

Highly Stereoselective Olefin Cyclopropanation of Diazoindoles Catalyzed by a C₂-Symmetric Spiroketal Bisphosphine/Au(I) ComplexZhong-Yan Cao,[†] Xiaoming Wang,[‡] Chen Tan,[†] Xiao-Li Zhao,[†] Jian Zhou,^{*,†} and Kuiling Ding[‡][†]Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062 China[‡]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China

Supporting Information

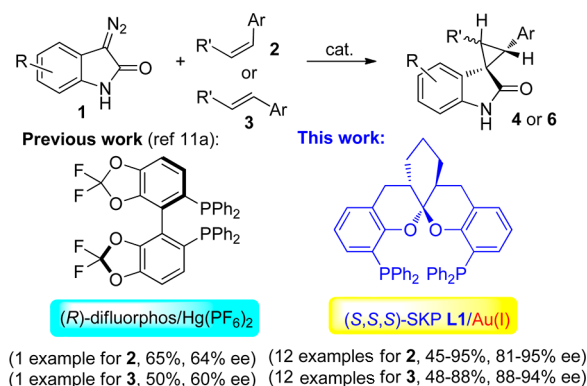
ABSTRACT: A spiroketal bisphosphine (SKP) derived chiral digold complex is identified as a powerful catalyst for the highly diastereo- and enantioselective synthesis of spirocyclopropyloxindoles from diazoindoles and a broad range of alkenes, including both *cis* and *trans* 1,2-disubstituted alkenes.

Since the pioneering work of Nozaki and Noyori,^{1a} the metal-catalyzed olefin cyclopropanation using diazo compounds has been established as a powerful strategy to access optically active cyclopropanes.² Despite significant achievements,^{3–6} it is still highly desirable to develop an efficient synthesis for 1,2,3-trisubstituted cyclopropanes from both *trans* and *cis* 1,2-disubstituted alkenes with full control of stereoselectivity.⁷ In this context, a successful protocol involving the acceptor-substituted diazoacetates has been recently developed by Sun and Tang using a chiral BOX/Cu^I catalyst.^{7g} By contrast, the corresponding process using donor–acceptor diazo compounds remains a challenge, since donor/acceptor substituted carbenoids are known to be much more sensitive to the steric features of olefinic substrates than acceptor-only ones.^{7e} Especially, electronically unbiased *trans*-1,2-disubstituted alkenes proved to be difficult substrates for cyclopropanation, as revealed by Davies' systematic studies on the Rh-catalyzed reactions of aryldiazoacetates with electron-rich *trans*-anethole (cyclopropanated in up to 87% ee) or electron-neutral *trans*- β -methyl styrene (only C–H insertion product).^{7e} Herein, we wish to report a highly stereoselective cyclopropanation of cyclic donor–acceptor diazoindoles with various types of alkenes, including both *cis* and *trans* 1,2-disubstituted alkenes, catalyzed by a novel dinuclear Au(I) complex derived from chiral spiroketal bisphosphine (SKP) **L1**.

The diazoindole **1** is a versatile synthon for the 3,3-disubstituted oxindoles,⁸ a type of privileged scaffolds in natural products and drugs.⁹ Particularly, spirocyclopropyl oxindoles are useful building blocks^{10,11a} and interesting targets in medicinal research,¹² but their synthesis via asymmetric olefin cyclopropanation using **1** was rarely explored, probably due to the relatively low reactivity toward alkenes.^{8a} To meet this challenge, Arai and our group independently reported the first example of the asymmetric cyclopropanation of olefins with diazoindole **1** by using either Rh₂(S-PTTL)₄¹³ or the (R)-difluorophos/Hg(II)^{11a} complex as the catalyst, respectively.

Although up to 99% ee has been achieved for the cyclopropanation of styrenes by mercury catalysis, the 1,2-disubstituted alkenes proved to be difficult substrates in terms of the enantioselectivity (Scheme 1). On the other hand, Au(I),

Scheme 1. Mercury Catalysis vs Gold Catalysis in the Olefin Cyclopropanation with Diazoindoles



isoelectronic with Hg(II), has been shown to be effective in the catalysis of olefin cyclopropanation with diazo reagents,¹⁵ but a highly enantioselective version has not yet been reported so far to our knowledge. Inspired by the leading work of Toste¹⁶ and Davies¹⁷ on the exploration of Au(I)-carbenoids in asymmetric catalysis, we thus turned to examine the potential of chiral gold catalysis in the cyclopropanation of the challenging olefins, as Au(I) has been demonstrated to be superior to Hg(II) in many reactions.¹⁴

