Communication

Highly Stereoselective Olefin Cyclopropanation of Diazooxindoles Catalyzed by a C2-Symmetric Spiroketal Bisphosphine/Au(I) Complex

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Highly Stereoselective Olefin Cyclopropanation of Diazooxindoles Catalyzed by a C_2-Symmetric Spiroketal Bisphosphine/Au(I) Complex

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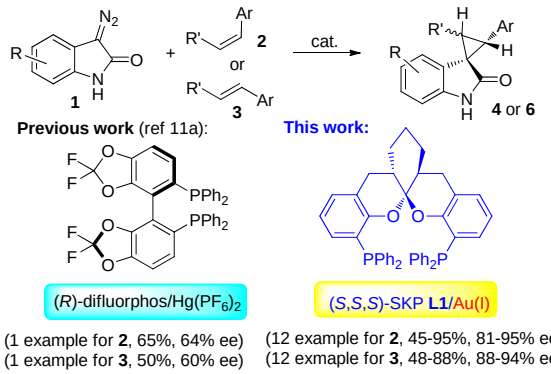
Supporting Information Placeholder

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 diazooxindoles 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 efficient synthesis of 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 diazooxindoles 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 SKP **L1**.

The diazooxindole **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 the synthesis of which via asymmetric olefin cyclopropanation using **1** was rarely explored, probably due to its relatively low reactivity towards alkenes.[8a] To meet this challenge, Arai and our group independently reported the first example of asymmetric cyclopropanation of olefins with diazooxindole **1** by using either Rh$_2$(*S*-PTTL)$_4$[13] or (*R*)-difluorphos/Hg(II)[11a] complex as the catalyst, respectively. Although up to 99% ee has been achieved for 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), isoelectronic with Hg(II), has been shown 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 Toste[16] and Davies[17] 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]

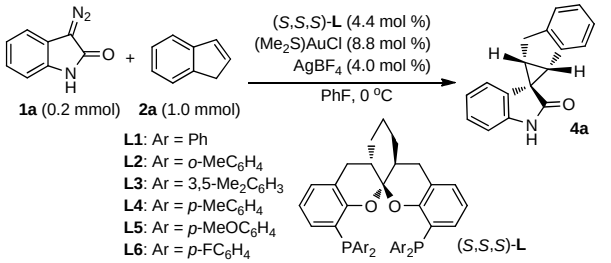


Scheme 1. Mercury catalysis vs gold catalysis in the olefin cyclopropanation with diazooxindoles

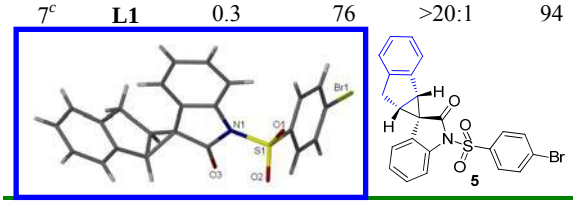
Indeed, an initial test proved that Au(I) catalyst was much more reactive than a variety of metal catalysts we tried in the olefin cyclopropanation of diazooxindole **1a** (Tables S1 and S2, supporting information, SI). This result prompted us to further develop its asymmetric version by screening various 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 $(Me_2S)AuCl$ and 4.0 mol % of $AgBF_4$, affording **4a** in 90% yield, with excellent dr and 90% ee (entry 1, Table 1). The dr value was determined by ^1H NMR analysis of an aliquot 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 at all in the absence of $AgBF_4$, and the amount of $AgBF_4$ obviously influenced the level of enantioselectivity. The best result was obtained with the Ag/Au ratio of 1:2, and erosion of enantioselectivity was observed when the ratio was over 1:2 (Table S4 in SI).

Table 1. Condition Optimization



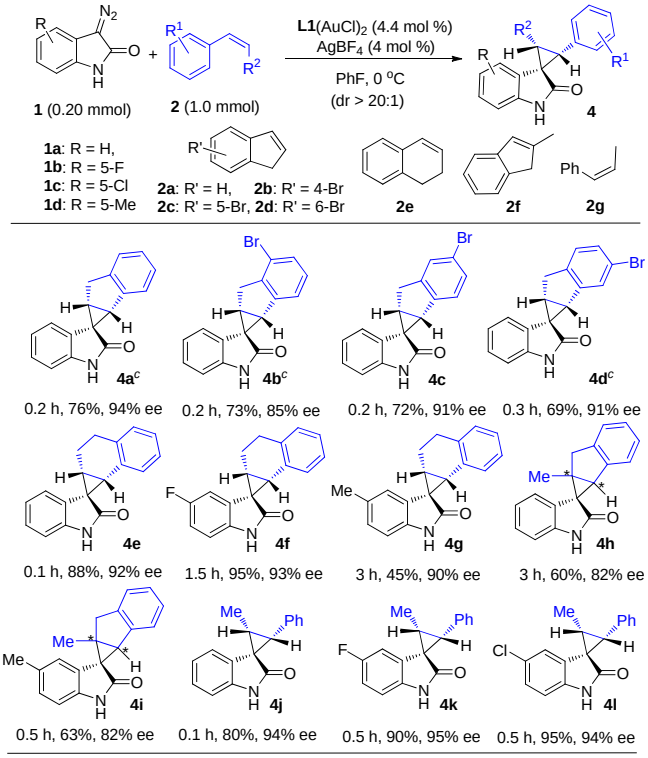
entry	L	time (h)	yield (%)[a]	dr	ee (%)[b]
1	**L1**	0.3	90	>20:1	90
2	**L2**	1	72	>20:1	74
3	**L3**	0.3	79	>20:1	84
4	**L4**	0.5	79	>20:1	87
5	**L5**	0.3	90	>20:1	86
6	**L6**	0.2	80	>20:1	54
7[c]	**L1**	0.3	76	>20:1	94



[a]Isolated yield. [b]Determined by HPLC analysis. [c]0.24 mmol **1a** and 0.2 mmol **2a** were used.

