Ligand Effects

International Edition: DOI: 10.1002/anie.201612243
German Edition: DOI: 10.1002/ange.201612243

C,O-Chelated BINOL/Gold(III) Complexes: Synthesis and Catalysis with Tunable Product Profiles

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Abstract: *Unprecedented stable BINOL/gold(III) complexes, adopting a novel C,O-chelation mode, were synthesized by a modular approach through combination of 1,1′-binaphthalene-2,2′-diols (BINOLs) and cyclometalated gold(III) dichloride complexes [(C^N)AuCl$_2$]. X-ray crystallographic analysis revealed that the bidentate BINOL ligands tautomerized and bonded to the Au^{III} atom through C,O-chelation to form a five-membered ring instead of the conventional O,O′-chelation giving a seven-membered ring. These gold(III) complexes catalyzed acetalization/cycloisomerization and carboalkoxylation of ortho-alkynylbenzaldehydes with trialkyl orthoformates.*

Gold catalysis has contributed to a diversity of novel organic transformation reactions streamlining organic synthesis with excellent atom economy and operational simplicity owing to its superior reactivity, excellent selectivity, and high functional-group tolerance.[1] Meticulous choice of ligand in gold catalysis is of significance to prevent the decomposition of simple gold salts in catalytic cycles and fine-tune the catalytic activity and product enantioselectivity.[1i,2] In particular, a variety of phosphine/gold(I) and N-heterocyclic carbene/gold(I) complexes have been developed as efficient catalysts for novel synthetic transformations. However, gold(I) complexes have two coordination sites with a linear geometry, thus leading to a challenge when arranging ligands around the gold(I) center for tuning catalytic activity and introducing a chiral environment.[1e,i,2a]

Gold(III) complexes have a square-planar geometry with four coordination sites, thus allowing easy fine-tuning through diverse ligand design in a modular approach. However, the development of gold(III) complexes for catalysis remains largely unexplored because of difficult access to the high oxidation state under mild reaction conditions and a lack of suitable non-redox ligands.[3] The great challenge in synthesizing stable gold(III) complexes comes from the facile reduction of gold(III) complexes to either gold(I) or gold(0) species.[4] For example, electron-rich tertiary phosphine and amine ligands[3h] are not compatible with the gold(III) ion owing to the possible gold(III) reduction. Thus, neutral or electron-deficient nitrogen-containing compounds, such as pyridines,[3a,b,f] Schiff bases,[3c] N-heterocyclic carbenes,[5] and triazole derivatives,[3g,h] have been used as ligands for gold(III) complexes (Figure 1 a). In principle, the stability of gold(III) ions significantly increases upon complexation with ligands. However, stable gold(III) complexes generally exhibit poor catalytic activity. Thus, a significant challenge in the successful development of gold(III) complexes as efficient catalysts is to strike a balance between stability and catalytic activity.[5,6]

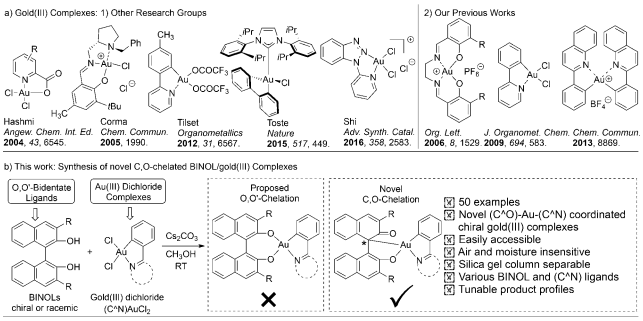

Figure 1. a) Gold(III) complexes previously reported by other research groups and our group. b) Synthesis of unprecedented stable BINOL/gold(III) complexes adopting a novel C,O-chelation mode.

Over the years, we have been developing gold(III) complexes, including Salen-based gold(III) complexes[7] and cyclometalated gold(III) dichloride complexes [(C^N)AuCl$_2$, C^N = 2-arylpyridyl],[8] as efficient catalysts for organic synthesis. In addition, we reported that the bis(cyclometalated) gold(III) complex [(C^N)$_2$AuBF$_4$] is able to enhance the stability of the Au^{III} cation with good catalytic activity.[6] To further explore the potential of gold(III) catalysis, it is important to develop easily assessable, stable, and tunable gold(III) complexes.