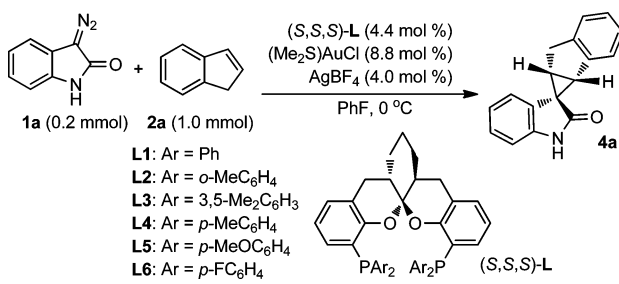
Indeed, an initial test proved that the Au(I) catalyst was much more reactive than a variety of metal catalysts we tried in the olefin cyclopropanation of diazoindole **1a** (Tables S1 and S2, Supporting Information, SI). This result prompted us to further develop its asymmetric version by screening various chiral phosphine ligands, and fortunately, SKP **L1**¹⁸ was identified to be optimal in terms of reactivity and stereoselectivity (Tables S3–5 in SI). Under the optimized reaction conditions, the complete conversion of **1a** was observed within 0.3 h at 0 °C in PhF in the presence of 4.4 mol % of **L1**, 8.8 mol % of (Me₂S)AuCl, and 4.0 mol % of AgBF₄, affording **4a** in

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90% yield, with excellent dr and 90% ee (entry 1, Table 1). The dr value was determined by ^1H NMR analysis of an aliquot

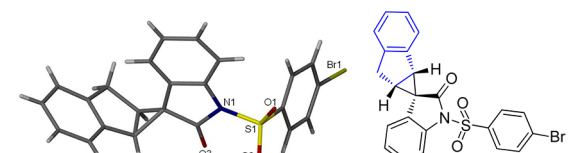
Table 1. Condition Optimization



1a (0.2 mmol) + 2a (1.0 mmol) $\xrightarrow[\text{PhF, 0 } ^\circ\text{C}]{\text{(S,S,S)-L (4.4 mol \%), (Me}_2\text{S)AuCl (8.8 mol \%), AgBF}_4 \text{ (4.0 mol \%)}} 4a$

L1: Ar = Ph
L2: Ar = *o*-MeC₆H₄
L3: Ar = 3,5-Me₂C₆H₃
L4: Ar = *p*-MeC₆H₄
L5: Ar = *p*-MeOC₆H₄
L6: Ar = *p*-FC₆H₄

entry	L	time (h)	yield (%) ^a	dr	ee (%) ^b
1	L1	0.3	90	>20:1	90
2	L2	1	72	>20:1	74
3	L3	0.3	79	>20:1	84
4	L4	0.5	79	>20:1	87
5	L5	0.3	90	>20:1	86
6	L6	0.2	80	>20:1	54
7 ^c	L1	0.3	76	>20:1	94



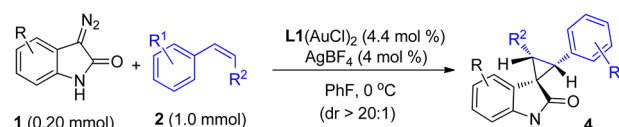
^aIsolated yield. ^bDetermined by HPLC analysis. ^c0.24 mmol of 1a and 0.2 mmol of 2a were used.

taken from the crude reaction mixture. A variety of SKP ligands (S,S,S)-L2–6 were further examined, but proved to be less effective than L1 (entries 2–6 vs 1). With the ratio of 1a and 2a varying from 1.0:5.0 to 1.2:1.0, the ee of product 4a was improved to 94% (entry 7). The relative and absolute configuration of product 4a was assigned by the X-ray analysis of its sulfamide derivative 5. It should be noted that no reaction took place in the absence of AgBF₄, and the amount of AgBF₄ obviously influenced the level of enantioselectivity. The best result was obtained with a Ag/Au ratio of 1:2, and erosion of the enantioselectivity was observed when the ratio was over 1:2 (Table S4 in SI).

The substrate scope of this protocol was first evaluated in the reactions of various *cis*-alkenes 2a–g with diazooxindoles 1a–d, by using 4.4 mol % of the catalyst precursor L1(AuCl)₂, prepared from L1 and (Me₂S)AuCl, and 4.0 mol % of AgBF₄ (Table 2). Both substituted indenenes 2a–d and 1,2-dihydronaphthalene 2e worked well with diazooxindole 1 to give polycyclic oxindoles 4a–g in excellent dr and high to excellent ee. *cis*-Trisubstituted alkene 2f also furnished products 4h–i, with two adjacent quaternary centers, in excellent dr with up to 82% ee. Acyclic *cis* alkene 2g was a viable substrate as well, giving the desired products 4j–l in good yields and excellent diastereo- and enantioselectivities.