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 $(Me_2S)AuCl$, and 4.0 mol % of $AgBF_4$ (Table 2). Both substituted indenes **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.

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



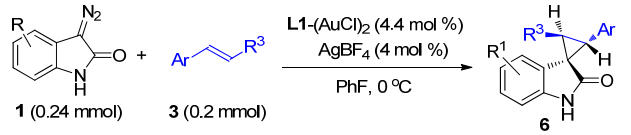
[a] Isolated yield. [b] Determined by chiral HPLC analysis. [c]0.24 mmol **1** and 0.2 mmol **2** were used.

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 the activation by a donating group, reacted with diazooxindole **1b-c** 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 3-8). 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 $AgBF_4$, which gave product **6g** in 71% yield with 92% ee (entry 9). Alkene **3c**, with a methoxy group at the allylic position, selectively gave the desired cyclopropanes **6i-j** in good yields and excellent ees (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 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%).

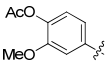
When α-methylstyrene was used, the construction of continuous quaternary stereogenic centers was achieved to afford products **9g-h** in excellent dr and up to 93% ee.

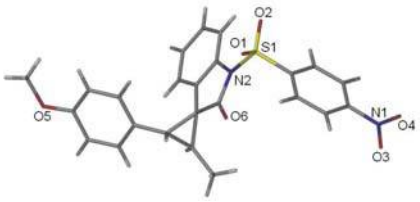
Table 3. SKP **L1**/Au(I) Catalyzed Cyclopropanation of *trans*-1,2-Disubstituted Alkenes **3**

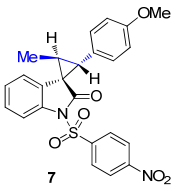


1e: R = 5-Br, **1f**: R = 7-Me, **1g**: R = 7-Et
1h: R = 5,7-Me_2, **1i**: R = 6,7-Me_2

(dr > 20:1 in all cases)

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_2OMe	**6i**	0.4	53	93
11	**1f**	**3c**: Ar = PMP, R^3 = CH_2OMe	**6j**	0.5	48	94
12	**1e**	**3d**: Ar =  R^3 = Me	**6k**	2.0	52	92
13[c]	**1f**	**3d**	**6l**	0.5	53	92

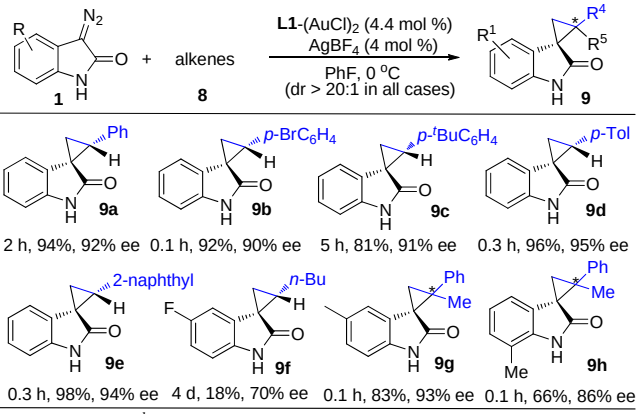




[a]Isolated yield. [b]Determined by chiral HPLC analysis. [c]At -30 °C. [d]Run on a 4.0 mmol scale, using 1.1 mol % of **L1**$(AuCl)_2$, and 1.0 mol % of $AgBF_4$ at -30 °C.

The high stereoselectivity and broad substrate scope achieved by SKP **L1**/Au(I) complex prompted us to get 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**$(AuCl)_2$ confirmed the formation of Au-Au interaction, with a bond length of 3.25 Å, as shown in Figure 1. Because the best result was obtained with the ratio of $AgBF_4$/**L1**$(AuCl)_2$ as 1:2, the active catalytic species might be a monocationic complex, and the exact structure of which is now in studies.

Table 4. SKP **L1**/Au(I) Catalyzed Cyclopropanation of Terminal and 1,1-Disubstituted Alkenes **8**[a,b]



[a]Isolated yield. [b]For details, see supporting information.

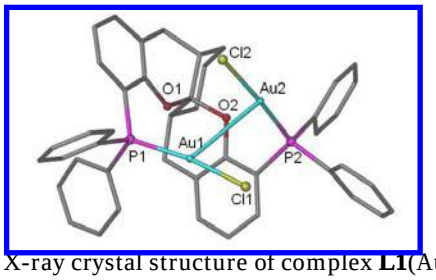


Figure 1. X-ray crystal structure of complex **L1**$(AuCl)_2$.

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 the 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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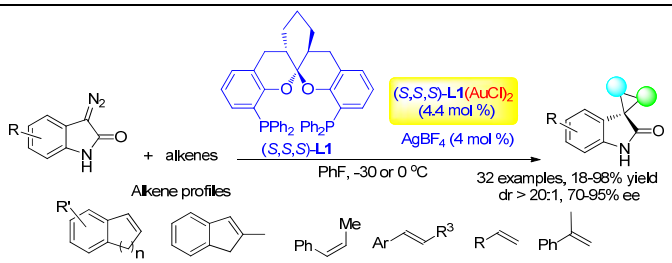
N2
R
O
N
H
+ alkenes
Alkene profiles
R'
n
PPh2 Ph2P
(S,S,S)-L1
PhF, -30 or 0 °C
(S,S,S)-L1(AuCl)2
(4.4 mol %)
AgBF4 (4 mol %)
32 examples, 18-98% yield
dr > 20:1, 70-95% ee
Me
Ph
Ar
R3
R
Ph