1,1′-Binaphthalene-2,2′-diols (BINOLs), which are readily bound to transition metals through both oxygen atoms to form a seven-membered ring,[9] are privileged ligands in asymmetric transition-metal catalysis.[10] The reported stabilization of cationic gold(III) complexes by catechol derivatives inspired us to examine BINOLs as the supporting ligands.[11] The two consecutive O-anionic centers on the BINOL ligands were able to donate sufficient electron density to stabilize a highly electrophilic Au^{III} center. However, such phenolate ligands are strong reductants, and even the preparation of gold(I) phenolate complexes was highly challenging and the compounds were very sensitive.[12] To

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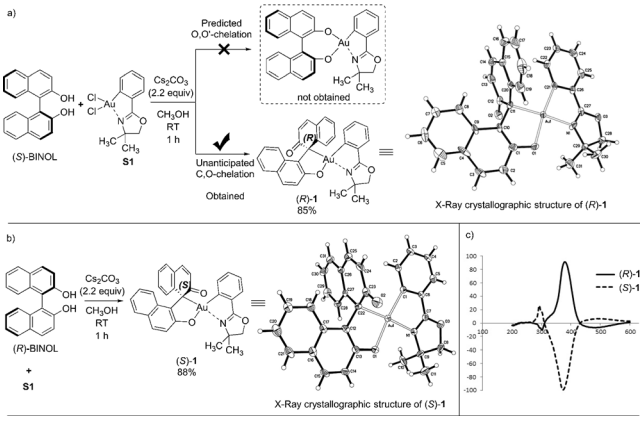
Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201612243.

fully utilize the four coordination sites of gold(III) complexes, we hypothesized that incorporating a BINOL ligand into a cyclometalated Au^{III} dichloride complex [(C^N)$AuCl_2$] by O,O′-chelation with the Au^{III} center by replacing the two chloride atoms would give a stable, neutral, and tetracoordinated gold(III) complex while maintaining tunable catalytic activity in organic synthesis. To our surprise, unprecedented gold(III) complexes in which the BINOL moiety adopted an unusual C,O-chelation mode with the Au^{III} center were obtained instead of the expected O,O′-chelation (Figure 1b).

Initially, an oxazoline-based gold(III) dichloride complex (**S1**) was prepared by a literature method.[13] Treatment of **S1** with commercially available (*S*)-BINOL in the presence of Cs_2CO_3 in methanol at room temperature afforded an orange-red solid [(*R*)-**1**] in 85% yield (Scheme 1a), and it was



Scheme 1. a) Formation of the stable gold(III) complex (*R*)-**1** derived from (*S*)-BINOL and cyclometalated gold(III) dichloride **S1** in an unusual C,O-chelation manner, and the X-ray crystal structure of (*R*)-**1**. Thermal ellipsoids are shown at 50% probability. b) Formation of the stable gold(III) complex (*S*)-**1**, and the X-ray crystal structure of (*S*)-**1**. Thermal ellipsoids are shown at 50% probability. c) Circular dichroism (CD) spectrum of (*R*)-**1** and (*S*)-**1**, 0.1 mg mL^{-1} in $CHCl_3$.

