DOI: 10.1002/chem.201103140

The More Gold—The More Enantioselective: Cyclohydroaminations of γ-Allenyl Sulfonamides with Mono-, Bis-, and Trisphospholane Gold(I) Catalysts

Lara-Isabel Rodríguez, Torsten Roth, Julio Lloret Fillol, Hubert Wadepohl, and Lutz H. Gade*[a]

Dedicated to Professor Peter Hofmann on the occasion of his 65th birthday

Abstract: A series of chiral mono-, di-, and trinuclear gold(I) complexes have been prepared and used as precatalysts in the asymmetric cyclohydroamination of *N*-protected γ-allenyl sulfonamides. The stereodirecting ligands were mono-, di-, and tridentate 2,5-diphenylphospholanes, which possessed C_1, C_2, and C_3 symmetry, respectively, thereby rendering the catalytic sites in the di- and trinuclear complexes symmetry equivalent. The C_3-symmetric trinuclear complex displayed the highest activity and enantioselectivity (up to 95% *ee*), whilst its mono- and dinuclear counterparts exhibited considerably lower enantioselectivities and activities. A similar trend was observed in a series of mono-, di-, and trinuclear 2,5-dimethylphospholane gold(I) complexes. Aurophilic interactions were established from the solid-state structures of the trinuclear gold(I) complexes, thereby raising the question as to whether these secondary forces were responsible for the different catalytic behavior observed.

Keywords: asymmetric catalysis · enantioselectivity · gold · hydroamination · modular ligands

Introduction

Enantioselective gold catalysis has experienced an explosive growth over the past decade, despite some inherent limitations of gold(I) catalysts in inducing stereoselectivity. Gold(I) usually favors a twofold linear coordination,[1,2] which places the ancillary ligand (the source of chiral induction) remote from the reactive site. To overcome this drawback, different strategies have been devised, such as the use of chiral counteranions[3] or, more recently, the construction of an encapsulating chiral pocket around the active center of a mononuclear gold catalyst.[4] Secondary forces have been proposed to have a remarkable effect on the conformational orientation of the complex and, therefore, in the observed catalytic properties.

For example, in 2005, Echavarren and co-workers studied the enantioselective alkoxycyclization of enynes using chiral monodentate and dinuclear phosphine–gold(I) complexes,[5] the latter of which induced significantly higher enantioselectivity than the former. Gagné and co-workers investigated the cycloisomerization of eneallenes,[6] and they suggested that conformational rigidity owing to metallophilic interactions may be a necessary structural feature in active dinuclear gold(I) catalysts to impose stereoinduction on the distant coordination site. Recently, Che and co-workers investigated a series of dinuclear gold(I) complexes and they proposed that there was a direct relationship between the existence of Au–Au interactions and the enantioselectivity of the intermolecular hydroarylation of allenes with indoles.[7]

In a recent profound mechanistic investigation of the role of dinuclear catalysts in gold-catalyzed oxidative heteroarylations of alkenes, Toste and co-workers observed that aurophilic interactions in solution (even if absent in the solid state) modulated the redox behavior of their catalysts.[8] This observation provided the first quantitative indication of the way in which two Au centers may influence each other in elementary reaction steps of catalytic cycles. Comparable mechanistic studies with the aim of assessing how the modification of the accessible conformational space modifies the stereoinduction in enantioselective gold-catalyzed reactions have not been reported.

Despite indications that dinuclear gold catalysts may display superior performance for certain reactions,[7–9] no examples of gold complexes of higher nuclearity have been studied in asymmetric catalysis to date. Nor has there been a systematic study of the influence of catalyst nuclearity for a specific structural type of chiral stereodirecting ligand. As noted above, aurophilic interactions may significantly influence the activity of the catalyst, considering the fact that they are similar in energy to hydrogen bonding and that their use has been well-established in, for example, the assembly of supramolecular structures.[10] Herein, we report

[a] Dr. L.-I. Rodríguez, Dipl.-Chem. T. Roth, Dr. J. Lloret Fillol, Prof. Dr. H. Wadepohl, Prof. Dr. L. H. Gade
Anorganisch-Chemisches Institut, Universität Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)
Fax: (+49) 6221-54-5609
E-mail: lutz.gade@uni-hd.de

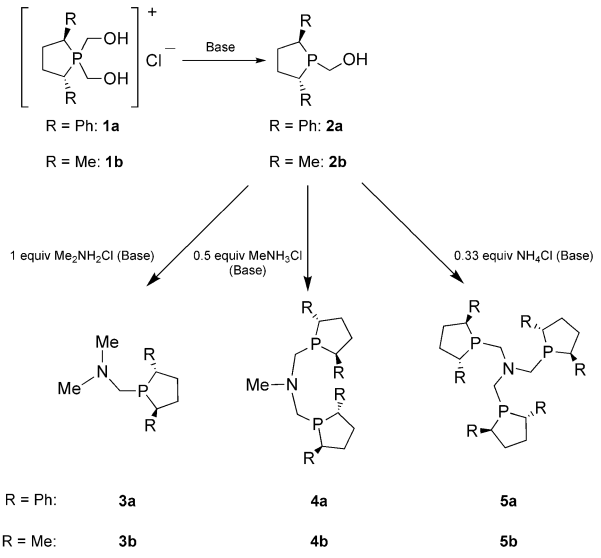
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201103140.

the synthesis of chiral mono-, di-, and trinuclear gold complexes and a systematic study of their activities and the enantioselectivities afforded in the asymmetric cyclohydroamination of *N*-protected γ-allenyl sulfonamides. In these di- and trinuclear complexes, the C_2- and C_3-symmetric chiral ligands rendered the catalytic sites symmetry-equivalent.[11,12]

Results and Discussion

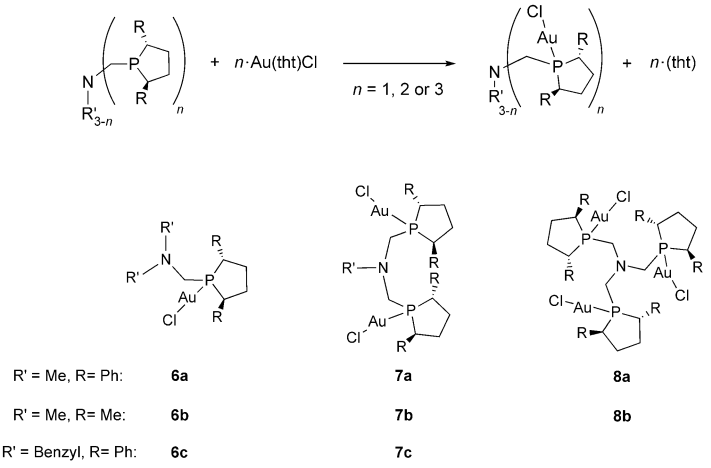
Synthesis and characterization of chiral phospholanomethylamine ligands and their gold(I) complexes: We recently reported a new class of chiral bidentate C_2- and tridentate C_3-symmetric diphenylphospholane (DPP) and dimethylphospholane (DMP) ligands.[13] Their corresponding Rh^I complexes were shown to be highly enantioselective hydrogenation catalysts for a range of prochiral alkenes.

