*S*)-(−)1,1′-binapthyl-2,2′-diformamide (1.394 g, 4.094 mmol) and triethylamine (2.3 mL, 16.38 mmol) in 50 mL of dichloromethane, a solution of trichloromethylcarbonate (triphosgene) (0.850 g, 2.87 mmol) in 10 mL of dichloromethane was added dropwise. The mixture was stirred for 3 h and then the solvent was removed on a rotary evaporator. The resulting residue was chromatographed (silica gel, diethylether/hexane, 5:1 as eluent), and the solvent was evaporated to obtain the product as a white solid. (74% yield). IR: 2118 cm^{-1} ν(C≡N). ^{1}H NMR (300 MHz, $CDCl_3$, 295 K), δ: 8.08 (d, J = 8.7 Hz, 2H), 8.00 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.7 Hz, 2H), 7.60 (dd, J = 7.0, 8.5 Hz, 2H), 7.41 (dd, J = 7.0, 8.5 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H). Anal. Calcd. for $C_{22}H_{12}N_2$: C, 86.82; H, 3.97; N, 9.20. Found: C, 86.37; H, 4.12; N, 9.46. $[\alpha]_D^{25}$ +66 (c 1, benzene).

(*S*)-2,2′-[NCAuCl]$_2$-binaphthyl ((*S*)-8). A 0.250 g portion of **7** (0.82 mmol) was added to a solution of [AuCl(tht)] (0.527 g, 1.64 mmol) in dichloromethane (20 mL). After 15 min of stirring at room temperature the volatiles were pumped off, and the pale gray residue was washed with *n*-hexane (3 × 5 mL) and crystallized from dichloromethane/*n*-hexane. The white solid obtained was decanted, washed with *n*-hexane (3 × 5 mL) and vacuum-dried, yielding 0.567 g (73%). IR: 2217 cm^{-1} ν(C≡N). ^{1}H NMR (300 MHz, $CDCl_3$, 295 K), δ: 8.24 (d, J = 8.8 Hz, 2H), 8.11 (d, J = 8.3 Hz, 2H), 7.88 (d, J = 8.8 Hz, 2H), 7.76 (ddd, J = 8.1, 6.8, 1.1 Hz, 2H), 7.53 (ddd, J = 8.1, 6.8, 1.1 Hz, 2H), 7.17 (dd, J = 8.6, 6.8 Hz, 2H). $[\alpha]_D^{25}$ −5.0 (c 1, $CHCl_3$). Anal. Calcd. for $C_{22}H_{12}N_2Au_2Cl_2$: C, 34.35; H, 1.57; N, 3.64. Found: C, 34.51; H, 1.80; N, 3.65.

(*S*)-2,2′-bis[NH{C(AuCl)(NMe$_2$)}]$_2$-binaphthyl ((*S*)-9). Dimethylamine (150 μL, 0.26 mmol) was added to a solution of **8** (0.100 g, 0.13 mmol) in THF (15 mL), and the resultant solution was stirred at 40 °C. After 3 h, the solution did not show ν(C≡N) IR absorption. Work up as for **2** yielded 0.084 g of a white solid (75%). ^{1}H RMN (400 MHz, Me_2CO-d_6, 295 K): δ (ppm) 8.17−8.10 (m, 4H), 8.07 (d, J = 8.1 Hz, 2H), 7.99 (br, 2H, N*H*), 7.54 (ddd, J = 15.1, 7.1, 0.8 Hz, 2H), 7.31 (ddd, J = 15.3, 8.3, 0.8 Hz, 2H), 6.99 (d, J = 7.9 Hz, 2H), 3.64 (s, 6H, N(C*H*$_3$)$_2$), 2.69 (s, 6H, N(C*H*$_3$)$_2$). $[\alpha]_D^{25}$ −121.0 (c 1, $CHCl_3$). Anal. Calcd for $C_{26}H_{26}Au_2Cl_2N_4$: C, 36.34; H, 3.05; N, 6.52. Found: C, 35.93; H, 2.95; N, 6.28.