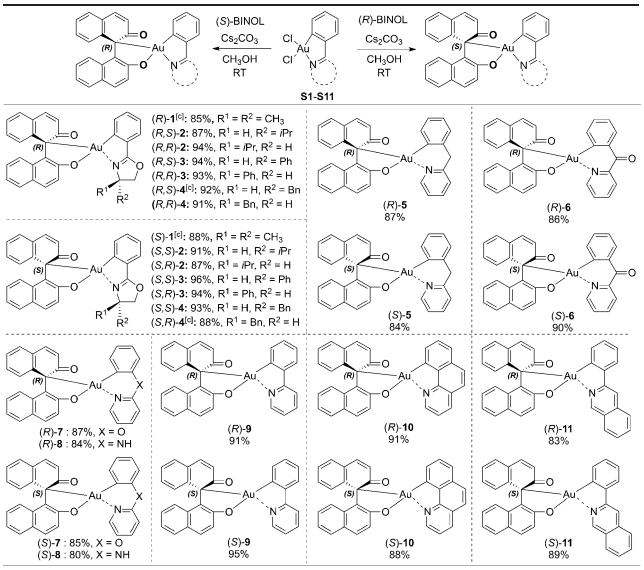
characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, and high-resolution ESI-MS. However, the unsymmetrical proton signal in the ^{1}H NMR spectra and the carbonyl signal ($\delta \approx 200$ ppm) appearing in the ^{13}C NMR spectra indicated that the structure of this gold(III) complex is not the proposed O,O′-chelated gold(III) complex. Notably, X-ray crystallographic analysis revealed that the structure of (*R*)-**1**,[14] in which the BINOL moiety adopted an unprecedented C,O-chelation mode with the Au^{III} center (Scheme 1a).[15] The O,O′-bidentate (*S*)-BINOL ligand tautomerized and bonded to the Au atom by C,O-chelation to form a five-membered ring instead of O,O′-chelation giving a seven-membered ring. The crystal structure reveals that the gold(III) atom in (*R*)-**1** adopts a square-planar geometry surrounded by *cis*-oxygen-nitrogen and *cis*-carbon-carbon atoms. The complex (*R*)-**1** was light, air, and moisture insensitive and could be isolated and stored at ambient conditions. It is stable upon exposure to air for months. Remarkably, an axial-to-central chirality transfer occurred during the complex formation between (*S*)-BINOL and [(C^N)$AuCl_2$]. The (*S*)-BINOL exclusively afforded the gold(III) complex (*R*)-**1** with the quaternary stereogenic carbon center in the *R* configuration. Moreover, **S1** reacted with (*R*)-BINOL under the same reaction conditions to afford the enantiomer, (*S*)-**1**, in 88% yield, which was also well-characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, high-resolution ESI-MS, and X-ray crystallographic analysis (Scheme 1b). Circular dichroism (CD) indicated the stereochemical properties of the enantiomers (*R*)-**1** and (*S*)-**1** (Scheme 1c).

A search of the literature revealed that this kind of peculiar C,O-chelation mode for BINOL derivatives with Pd^{II} and Pt^{II} have rarely been reported.[16] To our knowledge, we are the first to synthesize chiral BINOL–oxazoline hybrid gold(III) complexes [(*R*)-**1** and (*S*)-**1**] with an unusual C,O-chelation mode. The possible reasons for (*R*)-**1** and (*S*)-**1** accommodating the peculiar C,O binding mode would be enol–keto tautomerization of BINOL in the presence of Cs_2CO_3 and the higher tendency of the gold center to coordinate the carbanion rather than phenoxide.[16] This unprecedented C,O-chelation, rather than O,O′-chelation mode, of BINOL towards the Au^{III} center of the complex [Au(CN)Cl_2] represents a facile approach for generating strong Au–C and Au–O bonds, thus paving the way to stable gold(III) complexes. In this work, we are the first to develop a modular approach for synthesizing a series of novel chiral C,O-chelated BINOL–gold(III) complexes by a combination of diverse chiral (*S*)-BINOL and (*R*)-BINOL derivatives with various oxazoline- and pyridine-based cyclometalated gold(III) complexes.

The scope of using various oxazoline- and pyridine-based cyclometalated gold(III) dichloride complexes [(C^N)$AuCl_2$] for synthesizing chiral C,O-chelated BINOL–gold(III) complexes were studied (Table 1). Chiral oxazoline-based gold(III) dichloride complexes (**S2**–**S4**) were prepared by a literature method with modifications (see Schemes S2 and S3 in the Supporting Information).[13a,17] Treatment of (*S*)-BINOL and (*R*)-BINOL with these chiral oxazoline-based gold(III) dichloride complexes under the optimized reaction conditions, respectively, gave the four stereoisomers of a chiral BINOL-oxazoline hybrid cyclometalated gold(III) complex (**2**–**4**; with *R*,*S*-, *R*,*R*-, *S*,*S*-, and *S*,*R*-configurations, respectively) in 87–96% yield. Reactions of (*S*)-BINOL and (*R*)-BINOL with the *ortho*-substituted pyridine-based complexes **S5**–**S11**, respectively, afforded chiral gold(III) complexes **5**–**11** with *R*- and *S*-configurations in 80–95% yield.