Herein, the synthesis of several new chiral mono- and bidentate ligands is reported, by following a similar procedure as described previously, to evaluate the catalytic properties of their corresponding gold complexes and compare them with their trinuclear counterparts. Whereas ligands **4b**, **5a**, and **5b** were presented in our previous report, phospholanes **3a**, **3b**, and **4b** were synthesized for the first time in this work (Scheme 1).[14] All of these compounds were characterized by elemental analysis and high-resolution mass spectrometry as well as by ^{1}H NMR, ^{31}P NMR, and $^{13}C\{^1H\}$ NMR spectroscopy (analysis of the COSY, DEPT-135, HSQC, and HMBC spectra allowed the complete assignment of all of the ^{1}H NMR and ^{13}C NMR resonances).



Scheme 1. Synthesis of monodentate, C_2-bidentate, and C_3-tridentate phospholane ligands.

Only a few phospholane gold(I) complexes have been described in the literature to date.[7,15] Notable examples include the dinuclear gold(I) complexes prepared by Corma and co-workers using Me-DuPhos ligands, which efficiently performed the enantioselective hydrogenation of alkenes and imines.[15c] The gold complexes reported herein were synthesized by addition of an equimolar amount of the precursor [Au(tht)Cl] to a solution of the corresponding chiral phospholane ligand (Scheme 2) and were found to be highly soluble in polar organic solvents (CH_2Cl_2, $CHCl_3$, CH_3CN, acetone), with the exception of trinuclear complex **8b**, which precipitated as a pure crystalline solid from the reaction mixture (CH_2Cl_2/CH_3CN).



Scheme 2. General synthesis of chiral mono-, di-, and trinuclear phospholane gold(I) complexes.

In all cases, the formation of the metal complexes was accompanied by a shift in the $^{31}P\{^1H\}$ NMR singlet by approximately 40–45 ppm relative to the respective free ligands. The major ion peaks found in the high-resolution mass spectra (ESI(+)) corresponded to $[M+H]^+$ or to the loss of one chloride group ($[M-Cl]^+$), thus indicating that the ligand–metal interactions and the nuclearity of the complexes were maintained in solution. In all cases, the analytical data were in accordance with the formation of neutral gold(I) species. Single-crystal X-ray analysis of complexes **6a**, **6b**, **8a**, and **8b** corroborated the proposed solution-state structures (for full details and representations of complexes **6a** and **6b**, see the Supporting Information). All structures displayed the expected almost-linear coordination for gold (P-Au-Cl 172–178°). For mononuclear complexes **6a** and **6b**, no secondary metallophilic interactions were found in the solid state. Interestingly, short Au–Au contacts were observed in both C_3-symmetric complexes. In the crystals of DMP complex **8b**, the aurophilic interactions were intermolecular (Au–Au 3.432 Å), thereby connecting the complexes in a zigzag-type chain (Figure 1), which may explain the observed low solubility of compound **8b**.

In contrast, DPP complex **8a** displayed a short intramolecular Au–Au interaction between two of the three gold atoms (Au–Au 2.978 Å) whilst the third atom was neither engaged in inter- nor intramolecular interactions in the crystal structure (Figure 2). This feature revealed that at least two of the three gold atoms were sufficiently close to allow for aurophilic interaction in solution, which could potentially influence the catalytic properties of the system.

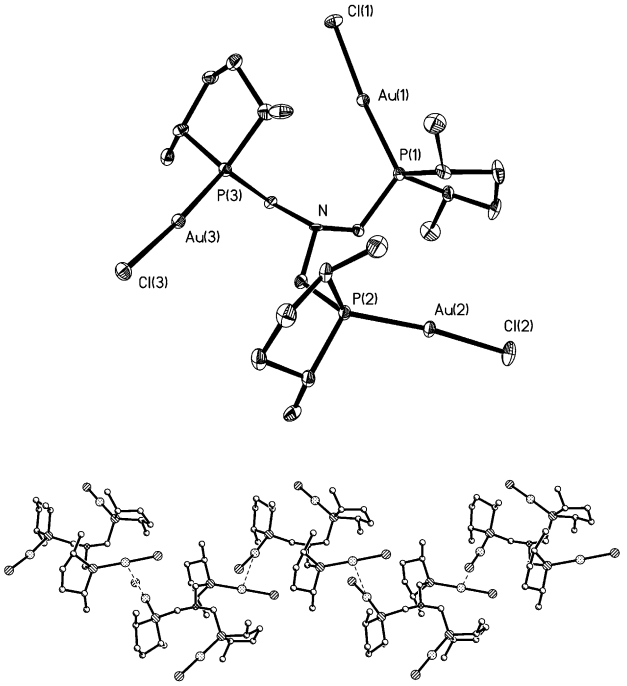


Figure 1. Top: Molecular structure of complex **8b**, ellipsoids set at 50% probability. H atoms and one molecule of CH_2Cl_2 are omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)–Au(1) 2.231(3), P(2)–Au(2) 2.226(2), P(3)–Au(3) 2.228(2); P(1)-Au(1)-Cl(1) 172.43(9), P(2)-Au(2)-Cl(2) 173.28(10), P(3)-Au(3)-Cl(3) 174.49(9). Bottom: Ball-and-stick structure of complex **8b**, which shows aggregation through Au···Au contacts (3.430 Å).

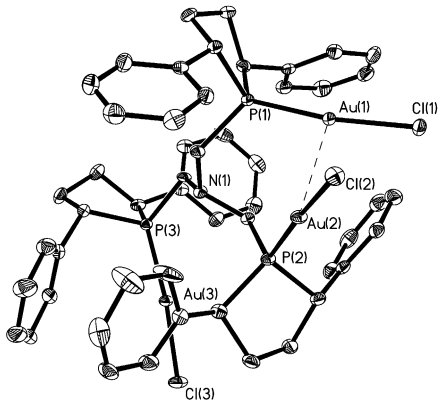


Figure 2. Molecular structure of complex **8a**, ellipsoids set at 50% probability. H atoms and one molecule of $CHCl_3$ are omitted for clarity. There was a statistical 60:40 disorder of two conformers that differed in orientation of the phenyl ring in the crystal structure, of which only the major component is shown. Selected bond lengths [Å] and angles [°]: Au(1)–Au(2) 2.9782(15), P(1)–Au(1) 2.2374(15), P(2)–Au(2) 2.2336(12), P(3)–Au(3) 2.2246(12); P(1)-Au(1)-Cl(1) 171.75(4), P(2)-Au(2)-Cl(2) 175.26(4), P(3)-Au(3)-Cl(3) 173.91(4).

Nevertheless, the aurophilic attractive forces were weak, as also observed previously for oligonuclear gold(I) compounds.[10] In a low-temperature VT NMR study of compound **8a**, a single ^{31}P NMR signal was observed over the temperature range 295–200 K, albeit significantly broadened at the lower temperatures, thus indicating the presence of intramolecular aggregation at even-lower temperatures (see the Supporting Information). This result indicated that the threefold symmetry of the precatalyst was essentially preserved on the experimental timescale under these conditions. Because the catalysis was performed at 323 K and above (see below), the general symmetry-based argument (see the Introduction) remained valid.

Unfortunately, all attempts to grow suitable crystals of dinuclear complexes **7a** or **7b** for X-ray diffraction failed. To obtain insight into the structural details of the dinuclear complexes, the *N*-benzyl-substituted diphospholane ligand derivative of compound **4a** and its corresponding gold complex (**9**) were prepared by following similar procedures. Figure 3 shows the molecular structure of complex **9**, which was characterized by an intramolecular aurophilic interaction (Au–Au 3.156 Å).