(*S*)-2,2′-bis[NH{C(AuCl)(N^{i}Pr$_2$)}]$_2$-binaphthyl ((*S*)-10). Isopropylamine (29 μL, 0.203 mmol) was added to a solution of **8** (0.071 g, 0.092 mmol) in THF (15 mL), and the resultant solution was stirred at 40 °C. After 3 h, the solution did not show ν(C≡N) IR absorption. Work up as for **2** yielded 0.072 g of a white solid (80%). ^{1}H NMR (400 MHz, $CDCl_3$, 295 K): δ (ppm) 8.44 (d, J = 12.0 Hz, 2H), 8.10 (d, J = 8.0 Hz, 2H), 7.99 (d, J = 12.0 Hz, 2H), 7.54 (t, J = 8.0 Hz, 2H), 7.44 (t, J = 8.0 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.19 (br, 2H, N*H*), 5.21 (m, 2H, N{C*H*-(CH$_3$)$_2$}), 3.52 (sep, J = 4.0 Hz, 2H, N{C*H*(CH$_3$)$_2$}), 1.27 (d, J = 4.0 Hz, 6H, N{CH(C*H*$_3$)$_2$}), 1.18 (d, J = 8.0 Hz, 6H, N{CH-(C*H*$_3$)$_2$}), 0.78 (d, J = 12.0 Hz, 6H, N{CH(C*H*$_3$)$_2$}), 0.43 (d, J = 8.0 Hz, 6H, N{CH(C*H*$_3$)$_2$}). $[\alpha]_D^{25}$ −171.0 (c 1, $CHCl_3$). Anal. Calcd for $C_{34}H_{42}Au_2Cl_2N_4$: C, 42.03; H, 4.36; N, 5.77. Found: C, 42.65; H, 4.06; N, 5.30.

(*S*)-1,1′-Binaphthyl-(3,3′-diphenyl)-2,2′-diisocyanide (11). Formic acid (72 μL, 1,91 mmol) was added to a 0 °C acetic anhidride (146 μL, 1.55 mmol). After the addition, the solution was stirred at 50 °C for 2 h and then cooled to room temperature. THF (1.5 mL) was added, the solution was cooled down to 0 °C, and (*S*)-2,2′-(3,3′-diphenyl)-binapthylamine[24] (261 mg, 0.597 mmol) was added and after 20 min the mixture was allowed to warm to ambient temperature, stirred for 10 h, and kept stirring at 50 °C for 2 h. Then, the volatiles were pumped off, and the crude formamide was chromatographed (silica gel, *n*-hexane:ethyl acetate 1:1 as eluent) yielding 0.215 g (73%) of 2,2′-(3,3′-diphenyl)binaphthyldiformamide that was used in the subsequent transformation.[26] To a solution of (*S*)-2,2′-(3,3′-diphenyl)-binaphthyldiformamide (0.190 g, 0.386 mmol) and triethylamine (215 μL, 16.38 mmol) in 16 mL of dichloromethane, a solution of trichloromethylcarbonate (triphosgene) (0. 084 g, 0.283 mmol) in 10 mL of dichloromethane was added dropwise. The mixture was stirred for 3 h, and then the solvent was removed on a rotary evaporator. The resulting residue was chromatographed (silica gel, CH_2Cl_2/hexane, 1:3 as eluent), and the solvent was evaporated to obtain the product as a white solid yielding 0.143 g (81%). IR (THF): 2114s cm^{-1} (C≡N). ^{1}H NMR (300 MHz, $CDCl_3$, 295 K), δ: 8.09 (s, 2H), 8.00 (d, J = 8.4 Hz, 2H), 7.69 (m, 4H), 7.61 (m, 2H), 7.53 (m, 4H), 7.47 (m, 2H), 7.42 (m, 2H), 7.23 (d, J = 8.4 Hz, 2H). Anal. Calcd. for $C_{34}H_{20}N_2$: C, 89.45; H, 4.42; N, 6.14. Found: C, 89.38; H, 4.54; N, 5.68. $[\alpha]_D^{25}$ +117.0 (c 1, $CHCl_3$).

(*S*)-2,2′-[NCAuCl]$_2$-3,3′-Ph$_2$-binaphthyl ((*S*)-12). A 0.100 g portion of **11** (0.219 mmol) was added to a solution of [AuCl-(tht)] (0.140 g, 0.438 mmol) in THF (20 mL). After 15 min of stirring at room temperature the volatiles were pumped off, and the pale gray residue was washed with *n*-hexane (3 × 5 mL) and crystallized from dichloromethane/*n*-hexane. The white solid

(26) The procedure described by Ugi et al. for other isocyanides (ref 13) was used, using triphosgene instead of phosgene as a dehydrating agent.

obtained was decanted, washed with *n*-hexane (3 × 5 mL), and vacuum-dried, yielding 0.174 g (86%). IR: 2211s ν(C≡N). ^{1}H NMR (400 MHz, $CDCl_3$, 295 K), δ: 8.23 (s, 2H), 8.14 (d, J = 8.0 Hz, 2H), 7.78 (t, J = 8.0 Hz, 2H), 7.57 (m, 10H), 7.52 (t, J = 8.0 Hz, 2H), 7.31 (t, J = 8.0 Hz, 2H). Anal. Calcd. for $C_{34}H_{20}N_2Au_2Cl_2$: C, 44.32; H, 2.19; N, 3.04. Found: C, 43.95; H, 2.15; N, 2.96.