As literature reported that the coordination mode of Pd^{II} and Pt^{II} with BINOL and VANOL exclusively adopted the O,O′-chelation, while the apparently more bulky ligands 3,3′-Me_2BINOL and VAPOL preferred the C,O-chelation.[16d] We proceeded to employ 3,3′-disubstituted BINOLs for the formation of the C,O-chelated BINOL–gold(III) complexes (Table 2). (*S*)-3,3′-Me_2BINOL and (*R*)-3,3′-Me_2BINOL were used to react with the oxazoline-based cyclometalated gold(III) dichloride **S1**, thus giving the C,O-chelation products (*R*)-**12** and (*S*)-**12** in 77 and 83% yield, respectively. Similarly, reaction of (*S*)-6,6′-dibromo-BINOL and (*R*)-6,6′-dibromo-BINOL with **S1** afforded (*R*)-**13** and (*S*)-**13**, respectively, in excellent yield (93 and 89%). Next, the scope of various sterically bulky 3,3′-disubstituted BINOLs were investigated.

Table 1: Scope of using oxazoline- and pyridine-based cyclometalated gold(III) dichloride complexes for the synthesis of **1**–**11**.[a,b]



[a] Reaction conditions: gold(III) dichloride complex (0.2 mmol), (*S*)-BINOL or (*R*)-BINOL (1.1 equiv), Cs_2CO_3 (2.2 equiv), methanol (10 mL), room temperature, reaction time: 1 h. [b] Yield of isolated product. [c] Configuration validated by X-ray crystallographic analysis.

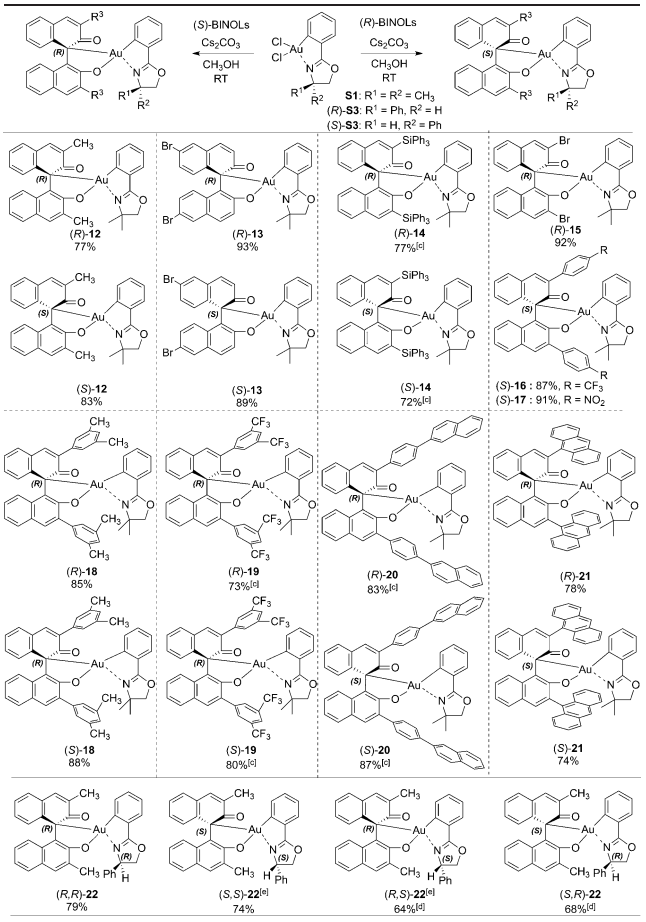
BINOLs with $SiPh_3$, Br, and aryl groups on 3,3′-positions were well-compatible with **S1** to form the cyclometalated gold(III) complexes **14**–**21** (72–92% yield) with the C,O-chelation. Furthermore, (*S*)-3,3′-Me_2BINOL and (*R*)-3,3′-Me_2BINOL reacted with the chiral oxazoline-based gold(III) dichloride complexes (*S*)-**S3** and (*R*)-**S3**, respectively, and afforded the four stereoisomers (*R*,*S*)-**22**, (*R*,*R*)-**22**, (*S*,*S*)-**22**, and (*S*,*R*)-**22** in yields ranging from 64 to 79%.