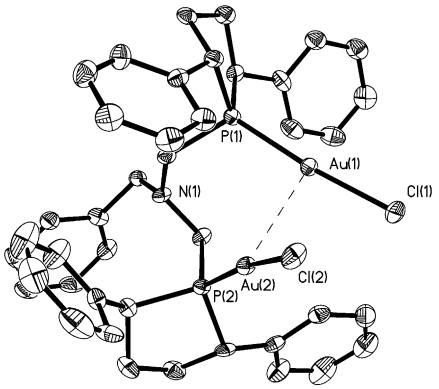
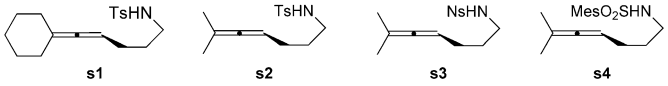


Figure 3. Molecular structure of complex **9**, ellipsoids set at 50% probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Au(1)–Au(2) 3.156(1), P(1)–Au(1) 2.227(2), P(2)–Au(2) 2.231(2); P(1)-Au(1)-Cl(1) 173.99(7), P(2)-Au(2)-Cl(2) 171.54(7).

Catalytic asymmetric cyclohydroamination of *N*-protected *γ*-allenyl sulfonamides: The use of allenes as reactive building blocks has emerged as a powerful tool for organic transformations in fields such as natural-product synthesis, pharmaceutical chemistry, and materials science.[16] Gold(I) complexes are known to activate allene groups toward nucleophilic attack and have been used to promote the formation of new C–C, C–N, and C–O bonds.[1c,r,17] Enantioselective intramolecular functionalization and isomerization of allenes have recently been successfully performed with chiral gold(I) complexes.[3,4a–c,6,18,19]

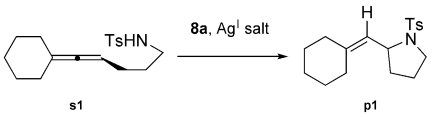
We chose the cyclohydroamination of γ-allenyl-*N*-sulfonamides as a suitable reference reaction within this area of gold catalysis. Our first tentative trials with the phospholane gold(I) complexes were carried out with trinuclear C_3-symmetric gold(I) complex **8a** and a cyclic *N*-protected γ-allenyl tosylamide (**s1**) as a reference system (Scheme 3).

Similar to previous work reported by Toste and co-workers,[19] silver salts as halide abstractors with non-coordinating counterions, such as $AgBF_4$ and AgOTf, were needed to



Scheme 3. Allenes used in this study.

Table 1. Screening of experimental conditions in the asymmetric cyclohydroamination reaction of allene **s1** with catalyst complex **8a**.[a]



Entry	Silver salt	Solvent	T [°C]	t [h]	*ee* [%][b]
1	–	toluene	50	120[d]	rac
2	$AgBF_4$	–	20	0.5	rac
3	AgOTf	–	20	0.5	rac
4	AgOBz (1.0)[c]	–	50	48	95
5	AgOBz (0.8)[c]	–	50	48	95
6	AgOBz (1.2)[c]	–	50	48	93
7	AgOBz	nitromethane	50	48	55
8	AgOBz	CH_2Cl_2	20	120	85
9	AgOBz	chlorobenzene	50	48	94
10	AgOPMB	toluene	50	48	95
11	AgOPNB	–	50	20	92
12	AgOPNB	–	20	48	94
13	AgODNB	–	50	20	92
14	CF_3CO_2Ag	–	50	20	84

[a] All reactions were carried out with 5 mol% of Au^I in 1 mL solvent. Full conversion was always observed by ^1H NMR spectroscopy. [b] Enantioselectivities determined by chiral HPLC. [c] Number of equivalents used with respect to Au^I are shown in parentheses. [d] 12% yield.

provide extremely active systems; however, no enantioselectivity was observed in these cases (Table 1, entries 2 and 3).

On the other hand, silver salts with more-coordinating anions, such as silver benzoate (AgOBz), were suitable chloride-abstracting agents, thereby achieving full conversions and high enantiomeric excesses (95% *ee* in both cases; Table 1, entries 4). An equimolar amount of silver salt with respect to gold was employed in all catalytic runs because an excess or deficit of the Ag^I salt showed no gain either in the activity or enantioselectivity (Table 1, entries 4–6), in contrast to previous reports.[4,5,20] Toluene and chlorobenzene were the optimal solvents, whilst the use of more-polar solvents, such as nitromethane or CH_2Cl_2, led to an erosion of the enantioselectivity (Table 1, entries 7, 8, and 9),

Next, we studied the electronic effect of the counteranion in the silver salt; in particular, a silver salt with the electron-donating *para*-methoxybenzoate counterion (AgOPMB) and the corresponding silver salts with the electron-withdrawing *para*-nitrobenzoate (AgOPNB) and 3,5-dinitrobenzoate counterions (AgODNB). Similar activities and selectivities to AgOBz were obtained with the electron-donating counteranion silver salt AgOPMB (Table 1, entry 10). On the other hand, the electron-withdrawing counteranion silver salts AgOPNB and AgODNB (Table 1, entries 11 and 13) were advantageous with respect to reaction times,[19] albeit with a slight decrease in enantioselectivity. However, if the reaction using AgOPNB was conducted at 20°C instead of 50°C, the loss of enantioselectivity was compensated at the expense of reaction time (Table 1, entry 12). The weaker coordinating trifluoroacetate counterion led to a slightly lower enantiomeric excess (Table 1, entry 14).

With the optimized system in hand, we evaluated the efficiency of mono- and dinuclear complexes **6a** and **7a** to compare their catalytic behavior to that observed for their trinuclear counterpart **8a** (Table 2). Whilst the C_3-symmetric

Table 2. Examination of the catalytic properties of complexes **6a**, **7a**, and **8a** in the hydroamination of allenes.[a]

Entry	Substrate	Silver salt	**6a** *ee* [%][b,c]	**7a** *ee* [%][b,c]	**8a** *ee* [%][b]	**8a** t [h]
1	**s1**	AgOBz	rac	36	95	48
2		AgOPNB	rac	36	92	20
3	**s2**	AgOBz	−21	22	94	48
4		AgOPNB	−23	29	91	12
5	**s3**	AgOBz	−15	33	91	24
6		AgOPNB	−11	40	87	10

[a] All reactions were carried out with 5 mol% of Au^I in toluene (1 mL) at 50°C. [b] Enantioselectivities determined by chiral HPLC. [c] Reaction time: 120 h.

complex provided high enantioselectivities (up to 95% *ee*), C_2-symmetric complex **7a** gave moderate *ee* values (22–40% *ee*). Surprisingly, monodentate complex **6a** produced racemic mixtures when substrate **s1** was studied. Moreover, unexpectedly, the opposite enantiomer of the desired pyrrolidine was afforded to that derived from substrates **s2** and **s3**.

We also found that complex **9**, the *N*-benzylated analogue of compound **7a**, afforded virtually identical enantioselectivity (20% *ee*) for the cyclization of substrate **s2**, thus indicating that the catalyst performance was not significantly influenced by structural variation at this position.

The electronic effect of the *N*-substitution of the allene was clearly reflected in the differences in reactivity between the substrates. Full conversion of the more-electron-withdrawing *N*-substituted substrate (**s3**) was achieved with complex **8a** (reaction time: 10 h), but with a slight deterioration of the enantiomeric excess (Table 2, entries 5 and 6). Increasing the reaction temperature (Table 2, entry 5) to 70°C and 100°C gave complete conversion after 18 h and 10 h, respectively. Remarkably, these elevated temperatures only led to a slight decrease in enantioselectivity (70°C: 89% *ee*; 100°C: 82% *ee*). This result demonstrated the robust nature of this trinuclear gold catalyst.