(*S*)-2,2′-bis[NH{C(AuCl)(NMe$_2$)}]$_2$-3,3′-Ph$_2$-binaphthyl ((*S*)-13). Dimethylamine (6.33 μL of a 2 M solution in THF, 0.120 mmol) was added to a solution of **12** (50 mg, 0.054 mmol) in THF (15 mL), and the resultant solution was stirred at room temperature until the solution did not show ν(C≡N) IR absorption. Work up as for **2** yielded 0.027 g of a white solid (50%). ^{1}H NMR (400 MHz, $CDCl_3$, 295 K), δ: 8.11 (s, 2H, major), 8.08 (s, 2H, minor), 8.07 (s, 2H, minor), 8.03 (d, J = 3.0 Hz, 2H), 7.86 (d, J = 3.0 Hz, 2H), 7. 96 (d, J = 3.0 Hz, 2H), 7.70−7.20 (m, 16H), 7.00 (s, 2H, N*H*, minor), 6.45 (s, 2H, N*H*, major), 6.41 (s, 2H, N*H*, minor), 3.29 (s, 6H, N(CH_3)$_2$, major), 3.16 (s, 6H, N(CH_3)$_2$, minor), 3.0 (s, 12H, N(CH_3)$_2$, minor), 2.40 (s, 12H, N(CH_3)$_2$, major), 2.35 (s, 12H, N(CH_3)$_2$, minor), 1.94 (s, 12H, N(CH_3)$_2$, minor). Stereoisomeric ratio: 2:1:1. $[\alpha]_D^{25}$ −96.0 (*c* 0.5, $CHCl_3$). Anal. Calcd. for $C_{38}H_{34}N_4Au_2Cl_2$: C, 45.12; H, 3.39; N, 5.54. Found: C, 45.34; H, 3.01; N, 5.46.

(*S*)-2,2′-bis[NH{C(AuCl)(NEt$_2$)}]$_2$-3,3′-Ph$_2$-binaphthyl ((*S*)-14). Diethylamine (7.4 μL, 0.072 mmol) was added to a solution of **12** (30 mg, 0.032 mmol) in THF (10 mL), and the resultant solution was stirred at room temperature until the solution did not show ν(CN) IR absorption. Work up as for **2** yielded 0.020 g (58%) of a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 295 K), δ: 8.14 (s, 2H), 8.10 (s, 2H), 8.05 (s, 2H), 8.04 (d, J = 4.0 Hz, 2H), 7.99 (d, J = 4.0 Hz, 2H), 7. 96 (d, J = 4.0 Hz, 2H), 7.70−7.10 (m, 16H), 6.94 (s, 2H, N*H*), 6.50 (s, 2H, N*H*), 6.39 (s, 2H, N*H*), 3.93 (m, 2H, N(CH_2CH$_3$)$_2$), 3.63 (m, 4H, N(CH_2CH$_3$)$_2$), 3.47 (m, 2H, N(CH_2CH$_3$)$_2$), 3.35 (m, 2H, N(CH_2CH$_3$)$_2$), 3.55 (m, 2H, N(CH_2CH$_3$)$_2$), 3.10 (m, 2H, N(CH_2CH$_3$)$_2$), 2.70 (m, 4H, N(CH_2CH$_3$)$_2$), 2.65 (m, 2H, N(CH_2CH$_3$)$_2$), 2.57 (m, 2H, N(CH_2CH$_3$)$_2$), 2.10 (m, 2H, N(CH_2CH$_3$)$_2$), 0.70 (m, 12H, N(CH$_2$CH_3)$_2$), 0.58 (t, J = 7.0 Hz, 6H, N(CH$_2$CH_3)$_2$), 0.23 (t, J = 7.0 Hz, 6H, N(CH$_2$CH_3)$_2$), 0.12 (t, J = 7.0 Hz, 6H, N(CH$_2$CH_3)$_2$), −0.01 (t, J = 7.0 Hz, 6H, N(CH$_2$CH_3)$_2$). Stereoisomeric ratio: 1:1:1. $[\alpha]_D^{25}$ −125.0 (*c* 0.5, $CHCl_3$). Anal. Calcd. for $C_{42}H_{42}N_4Au_2Cl_2$: C, 47.25; H, 3.97; N, 5.25. Found: C, 47.17; H, 4.27; N, 5.17.