The axial-to-central chirality transfer from the chiral BINOL to the resulting gold(III) complexes was again confirmed by X-ray crystallographic analysis (Figure 2).[14] Reaction of (*S*)-BINOL with (*S*)-**S4**, and reaction of with (*R*)-BINOL with (*R*)-**S4** afforded the corresponding (*R*,*S*)-**4** and (*S*,*R*)-**4**, thus indicating that the axial chirality on the chiral BINOL exclusively transferred to the resulting optically pure gold(III) complexes. This kind of efficient axial-to-central chirality transfer was also applicable to the synthesis of (*R*,*S*)-**22** and (*S*,*S*)-**22**.

Reaction of *rac*-BINOL with the chiral oxazoline-based gold(III) dichloride complex (*S*)-**S4** was conducted under the standard reaction conditions. Diastereoisomers (*R*,*S*)-**4** and (*S*,*S*)-**4** were well-separated by column chromatography on silica gel in 46 and 44% yield, respectively (Scheme 2a). These results indicated that chiral BINOL–gold(III) complexes could be synthesized from chiral oxazoline-based gold(III) dichloride complexes and inexpensive racemic BINOL. A gram-scale reaction of *rac*-BINOL with **S1** was conducted (Scheme 2b). *rac*-BINOL (1.58 g, 5.5 mmol) reacted with **S1** (2.21 g, 5.0 mmol) in the presence of Cs_2CO_3 in methanol at room temperature for 1 hour to afford *rac*-**1** in 95% yield (3.10 g).

With *rac*-**1** in hand, we proceeded to examine the catalytic activity of the newly developed C,O-chelated BINOL/gold-

Table 2: Scope of using chiral 3,3′-disubstituted BINOL ligands for the synthesis of **12**–**22**.[a,b]



[a] Reaction conditions: gold(III) dichloride complex (0.1 mmol), (*S*)-3,3′-disubstituted BINOL or (*R*)-3,3′-disubstituted BINOL (1.1 equiv), Cs_2CO_3 (2.2 equiv), methanol (5 mL), room temperature, reaction time: 1 h. [b] Yield of isolated product. [c] 0.05 mmol. [d] 24 h. [e] Configuration validated by X-ray crystallographic analysis.

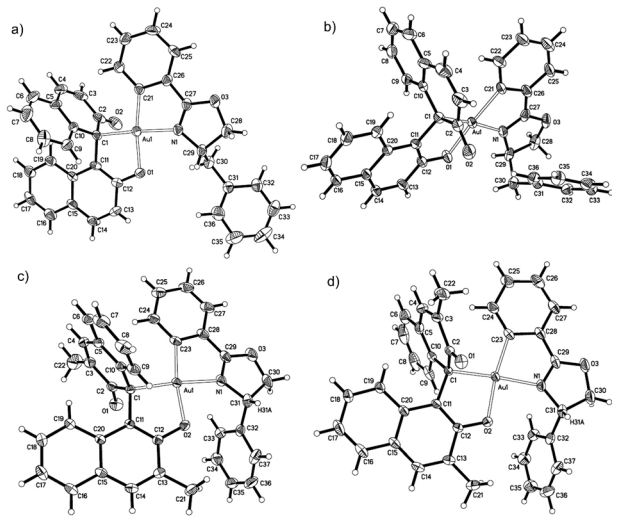
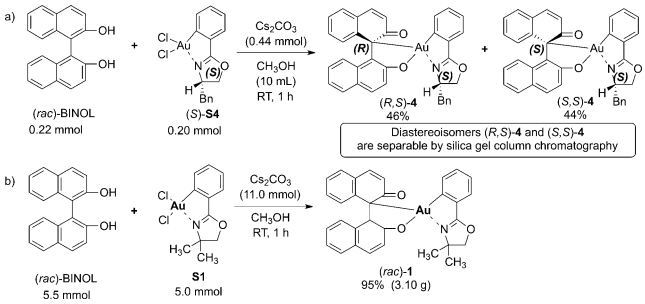