On the other hand, with the mesityl-substituted allene (**s4**), longer reaction times were needed to achieve high or full conversion with complex **8a** (AgOBz: 67% conversion, 87% *ee*, 5 days; AgOPNB: 100% conversion, 84% *ee*, 48 h), whilst less than 5% conversion was observed when the related mono- and dinuclear complexes **6a** and **7a** were used instead.

Figure 4 shows the trend in enantioselectivity for the cyclohydroamination reaction versus the DPP gold complex employed. To assess the scope of this approach, we carried

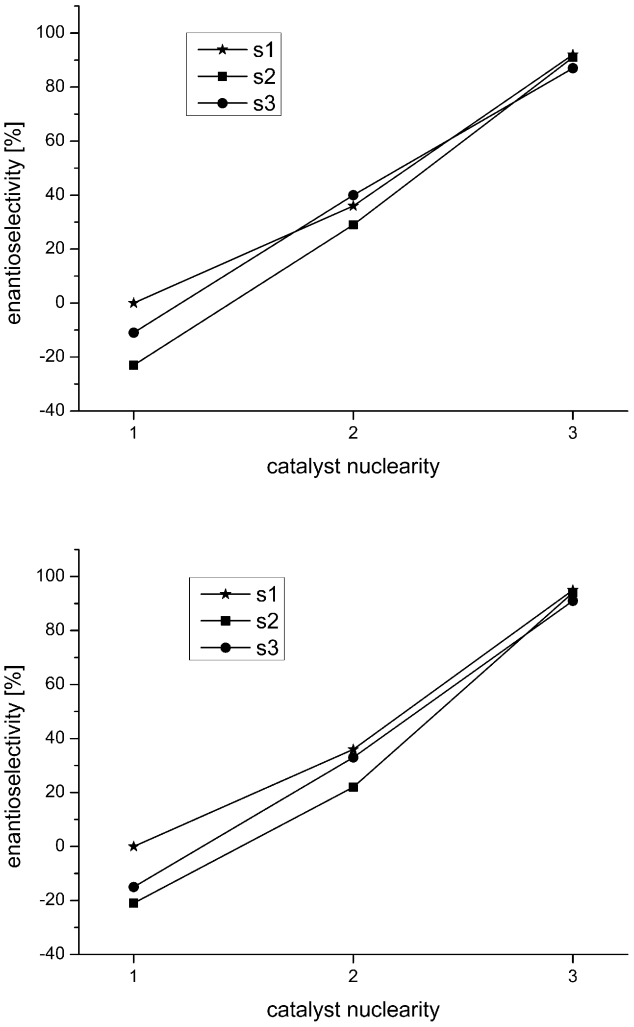


Figure 4. Plot of enantioselectivity versus the nuclearity of the gold complex (**6a**, **7a**, and **8a**). Halide abstractor: AgOPNB (top) and AgOBz (bottom).

out an analogous study with DMP complexes **6b**, **7b**, and **8b**, which contained methyl groups instead of phenyl substituents at positions 2 and 5 on the phospholane ring. As in the case of the DPP series, chiral trinuclear complex **8b** promoted the reaction of substrate **s2** to afford the corresponding pyrrolidine with the highest enantioselectivity (AgOBz: 38% conversion, 75% *ee*, 120 h; AgOPNB: 100% conversion, 75% *ee*, 72 h). However, compound **8b** was less active than compound **8a**, presumably owing to its low solubility in the reaction medium, whilst C_2-symmetric complex **7b** was significantly more active than its Ph-substituted analogue (AgOBz: 98% conversion, 34% *ee*, 120 h; AgOPNB: 100% conversion, 35% *ee*, 48 h).[21]

Conclusion

A series of chiral mono, di-, and trinuclear gold(I)–phospholane complexes were prepared and used in the first examples of chiral trinuclear gold(I) complexes employed in enantioselective catalysis. This result opened up the possibility of studying a series of chiral catalysts with increasing nuclearity from combining symmetry-equivalent sites.

Using the gold(I)-catalyzed cycloamination of γ-allenyl sulfonamides as a reference reaction allowed us to study the influence of the nuclearity of the catalysts on their catalytic performance. Interestingly, C_3-symmetric trinuclear complex **8a** surpassed its mono- and dinuclear congeners both in terms of activity and enantioselectivity (up to 95% *ee*). Aurophilic interactions may be responsible for this intriguing behavior.

Experimental Section

General: All manipulations were carried out under the exclusion of air and moisture by using standard Schlenk and glove-box techniques, unless otherwise stated. Argon 5.0, purchased from Messer Group GmbH, was used after drying over Granusic© phosphorus pentoxide (granulated). Solvents were dried according to literature procedures[22] and stored in glass ampules under an argon atmosphere. Et_2O and *n*-pentane were distilled from sodium/potassium alloy, benzene and *n*-hexane from potassium, MeOH over magnesium, CH_2Cl_2 and $CHCl_3$ from calcium hydride, and toluene from sodium. The same procedures were used to dry the deuterated solvents. Degassed solvents were obtained by three successive freeze–pump–thaw cycles. Triethylamine was degassed. (2*S*,5*S*)-1-Hydroxy-1-oxo-2,5-diphenylphospholane,[23] (2*R*,5*R*)-bis(1,1-hydroxymethyl)-2,5-diphenylphospholanium chloride (**1a**),[13] (2*R*,5*R*)-bis(1,1-hydroxymethyl)-2,5-dimethylphospholanium chloride (**1b**),[13] bis((2*R*,5*R*)-2,5-dimethylphospholanomethyl)methylamine (**4b**),[13] benzyl-bis((2*S*,5*S*)-2,5-diphenylphospholanomethyl)amine (**4c**),[13] tris((2*R*,5*R*)-2,5-diphenylphospholanomethyl)amine (**5a**),[13] tris(((2*R*,5*R*)-2,5-dimethyl-phospholan-1-yl)methyl)amine (**5b**),[13] [Au(tht)Cl] (tht = tetrahydrothiophene),[24] hydroamination substrates **s1**[19] and **s2**,[25] and silver salts AgOPNB, AgOPMB, and AgODNB[26] were prepared according to literature procedures. All other chemicals were used as received without further purification. NMR spectra were recorded on Bruker Avance II (400 MHz) and Bruker Avance III (600 MHz) instruments. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced to residual proton solvent signals or carbon resonances.[27] H_3PO_4 (^{31}P) and was used as an external standard. The following abbreviations were used: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), m (multiplet), br (broad signal). Enantioselectivities were measured on a HPLC Agilent Technologies 1200 Series instrument using a chiral Daicel Chiracel AD-H column. Optical rotation data were acquired by using a PerkinElmer Model 341 polarimeter. High-resolution mass spectra were aquired on Bruker ApexQe hybrid 9.4 T FT-ICR (ESI) and JEOL JMS-700 magnetic sector (FAB) spectrometers at the mass spectrometry facility of the Institute of Organic Chemistry, the University of Heidelberg. Elemental analysis was carried out in the Microanalysis Laboratory of the Heidelberg Chemistry Department.

Representative procedure for the preparation of complexes 6a, 7a, 7b, 8a, and 9: To a stirring solution of compound **3a** (0.118 g, 0.40 mmol) in CH_2Cl_2 (7 mL), [Au(tht)Cl] (0.127 g, 0.40 mmol) was added under exclusion of ambient light. After stirring for 10 min, the volatile compounds were removed in vacuo. Recrystallization of the residue from CH_2Cl_2 and Et_2O gave compound **6a** as a white microcrystalline solid. For compound numbering, see the Supporting Information.