Experimental Procedure for X-ray Crystallography. Suitable single crystals of **2** and **9** were obtained by layering hexane in a THF solution of the corresponding compound. Crystals were mounted in glass fibers, and diffraction measurements were made using a Bruker SMART CCD and Varian Supernova area-detector diffractometers with Mo−K$_a$ radiation (λ = 0.71073 Å).[27] Intensities were integrated from several series of exposures, each exposure covering 0.3° in ω, the total data set being a hemisphere.[28] Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.[29] The structures were solved by direct methods and refined by least-squares on weighted F^2 values for all reflections (see Table 3).[30] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All the hydrogen atoms, including those involved in hydrogen bonding, were calculated with a riding model.[31] Complex neutral-atom scattering factors were used.[32] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary publications with the deposition numbers CCDC-777502 for **2** and CCDC-777503 for **9**. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3

	2	**9**
empirical formula	$C_{14}H_{15}AuClN_3$	$C_{26}H_{26}Au_2Cl_2N_4$
formula weight	457.71	859.34
temperature	293(2) K	298(2)
wavelength (Å)	0.71073	0.71073
crystal system	orthorhombic	orthorhombic
space group	*P*2(1)2(1)2(1)	*P*2(1)2(1)2(1)
a (Å)	9.6832(2)	7.372(5)
b (Å)	16.2667(3)	16.075(12)
c (Å)	19.8061(4)	23.682(18)
β (deg)	90.00	90.00
V (Å^3)	3119.73(11)	2807(4)
Z	8	4
D_{calc} (g cm^{-3})	1.949	2.034
absorption coefficient (mm^{-1})	9.592	10.654
F(000)	1727	1608
crystal size (mm)	0.3345 × 0.3196 × 0.0834	0.20 × 0.04 × 0.04
θ range for data collection	2.94 to 26.37°	1.53 to 26.60°
reflections collected	31001	24822
independent reflections	6368 [*R*(int) = 0.0620]	5813 [*R*(int) = 0.1343]
absorption correction	analytical	multiscan
data/restraints/parameters	6368/0/345	5813/0/312
Flack parameter	−0.013(11)	0.00(3)
goodness-of-fit on F^2	1.040	1.013
R_1 [$I > 2\sigma(I)$]	0.0430	0.0495
wR_2 (all data)	0.0838	0.1670

General Procedures for the Catalytic Reactions. All the reactions were carried out under N_2 in solvents dried using a Solvent Purification System (SPS). Thin layer chromatography (TLC) was carried out using TLC-aluminum sheets with 0.2 mm of silica gel (Merck 60 F254). Chromatography purifications were carried out using flash grade silica gel (SDS S-2 Chromatogel 60 ACC, 40−60 μm). NMR spectra were recorded at 25 °C on a Bruker Avance 400 Ultrashield. 2,2-Diphenyl-4,5-hexadien-1-ol,[33] and propargyl pivaloate,[34] were synthesized employing published procedures. Chiral HPLC was performed on a Hewlett-Parkard chromatograph equipped with a 25 cm Chiracel OD-H column.

Intramolecular Hydroalkoxylation of 2,2-Diphenyl-4,5-hexadien-1-ol. A mixture of the neutral gold carbene (0.05 equiv) and AgOTs (0.05 equiv) in toluene (1 mL) was stirred at room temperature for 10 min, and treated with 2,2-diphenyl-4,5-hexadien-1-ol (1 equiv) in toluene. The resulting suspension was stirred at room temperature and followed by TLC. Column chromatography of the reaction mixture (hexane/EtOAc 20:1) gave 2-vinyltetrahydrofurane as a colorless oil.

(27) (a) *SMART V5.051 diffractometer control software*; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1998. (b) *CrysAlisPro*, Version 1.171.33.48; Oxford Diffraction Ltd.: Abingdon, U.K.

(28) (a) *SAINT V6.02 integration software*; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1999. (b) *CrysAlisPro*, Version 1.171.33.48; Oxford Diffraction Ltd.: Abingdon, U.K.

(29) (a) Sheldrick, G. M. *SADABS: A program for absorption correction with the Siemens SMART system*; University of Göttingen: Göttingen, Germany, 1996. (b) *CrysAlisPro*, Version 1.171.33.48; Oxford Diffraction Ltd.: Abingdon, U.K.

(30) *SHELXTL program system version 5.1*; Bruker Analytical X-ray Instruments Inc.: Madison, WI, 1998.

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Cyclopropanation of Styrene with Propargyl Pivaloate. The gold catalyst was generated by mixing the corresponding neutral gold carbene (0.05 equiv), $AgSbF_6$ (0.05 equiv), and NO_2Me (3 mL) and stirring at room temperature for 10 min. Then, propargyl pivaloate (1 equiv) in NO_2Me (3 mL) and styrene (4 equiv) were added. The resulting suspension was stirred at room temperature and followed by TLC. The resulting mixture was concentrated and column chromatography purified (hexane/Et_2O 97:3) to yield the analytically pure cyclopropane.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.