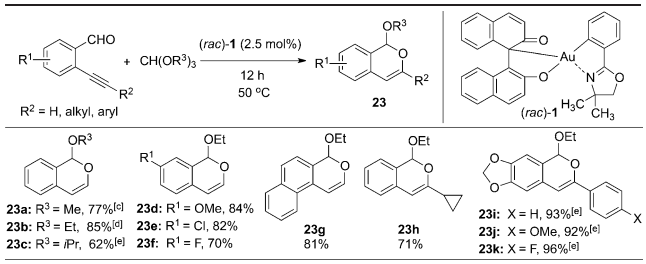
Figure 2. X-ray crystal structures of a) (*R*,*S*)-**4**, b) (*S*,*R*)-**4**, c) (*R*,*S*)-**22**, and d) (*S*,*S*)-**22**. Displacement ellipsoids are drawn at the 50% probability level. Solvent molecules are omitted for clarity.



Scheme 2. a) Access to the chiral diastereoisomers (*R*,*S*)-**4** and (*S*,*S*)-**4** from reaction of *rac*-BINOL and (*S*)-**S4**. b) A gram-scale synthesis *rac*-**1** from *rac*-BINOL and **S1**.

(III) complexes in organic transformations of *ortho*-alkynylbenzaldehydes.[18] Treatment of various *ortho*-alkynylbenzaldehydes with trialkyl orthoformates in the presence of 2.5 mol% of *rac*-**1** gave the six-membered acetal products **23a–k** in 62–96% yield without the five-membered counterpart as reported in literature[18d] (Table 3). These findings

Table 3: Gold(III) complex *rac*-**1** catalyzed tandem acetalization/cycloisomerization of *ortho*-alkynylbenzaldehydes with trialkyl orthoformates.[a,b]



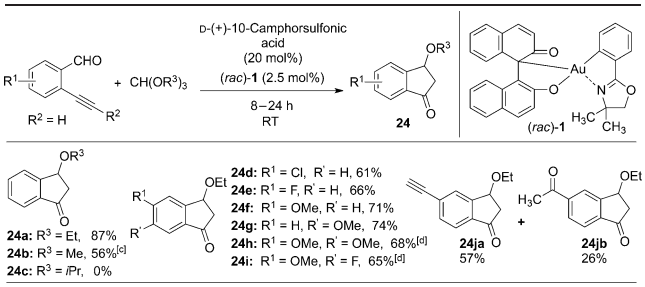
[a] Reaction conditions: *ortho*-alkynylbenzaldehyde (0.5 mmol), CH(OR^3)$_3$ (3.0 mmol, 6.0 equiv), DCE (3.0 mL), 50 °C, 12 h. [b] Yield of isolated product. [c] At room temperature. [d] 8 h. [e] 24 h. DCE = dichloroethane.

showed that the catalysis of *rac*-**1** towards tandem acetalization/cycloisomerization of *ortho*-alkynylbenzaldehydes with trialkyl orthoformates has excellent regioselectivity.

Interestingly, when sulfonic acid (20 mol%) was added to the reaction mixture with 2.5 mol% *rac*-**1**, a carboalkoxylation product (**24a**)[19] was exclusively formed in 87% yield, but the tandem acetalization/cycloisomerization product **23b** was not obtained. The drastic change in product distribution indicated that the product selectivity of *rac*-**1** towards *ortho*-alkynylbenzaldehyde is adjusted by addition of acid. Encouraged by these findings, we set out to optimize the reaction conditions by screening various gold(I) and gold(III) catalysts, as well as Brønsted acids, loading of catalysts and sulfonic acid, amount of trimethyl orthoformate, as well as solvents (see Tables S1–S4). As summarized in the Supporting Information, no carboalkoxylation product was obtained when a simple gold(I) salt (AuCl), phosphine/gold(I) complexes (LAuCl; L = PPh_3 and JohnPhos), and mono- and bis(cyclometalated) gold(III) complexes [(C^N)$AuCl_2$ and (C^N)$_2AuBF_4$] were used. We found that using 2.5 mol% *rac*-**1**, 20 mol% camphorsulfonic acid, and 6.0 equivalents of $CH(OEt)_3$ in DCE gave the best yield (87%).