Chlorido((((2*S*,5*S*)-2,5-diphenylphospholan-1-yl-κ*P*)methyl)-*N*,*N*-dimethylamine)gold(I) (6a): Yield: 0.117 g (56%); $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, 298 K): $\delta = 43.0$ ppm (s); ^1H NMR (600.1 MHz, $CDCl_3$, 298 K): $\delta = 7.49$–7.25 (10H; ArH), 4.22–4.15 (m, 1H; H6), 3.82–3.69 (m, 1H; H3), 2.87–2.77 (m, 1H; H2′), 2.72–2.54 (m, 2H; H4′ and H5′), 2.46 (dd, $^2J(H,H) = 13.9$ Hz, $^2J(H,P) = 3.7$ Hz, 1H; H2), 2.26 (s, 6H; H1), 2.33–2.20 ppm (m, 2H; H4 and H5); $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$,

298 K): $\delta = 139.4$ (s; C_{ipso}), 134.2 (d, $^2J(C,P) = 4.8$ Hz; $C_{ipso'}$), 129.3–127.7 (ArC), 56.3 (d, $^1J(C,P) = 38.8$ Hz; C2), 47.4 (d, $^3J(C,P) = 6.9$ Hz; C1), 46.9 (d, $^1J(C,P) = 31.0$ Hz; C3), 46.8 (d, $^1J(C,P) = 29.8$ Hz; C6), 35.0 (d, $^2J(C,P) = 5.0$ Hz; C4), 31.1 ppm (s, C5); HRMS (ESI(+)): *m/z* (%) calcd: 530.1079; found: 530.1054 (100) $[M+H]^+$; elemental analysis calcd (%) for $C_{19}H_{24}NPAuCl$: C 43.07, H 4.57, N 2.64; found: C 42.77, H 4.57, N 2.63.

Dichlorido(bis(((2*S*,5*S*)-2,5-diphenylphospholan-1-yl-κ^2*P*)methyl)-*N*-methylamine)digold(I) (7a): Yield: 0.185 g (54%); $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, 298 K): $\delta = 43.7$ ppm (s); ^1H NMR (600.1 MHz, $CDCl_3$, 298 K): $\delta = 7.38$–7.22 (20H; ArH), 4.15–4.06 (m, 2H; H-6), 3.57–3.48 (m, 2H; H3), 3.28 (dd, $^2J(H,H) = 14.2$ Hz, $^2J(H,P) = 6.2$ Hz; H2), 2.63–2.48 (m, 4H; H4 and H5), 2.33 (d, $^2J(H,H) = 14.2$ Hz, 2H; H2′), 2.27–2.11 (m, 4H; H4′ and H5′), 2.15 ppm (s, 3H; H1); ^{13}C NMR (150.9 MHz, $CDCl_3$, 298 K): $\delta = 139.0$ (s; C_{ipso}), 133.7 (d, $^2J(C,P) = 5.0$ Hz; $C_{ipso'}$), 129.4–127.8 (ArC), 55.6 (dd, $^1J(C,P) = 36.0$ Hz, $^3J(C,P) = 7.0$ Hz; C2), 47.6 (d, $^1J(C,P) = 30.4$ Hz; C3), 47.0 (d, $^1J(C,P) = 29.6$ Hz; C6), 46.7 (t, $^3J(C,P) = 5.5$ Hz; C1), 35.6 (d, $^2J(C,P) = 5.3$ Hz; C4), 31.4 ppm (s; C5); HRMS (ESI(+)): *m/z* (%) calcd: 964.1577; found: 964.1582 (100) $[M-Cl]^+$; elemental analysis calcd (%) for $C_{35}H_{39}NP_2Au_2Cl_2$: C 42.02, H 3.93, N 1.40; found: C 42.24, H 3.86, N 1.70.

Dichlorido(bis(((2*S*,5*S*)-2,5-dimethylphospholan-1-yl-κ^2*P*)methyl)-*N*-methylamine)digold(I) (7b): Yield: 0.322 g (71%); $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, 298 K): $\delta = 36.6$ ppm (s); ^1H NMR (600.1 MHz, $CDCl_3$, 298 K): $\delta = 3.45$–3.29 (m, 4H; H2), 2.77 (s, 3H; H1), 2.69–2.60 (m, 2H; H3), 2.53–2.43 (m, 2H; H6), 2.34–2.18 (m, 4H; H4 and H5), 1.60–1.50 (m, 2H; H4′), 1.49–1.40 (m, 2H; H5′), 1.31 (dd, $^3J(H,P) = 20.6$ Hz, $^3J(H,P) = 7.1$ Hz; Me6), 1.27 ppm (dd, $^3J(H,P) = 14.7$ Hz, $^3J(H,P) = 7.3$ Hz; Me3); $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 298 K): $\delta = 53.9$ (dd, $^1J(C,P) = 41.1$ Hz, $^3J(C,P) = 6.3$ Hz; C2), 48.1 (t, $^3J(C,P) = 6.3$ Hz; C1), 35.8 (d, $^2J(C,P) = 1.8$ Hz; C4), 35.5 (d, $^1J(C,P) = 34.0$ Hz; C3), 35.3 (d, $^1J(C,P) = 36.3$ Hz; C6), 35.3 (d, $^2J(C,P) = 4.7$ Hz; C5), 20.5 (d, $^2J(C,P) = 6.7$ Hz; Me6), 13.4 ppm (d, $^2J(C,P) = 3.0$ Hz; Me3); HRMS (ESI(+)): *m/z* (%) calcd: 716.0951; found: 716.0953 (40) $[M-Cl]^+$; elemental analysis calcd (%) for $C_{15}H_{31}NP_2Au_2Cl_2$: C 23.95, H 4.15, N 1.86; found: C 23.65, H 4.03, N 2.02.

Trichlorido(tris(((2*S*,5*S*)-2,5-diphenylphospholan-1-yl-κ^3*P*)methyl)-amine)trigold(I) (8a): Yield: 0.143 g (53%); $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, 298 K): $\delta = 41.1$ ppm (s); ^1H NMR (600.1 MHz, $CDCl_3$, 298 K): $\delta = 7.36$–7.16 (30H; ArH), 4.13–4.06 (m, 3H; H2), 3.98–3.88 (m, 3H; H1), 3.88–3.80 (m, 3H; H5), 2.78–2.66 (m, 3H; H4), 2.56–2.40 (m, 6H; H3 and H3′), 2.05–1.95 (m, 3H; H4′), 1.73 ppm (dd, $^2J(H,H) = 14.2$ Hz, $^2J(H,P) = 2.1$ Hz, 3H; H1′); $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 298 K): $\delta = 139.5$ (d, $^2J(C,P) = 0.5$ Hz; C_{ipso}), 133.5 (d, $^2J(C,P) = 5.8$ Hz; $C_{ipso'}$), 129.5–127.8 (ArC), 54.0 (dt, $^1J(C,P) = 38.7$ Hz, $^3J(C,P) = 5.9$ Hz; C1), 47.3 (d, $^1J(C,P) = 31.8$ Hz; C2), 46.9 (d, $^1J(C,P) = 30.7$ Hz; C5), 36.9 (d, $^2J(C,P) = 5.2$ Hz; C4), 31.3 ppm (s; C3); HRMS (ESI(+)): *m/z* (%) calcd: 1434.1843; found: 1434.1853 (51) $[M-Cl]^+$; elemental analysis calcd (%) for $C_{51}H_{54}NP_3Au_3Cl_3$: C 41.64, H 3.70, N 0.95; found: C 41.28, H 3.67, N 0.98.