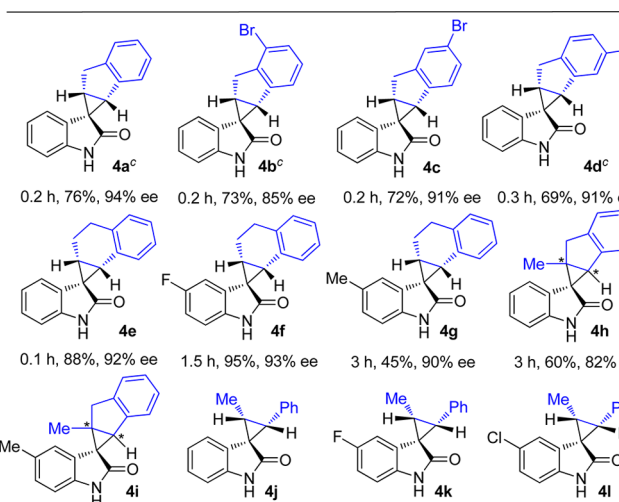
To our delight, the scope of olefins could be extended to *trans*-1,2-disubstituted alkenes as well, as shown in Table 3. It is noteworthy that electron-neutral alkene 3a, without activation by a donating group, reacted with diazooxindole 1b–c

Table 2. SKP L1/Au(I) Catalyzed Cyclopropanation of *cis*-1,2-Disubstituted Alkenes 2^{a,b}



1 (0.20 mmol) + 2 (1.0 mmol) $\xrightarrow[\text{PhF, 0 } ^\circ\text{C}]{\text{L1(AuCl)}_2 \text{ (4.4 mol \%), AgBF}_4 \text{ (4.0 mol \%)}} 4$ (dr > 20:1)

1a: R = H, 1b: R = 5-F
1c: R = 5-Cl, 1d: R = 5-Me
2a: R' = H, 2b: R' = 4-Br
2c: R' = 5-Br, 2d: R' = 6-Br
2e: 1,2-dihydronaphthalene
2f: 1,2-disubstituted alkene
2g: acyclic *cis* alkene



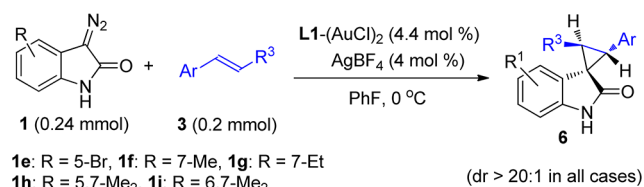
4a^c: 0.2 h, 76%, 94% ee
4b^c: 0.2 h, 73%, 85% ee
4c: 0.2 h, 72%, 91% ee
4d^c: 0.3 h, 69%, 91% ee
4e: 0.1 h, 88%, 92% ee
4f: 1.5 h, 95%, 93% ee
4g: 3 h, 45%, 90% ee
4h: 3 h, 60%, 82% ee
4i: 0.5 h, 63%, 82% ee
4j: 0.1 h, 80%, 94% ee
4k: 0.5 h, 90%, 95% ee
4l: 0.5 h, 95%, 94% ee

^aIsolated yield. ^bEe values determined by chiral HPLC analysis. ^c0.24 mmol 1 and 0.2 mmol 2 were used.

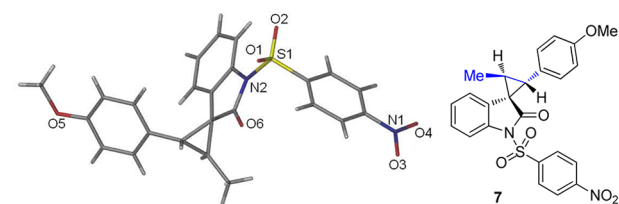
smoothly and selectively to give the desired cyclopropanes 6a–b in high yields with up to 90% ee, without C–H insertion products being detected by GC–MS or LC–MS analysis of the crude reaction mixture (entries 1–2). As expected, *trans*-anethole 3b also reacted smoothly with diazooxindoles to give cyclopropanes 6c–h in good yields and excellent ee values (entries 3–9). The high efficiency of the SKP L1/Au(I) was further exhibited by a 4.0 mmol scale reaction of 1h and 3b with only 1.1 mol % of L1(AuCl)₂ and 1.0 mol % of AgBF₄, which gave product 6g in 71% yield with 92% ee (entry 8). Alkene 3c, with a methoxy group at the allylic position, selectively gave the desired cyclopropanes 6i–j in good yields and excellent ee's (entries 10–11). The relative and absolute configuration of product 6c was unambiguously determined by the X-ray analysis of its derivative 7, and those of other products were tentatively assigned by analogy.

The SKP L1/Au(I) catalyst also allowed the highly stereoselective cyclopropanation of diazooxindole 1 with monosubstituted or 1,1-disubstituted alkenes (Table 4). Styrene derivatives afforded the desired products 9a–e in excellent yield and ee. 1-Hexene reacted with 1b to give product 9f with 70% ee, albeit in a modest yield (18%). When α -methylstyrene was used, the construction of continuous quaternary stereogenic centers was achieved to afford products 9g–h in excellent dr and up to 93% ee.