With the optimized reaction conditions, we investigated the scope of this gold(III)-catalyzed carboalkoxylation reaction of *ortho*-ethynylbenzaldehydes (Table 4). Using trimethyl orthoformate, the corresponding indanone **24b** was obtainied with lower yield (56%). Yet, no carboalkoxylation

Table 4: Carboalkoxylation of *ortho*-alkynylbenzaldehydes with trialkyl orthoformates catalyzed by *rac*-**1**.[a,b]



[a] Reaction conditions: *ortho*-ethynylbenzaldehyde (0.5 mmol), CH(OR^3)$_3$ (3.0 mmol, 6.0 equiv), D-(+)-10-Camphorsulfonic acid (20 mmol%), DCE (3.0 mL), room temperature, 24 h. [b] Yield of isolated product. [c] 8 h. [d] At 60 °C. DCE = dichloroethane.

product was found when triisopropyl orthoformate was used. Substrates with electron-withdrawing groups (Cl, F), electron-donating groups (OMe), as well as two substituents on the aryl ring were well-tolerated (products **24d–i** in 61–74% yield). The reaction of an ethynyl-substituted substrate proceeded smoothly under the standard reaction conditions, thus giving the corresponding indanone **24ja** in 57% yield together with **24jb** (hydration product of **24ja**) in 26% yield.

As shown in Table 3, reaction of *ortho*-alkynylbenzaldehydes with trialkyl orthoformates catalyzed by *rac*-**1** gave six-membered acetal products (**23**). In contrast, addition of camphorsulfonic acid led instead to the carboalkoxylation products **24** (Table 4). One possibility might be the acid-promoted formation of acetals from 2-alkynylbenzaldehydes and subsequent carboalkoxylation reaction[19] to give **24** (mechanistic studies of these reaction pathways are ongoing in our laboratory).

In this work, the new approach of synthesizing novel C,O-chelated BINOL–gold(III) complexes has opened up a new research direction for gold catalysis based on high-valent gold(III) chemistry. It is envisioned that further development of gold(III) catalysis will lead to the discovery of novel organic transformation reactions which would have significantly different reactivity, selectivity, and substrate scope compared with gold(I) catalysis. Moreover, it is worth exploring the unique chiral environment around the Au^{III} center in asymmetric catalysis. Our preliminary studies showed that by using the chiral BINOL/gold(III) complex (*R*,*R*)-**2** (2.5 mol%) as a catalyst, carboalkoxylation of *ortho*-alkynylbenzaldehyde with CH_3OH gave **24b** in 52% yield with 41% *ee* (see Figure S1).

Acknowledgments

We are grateful for the financial support of Hong Kong Research Grants Council (PolyU 153006/15P), State Key Laboratory of Chirosciences, and Department of Applied Biology and Chemical Technology. We thank Prof. Zhou Zhongyuan for X-ray crystallographic analysis.

Conflict of interest

The authors declare no conflict of interest.

Keywords: chelates · gold · isomerization · ligand effects · structure elucidation

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Manuscript received: December 17, 2016
Final Article published: ■■ ■■, ■■■■

Communications

Ligand Effects

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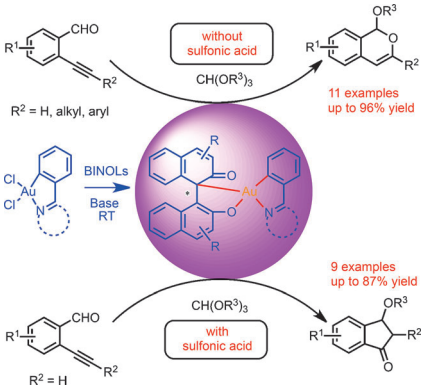
C,O-Chelated BINOL/Gold(III) Complexes: Synthesis and Catalysis with Tunable Product Profiles



Gold(III) and C,O: Stable BINOL/gold(III) complexes adopting an unusual C,O-chelation mode were synthesized by a modular approach through combination of BINOLs and cyclometalated gold(III) dichloride complexes. These gold(III) complexes catalyzed acetalization/cycloisomerization and carboalkoxylation of *ortho*-alkynylbenzaldehydes with trialkyl orthoformates.