Dichlorido(bis(((2*S*,5*S*)-2,5-diphenylphospholan-1-yl-κ^2*P*)methyl)-*N*-benzylamine)digold(I) (9): The corresponding ligand for the preparation of this complex was synthesized according to a literature procedure.[13] Yield: 0.207 g (66%); $^{31}P\{^1H\}$ NMR (242.9 MHz, CD_3Cl, 298 K): $\delta = 43.5$ ppm (s); ^1H NMR (600.1 MHz, CD_3Cl, 25 °C): $\delta = 7.37$–7.10 (25H; ArH), 4.28 (d, $^2J(H,H) = 12.7$ Hz, 1H; H1), 4.07–4.00 (m, 2H; H3), 3.44–3.35 (m, 4H; H2 and H6), 2.57 (d, $^2J(H,H) = 12.7$ Hz, 1H; H1′), 2.47–2.35 (m, 4H; H4 and H5), 2.15 (dd, $^2J(H,H) = 14.4$ Hz, $^2J(H,P) = 4.2$ Hz, 2H; H2′), 2.07–1.93 ppm (m, 4H; H4′ and H5′); ^{13}C NMR (150.9 MHz, C_6D_6, 298 K): $\delta = 139.6$ (s; C_{ipso}), 136.4 (s; $C_{ipso'}$), 133.7 (d, $^2J(C,P) = 4.9$ Hz; $C_{ipso''}$), 130.3–127.8 (ArC), 61.1 (t, $^3J(C,P) = 6.2$ Hz; C1), 52.1 (dd, $^1J(C,P) = 40.2$ Hz, $^3J(C,P) = 6.8$ Hz; C2), 47.1 (d, $^1J(C,P) = 30.3$ Hz; C6), 47.1 (d, $^1J(C,P) = 31.3$ Hz; C3), 35.7 (d, $^2J(C,P) = 4.8$ Hz; C4/C5), 31.2 ppm (s; C4/C5); HRMS (FAB(+)): *m/z* (%) calcd: 1040.1890; found: 1040.1847 (100) $[M-Cl]^+$; elemental analysis calcd (%) for $C_{41}H_{43}Au_2Cl_2NP_2$: C 45.74, H 4.03, N 1.30; found: C 45.47, H 4.08, N 1.32.

Chlorido((((2*S*,5*S*)-2,5-dimethylphospholan-1-yl-κ*P*)methyl)-*N*,*N*-dimethylamine)gold(I) (6b): A mixture of MeONa (0.317 g, 5.87 mmol) and phospholanium salt **1b** (0.250 g, 1.18 mmol) was stirred in MeOH (10 mL) for 10 min. A solution of Me_2NH_2Cl (0.100 g, 1.22 mmol) in MeOH (2 mL) was then added and the mixture was stirred overnight. $^{31}P\{^1H\}$ NMR spectroscopy showed the presence of a single set of signals that were attributed to monodentate ligand **3b**. The mixture was then distilled. The amount of ligand was determined by addition of an internal reference (PPh_3) to a small aliquot of the distilled solution. [Au(tht)Cl] (0.133 g, 0.42 mmol) was added in situ. The volatile compounds were partially removed in vacuo until precipitation of a crystalline white product was observed, which was filtered off and washed with cold Et_2O. Overall yield: 0.093 g (13%); $^{31}P\{^1H\}$ NMR (242.9 MHz, $CDCl_3$, 298 K): $\delta = 36.9$ ppm (s); ^1H NMR (600.1 MHz, $CDCl_3$, 298 K): $\delta = 3.00$–2.88 (m, 2H; H2), 2.64–2.55 (m, 1H; H3), 2.52 (s, 3H; H1), 2.42–2.33 (m, 1H; H6), 2.30–2.18 (m, 2H; H4/H5), 2.02–1.40 (m, 2H; H4/H5), 1.35 (dd, $^3J(H,P) = 20.4$ Hz, $^3J(H,P) = 7.1$ Hz; Me6), 1.25 ppm (dd, $^3J(H,P) = 14.5$ Hz, $^3J(H,P) = 7.3$ Hz; Me3); $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, 298 K): $\delta = 54.6$ (d, $^1J(C,P) = 41.9$ Hz; C2), 47.6 (d, $^3J(C,P) = 7.0$ Hz; C1), 35.6 (d, $^1J(C,P) = 34.5$ Hz; C3), 35.6 (d, $^2J(C,P) = 1.8$ Hz; C4/C5), 35.2 (d, $^2J(C,P) = 4.3$ Hz; C4/C5), 35.0 (d, $^1J(C,P) = 37.4$ Hz; C6), 20.4 (d, $^2J(C,P) = 6.8$ Hz; Me6), 13.0 ppm (d, $^2J(C,P) = 2.6$ Hz; Me3); elemental analysis calcd (%) for $C_9H_{20}NPAuCl$: C 26.65, H 4.97, N 3.45; found: C 26.19, H 4.87, N 3.32.

Trichlorido(tris(((2*S*,5*S*)-2,5-dimethylphospholan-1-yl-κ^3*P*)methyl)-amine)trigold(I) (8b): To a stirring solution of compound **5b** (0.238 g, 0.59 mmol) in CH_2Cl_2/MeCN (1:1, 30 mL), [Au(tht)Cl] (0.570 g, 1.78 mmol) was added in the dark. After stirring for 10 min, a white crystalline solid formed, which was filtered off and washed with CH_2Cl_2 (1×5 mL) and Et_2O (2×5 mL). Yield: 0.569 g (87%); $^{31}P\{^1H\}$ NMR (242.9 MHz, [D$_6$]DMSO, 298 K): $\delta = 30.1$ ppm (br s); ^1H NMR (600.1 MHz, [D$_6$]DMSO, 298 K): $\delta = 4.12$–3.91 (m, 6H; H1), 2.79–2.67 (m, 6H; H2 and H5), 2.28–2.08 (m, 6H; H3 and H4), 1.73–1.62 (m, 3H; H3′/H4′), 1.49–1.40 (m, 3H; H3′/H4′), 1.27–1.16 ppm (m, 18H; Me2 and Me5); $^{13}C\{^1H\}$ NMR (150.9 MHz, [D$_6$]DMSO, 298 K): $\delta = 51.0$ (br s; C1), 35.8 (s; C3/C4), 35.5 (d; $^2J(C,P) = 4.8$ Hz; C3/C4), 35.2 (d, $^1J(C,P) = 34.1$ Hz; C2/C5), 34.6 (d, $^1J(C,P) = 35.2$ Hz; C2/C5), 20.4 (d, $^2J(C,P) = 7.0$ Hz; Me2/Me5), 13.2 ppm (d, $^2J(C,P) = 2.0$ Hz; Me2/Me5); HRMS (ESI(+)): *m/z* (%):1136.0227 (85) (calcd: 1136.0229) $[M+K]^+$, 1120.0490 (23) (calcd: 1120.0490) $[M+Na]^+$, 1062.0902 (40) (calcd: 1062.0904) $[M-Cl]^+$; elemental analysis calcd (%) for $C_{21}H_{42}NP_3Au_3Cl_3$: C 22.96, H 3.85, N 1.27; found: C 22.69, H 3.83, N 1.29.