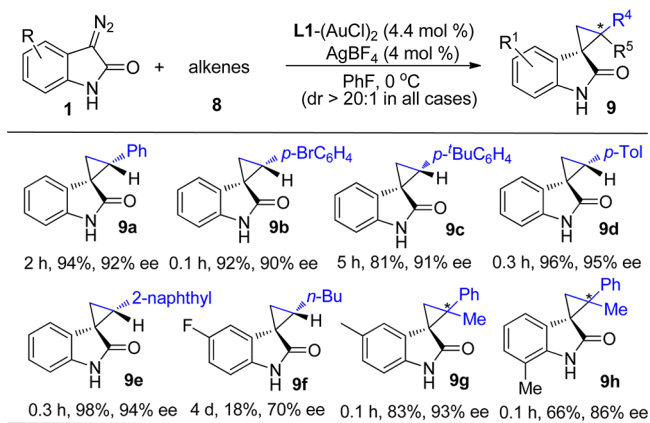
The high stereoselectivity and broad substrate scope achieved by the SKP L1/Au(I) complex prompted us to obtain more structure information, as SKP ligands contained a unique spiroketal backbone, different from the widely used axially chiral diphosphine ligands in gold catalysis.¹⁹ The X-ray diffraction analysis of the catalyst precursor L1(AuCl)₂

Table 3. SKP L1/Au(I) Catalyzed Cyclopropanation of *trans*-1,2-Disubstituted Alkenes 3

entry	1	3	6	time (h)	yield (%) ^a	ee (%) ^b
1 ^c	1b	3a: Ar = Ph, R ³ = Me	6a	0.3	88	90
2 ^c	1c	3a: Ar = Ph, R ³ = Me	6b	0.5	82	88
3	1a	3b: Ar = PMP, R ³ = Me	6c	0.3	76	90
4	1d	3b: Ar = PMP, R ³ = Me	6d	0.3	81	94
5 ^c	1f	3b: Ar = PMP, R ³ = Me	6e	2.0	72	91
6	1g	3b: Ar = PMP, R ³ = Me	6f	5.0	65	92
7	1h	3b: Ar = PMP, R ³ = Me	6g	2.0	72	94
8 ^d	1h	3b: Ar = PMP, R ³ = Me	6g	40	71	92
9	1i	3b: Ar = PMP, R ³ = Me	6h	1.0	83	88
10	1d	3c: Ar = PMP, R ³ = CH ₂ OMe	6i	0.4	53	93
11	1f	3c: Ar = PMP, R ³ = CH ₂ OMe	6j	0.5	48	94
12	1e	3d: Ar = MeO-C ₆ H ₄ -OMe, R ³ = Me	6k	2.0	52	92
13 ^c	1f	3d	6l	0.5	53	92

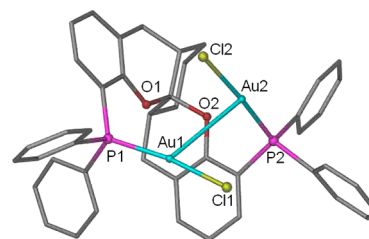


^aIsolated yield. ^bDetermined by chiral HPLC analysis. ^cAt -30 °C. ^dRun on a 4.0 mmol scale, using 1.1 mol % of L1(AuCl)₂ and 1.0 mol % of AgBF₄ at -30 °C.

Table 4. SKP L1/Au(I) Catalyzed Cyclopropanation of Terminal and 1,1-Disubstituted Alkenes 8^{a,b}

^aIsolated yield. ^bFor details, see Supporting Information.

confirmed the formation of Au–Au interaction, with a bond length of 3.25 Å, as shown in Figure 1. Because the best result

**Figure 1.** X-ray crystal structure of complex L1(AuCl)₂.

was obtained with the ratio of AgBF₄/L1(AuCl)₂ as 1:2, the active catalytic species might be a monocationic complex; the exact structure is currently being studied.

In conclusion, we have developed a highly diastereo- and enantioselective cyclopropanation of diazooxindoles with various alkenes, including both *cis* and *trans* 1,2-disubstituted alkenes, which contributes to the synthesis of substituted spirocyclopropyloxindoles that are useful in medicinal research. The high efficiency observed in this reaction suggests the potential wide application of gold-stabilized donor/acceptor carbenoids in the development of asymmetric cyclopropanations. Our results also imply that spiroketal bisphosphine ligands might find more application in gold catalyzed asymmetric reactions, which are still very limited.¹⁹ Further studies are in progress to investigate the range of new synthetic applications of gold-stabilized donor/acceptor carbenoids.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental procedures, characterization data, copies of NMR spectra, and HPLC traces for all compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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