General procedure for the cyclohydroamination reaction: A mixture of the gold(I) complex (0.015 mmol Au) and the corresponding silver(I) salt (0.015 mmol) was stirred in the solvent (dry and degassed, 0.5 mL) at RT for 10 min in the dark. Then, a solution of the γ-allenyl sulfonamide (0.3 mmol) in solvent (dry and degassed, 0.5 mL) was added and the reaction mixture was stirred at the denoted temperature (20 °C or 50 °C). The progress of the reaction was monitored by ^1H NMR spectroscopy.

Upon completion, the crude mixture was loaded directly onto a silica gel column. Purification by column chromatography on silica gel (pentane/EtOAc = 5:1) gave the cyclized product.

X-ray diffraction study: For the crystal data and details of the structure determination, see the Supporting Information. Full shells of intensity data were collected at low temperature ($T = 100$ K) with a Bruker AXS Smart 1000 CCD diffractometer ($Mo_{K\alpha}$ radiation, graphite monochromator, $\lambda = 0.71073$ Å). Data were corrected for air and detector absorption, and Lorentz and polarization effects;[28] absorption by the crystal was treated numerically[29] (complexes **6b** and **8a**) or with a semiempirical multiscan method.[29–31] The structures were solved by conventional direct methods[32,33] (complexes **6a**, **8a**, and **9**) or by the heavy-atom method combined with structure expansion by direct methods applied to difference structure factors[34] (complexes **6b** and **8b**) and refined by full-matrix least-squares methods based on F^2 against all of the unique reflections.[33,365] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions and refined with a riding model. Crystals of compound **8b** were twinned; after de-twinning (approx. twin fractions 0.71:0.29), refinement was carried out against all observations involving domain 1. Adp and geometry restraints were applied to the disordered phenyl rings in compound **8a**. Owing to severe disorder and fractional occupancy, electron density attributed to

the solvent of crystallization (CH_2Cl_2 and Et_2O) was removed from the structure (and the corresponding F_{obs}) of compound **9** with the BYPASS procedure,[36] as implemented in PLATON (SQUEEZE).[37]

CCDC-846159 (**6a**), CCDC-846160 (**6b**), CCDC-846161 (**8a**), CCDC-846162 (**8b**), and CCDC-846163 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft for their financial support (SFB 623, TP B6), the Fundación Ramón Areces for the award of a postdoctoral fellowship to L.I.R., and the European Union for the award of a Marie Curie EIF postdoctoral fellowship (to J.L.F.).

[1] a) F. D. Toste, *Beilstein J. Org. Chem.* **2011**, *7*, 553–553; b) A. Pradal, P. Y. Toullec, V. Michelet, *Synthesis* **2011**, 1501–1514; c) N. Krause, C. Winter, *Chem. Rev.* **2011**, *111*, 1994–2009; d) A. S. K. Hashmi, M. Rudolph, *Chem. Commun.* **2011**, *47*, 6536–6544; e) M. Bandini, *Chem. Soc. Rev.* **2011**, *40*, 1358–1367; f) H. Schmidbaur, A. Schier, *Organometallics* **2010**, *29*, 2–23; g) C. Nevado, *Chimia* **2010**, *64*, 247–251; h) A. S. K. Hashmi, *Angew. Chem.* **2010**, *122*, 5360–5369; *Angew. Chem. Int. Ed.* **2010**, *49*, 5232–5241; i) A. Fürstner, *Chem. Soc. Rev.* **2009**, *38*, 3208–3221; j) N. Marion, S. P. Nolan, *Chem. Soc. Rev.* **2008**, *37*, 1776–1782; k) G. J. Hutchings, M. Brust, H. Schmidbaur, *Chem. Soc. Rev.* **2008**, *37*, 1759–1765; l) A. S. K. Hashmi, M. Rudolph, *Chem. Soc. Rev.* **2008**, *37*, 1766–1775; m) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351–3378; n) A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266–3325; o) R. A. Widenhoefer, *Chem. Eur. J.* **2008**, *14*, 5382–5391; p) N. Bongers, N. Krause, *Angew. Chem.* **2008**, *120*, 2208–2211; *Angew. Chem. Int. Ed.* **2008**, *47*, 2178–2181; q) D. J. Gorin, F. D. Toste, *Nature* **2007**, *446*, 395–403; r) A. Fürstner, P. W. Davies, *Angew. Chem.* **2007**, *119*, 3478–3519; *Angew. Chem. Int. Ed.* **2007**, *46*, 3410–3449; s) L. M. Zhang, J. W. Sun, S. A. Kozmin, *Adv. Synth. Catal.* **2006**, *348*, 2271–2296; t) R. A. Widenhoefer, X. Q. Han, *Eur. J. Org. Chem.* **2006**, 4555–4563; u) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem.* **2006**, *118*, 8064–8105; *Angew. Chem. Int. Ed.* **2006**, *45*, 7896–7936; v) I. J. B. Lin, C. S. Vasam, *Can. J. Chem.* **2005**, *83*, 812–825; w) A. S. K. Hashmi, *Angew. Chem.* **2005**, *117*, 7150–7154; *Angew. Chem. Int. Ed.* **2005**, *44*, 6990–6993; x) G. J. Hutchings, *Catal. Today* **2002**, *72*, 11–17.

[2] a) P. Schwerdtfeger, H. L. Hermann, H. Schmidbaur, *Inorg. Chem.* **2003**, *42*, 1334–1342; b) M. A. Carvajal, J. J. Novoa, S. Álvarez, *J. Am. Chem. Soc.* **2004**, *126*, 1465–1477.

[3] a) G. L. Hamilton, E. J. Kang, M. Mba, F. D. Toste, *Science* **2007**, *317*, 496–499; b) R. L. LaLonde, Z. J. Wang, M. Mba, A. D. Lackner, F. D. Toste, *Angew. Chem.* **2010**, *122*, 608–611; *Angew. Chem. Int. Ed.* **2010**, *49*, 598–601; c) K. Aikawa, M. Kojima, K. Mikami, *Angew. Chem.* **2009**, *121*, 6189–6193; *Angew. Chem. Int. Ed.* **2009**, *48*, 6073–6077.

[4] a) H. Teller, S. Flügge, R. Goddard, A. Fürstner, *Angew. Chem.* **2010**, *122*, 1993–1997; *Angew. Chem. Int. Ed.* **2010**, *49*, 1949–1953; b) A. Z. González, F. D. Toste, *Org. Lett.* **2010**, *12*, 200–203; c) F. López, I. Alonso, B. Trillo, S. Montserrat, G. Ujaque, L. Castedo, A. Lledós, J. L. Mascareñas, *J. Am. Chem. Soc.* **2009**, *131*, 13020–13030; d) K. Tomioka, Y. Matsumoto, K. B. Selim, H. Nakanishi, K. Yamada, Y. Yamamoto, *Tetrahedron Lett.* **2010**, *51*, 404–406.

[5] M. P. Muñoz, J. Adrio, J. C. Carretero, A. M. Echavarren, *Organometallics* **2005**, *24*, 1293–1300.

[6] a) M. A. Tarselli, A. R. Chianese, S. J. Lee, M. R. Gagné, *Angew. Chem.* **2007**, *119*, 6790–6793; *Angew. Chem. Int. Ed.* **2007**, *46*, 6670–6673; b) M. A. Tarselli, A. R. Chianese, S. J. Lee, M. R. Gagné, *Angew. Chem.* **2007**, *119*, 6790–6793.

[7] M. Z. Wang, C. Y. Zhou, Z. Guo, E. L. M. Wong, M. K. Wong, C. M. Che, *Chem. Asian J.* **2011**, *6*, 812–824.

[8] E. Tkatchouk, N. P. Mankad, D. Benitez, W. A. Goddard, III, F. D. Toste, *J. Am. Chem. Soc.* **2011**, *133*, 14293–14300.

[9] a) F. Liu, D. Y. Qian, L. Li, X. L. Zhao, J. L. Zhang, *Angew. Chem.* **2010**, *122*, 6819–6822; *Angew. Chem. Int. Ed.* **2010**, *49*, 6669–6672; b) F. Liu, D. Y. Qian, L. Li, X. L. Zhao, J. L. Zhang, *Angew. Chem.* **2010**, *122*, 6819–6822.

[10] a) D. Michael, P. Mingos, J. Yau, S. Menzer, D. J. Williams, *Angew. Chem.* **1995**, *107*, 2045–2047; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1894–1895; b) R. E. Bachman, M. S. Fioritto, S. K. Fetics, T. M. Cocker, *J. Am. Chem. Soc.* **2001**, *123*, 5376–5377; c) H. Schmidbaur, *Nature* **2001**, *413*, 31–33; d) H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2008**, *37*, 1931–1951; e) M. C. Gimeno, A. Laguna, *Chem. Soc. Rev.* **2008**, *37*, 1952–1966.

[11] H. B. Kagan, T.-P. Dang, *J. Am. Chem. Soc.* **1972**, *94*, 6429–6433.

[12] a) C. Moberg, *Angew. Chem.* **1998**, *110*, 260–281; *Angew. Chem. Int. Ed.* **1998**, *37*, 248–268; b) M. C. Keyes, W. B. Tolman, *Adv. Catal. Processes* **1997**, *2*, 189–219; c) S. E. Gibson, M. P. Castaldi, *Chem. Commun.* **2006**, 3045–3062; d) S. E. Gibson, M. P. Castaldi, *Angew. Chem.* **2006**, *118*, 4834–4837; *Angew. Chem. Int. Ed.* **2006**, *45*, 4718–4720; e) C. Moberg, *Angew. Chem.* **2006**, *118*, 4838–4840; *Angew. Chem. Int. Ed.* **2006**, *45*, 4721–4723; f) L. H. Gade, S. Bellemin-Laponnaz, *Chem. Eur. J.* **2008**, *14*, 4142–4152.

[13] J. Lloret Fillol, A. Kruckenberg, P. Scherl, H. Wadepohl, L. H. Gade, *Chem. Eur. J.* **2011**, *17*, 14047.

[14] Ligand **3b** was not isolated owing to its volatility; therefore, it was used in situ for the preparation of its corresponding gold complex.

[15] a) S. Attar, W. H. Bearden, N. W. Alcock, E. C. Alyea, J. H. Nelson, *Inorg. Chem.* **1990**, *29*, 425–433; b) K. Owsianik, M. Zablocka, B. Donnadieu, J. P. Majoral, *Angew. Chem.* **2003**, *115*, 2226–2229; *Angew. Chem. Int. Ed.* **2003**, *42*, 2176–2179; c) C. González-Arellano, A. Corma, M. Iglesias, F. Sánchez, *Chem. Commun.* **2005**, 3451–3453; d) S. Durben, T. Baumgartner, *Inorg. Chem.* **2011**, *50*, 6823–6836.

[16] a) N. Krause, A. S. K. Hashmi, in *Modern Allene Chemistry, Vol. 1–2*, Wiley-VCH, Weinheim, **2004**; b) C. Mukai, F. Inagaki, S. Kitagaki, *Synlett* **2011**, 594–614; c) F. López, J. L. Mascareñas, *Chem. Eur. J.* **2011**, *17*, 418–428.

[17] a) C. F. Bender, R. A. Widenhoefer, *Chem. Commun.* **2008**, 2741–2743; b) X. Q. Han, R. A. Widenhoefer, *Angew. Chem.* **2006**, *118*, 1779–1781; *Angew. Chem. Int. Ed.* **2006**, *45*, 1747–1749.

[18] a) H. Li, S. Du Lee, R. A. Widenhoefer, *J. Organomet. Chem.* **2011**, *696*, 316–320; b) Z. B. Zhang, R. A. Widenhoefer, *Angew. Chem.* **2007**, *119*, 287–289; *Angew. Chem. Int. Ed.* **2007**, *46*, 283–285; c) Z. B. Zhang, C. F. Bender, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2007**, *129*, 14148–14149; d) C. Liu, R. A. Widenhoefer, *Org. Lett.* **2007**, *9*, 1935–1938.

[19] R. L. LaLonde, B. D. Sherry, E. J. Kang, F. D. Toste, *J. Am. Chem. Soc.* **2007**, *129*, 2452–2453.

[20] D. Weber, M. R. Gagné, *Org. Lett.* **2009**, *11*, 4962–4965.

[21] Full conversion was achieved in 24 h with mononuclear complex **6b** and substrate **s2** at 20 °C, by using $AgBF_4$ as the chloride-abstracting agent and CH_2Cl_2 as the solvent. For complexes **7b** and **8b**, as well as for the DPP series, full conversion was reached in less than 1 h under the same experimental conditions. No enantioselectivity was found in any of these cases. Mononuclear complex **6b** did not yield the desired pyrrolidine with either AgOBz or AgOPNB.

[22] W. L. F. Armarego, C. L. L. Chai, *Purification of Laboratory Chemicals*, Butterworth-Heinemann, Amsterdam, **2003**.

[23] F. Guillen, M. Rivard, M. Toffano, J.-Y. Legros, J.-C. Daran, J.-C. Fiaud, *Tetrahedron* **2002**, *58*, 5895–5904.

[24] R. Uson, A. Laguna, M. Laguna, D. A. Briggs, H. H. Murray, J. P. Fackler Jr., *Inorg. Synth.* **1989**, *26*, 85–91.

[25] C. Jonasson, A. Horváth, J.-E. Bäckvall, *J. Am. Chem. Soc.* **2000**, *122*, 9600–9609.

[26] G. M. Rubottom, R. C. Mott, J. H. D. Juve, *J. Org. Chem.* **1981**, *46*, 2717–2721.

[27] H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512–7515.
[28] SAINT, Bruker AXS, **1997–2008**.
[29] G. M. Sheldrick, SADABS, Bruker AXS, **2004–2008**.
[30] G. M. Sheldrick, TWINABS, Bruker AXS, **2008**.
[31] R. H. Blessing, *Acta Crystallogr. Sect. A* **1995**, *51*, 33.
[32] G. M. Sheldrick, SHELXS-97, University of Göttingen, Germany, **1997**.
[33] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112.
[34] a) P. T. Beurskens, G. Beurskens, R. de Gelder, J. M. M. Smits, S. Garcia-Granda, R. O. Gould, DIRDIF-2008, Radboud University Nijmegen, The Netherlands, **2008**; b) P. T. Beurskens in *Crystallographic Computing 3*, (Eds.: G. M. Sheldrick, C. Krüger, R. Goddard), Clarendon Press, Oxford, UK, **1985**, p. 216.
[35] G. M. Sheldrick, SHELXL-97, University of Göttingen, **1997**.
[36] P. van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, 194.
[37] a) A. L. Spek, PLATON, Utrecht University, The Netherlands; b) A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7.

Received: October 5, 2011
Revised: December 3, 2011
Published online: February 23, 2012

