Gold(III)-catalysed *cis*-to-*trans* cyclopropyl isomerization

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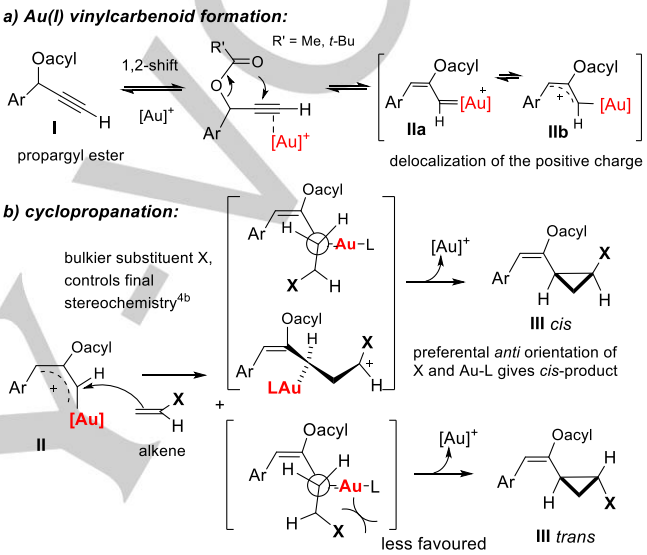
Abstract: Novel chiral gold(III) complexes, based on bisoxazoline (BOX) and 2-pyridyl-(-)menthol ligands, were prepared and characterised (X-ray), and their catalytic properties in cyclopropanation reactions of propargyl esters with alkenes were explored. The BOX-Au(III) catalysts gave excellent results for fast cyclopropanation and subsequent in situ *cis*-to-*trans* vinylcyclopropyl isomerization. Au(I) and Au(III) catalytic species showed different abilities to tune the reactions and transform the initially formed *cis* into the isomerized *trans* product. The appropriate choice of gold(I) or gold(III) complexes enabled highly stereoselective formation of *cis* or *trans* products (up to 99% dr), in high yields (63-98%). The pure *cis* isomers were used in isomerization studies, showing that rapid *cis*-to-*trans* isomerization took place at r.t. in the presence of BOX-Au(III) catalysts.

Introduction

The intensive development of gold chemistry the last decade has mainly focussed on the discovery and understanding of new gold(I)-catalysed reactions as well as the introduction of a variety of ligands for construction of new gold(I)-ligated complexes. Gold(III) catalysts opened the field of gold catalysis in organic synthesis.[1] However, gold(III) catalysts have not found widespread usage in later years, and with some exceptions,[2,3] the Au(III) complexes have mainly been limited to ligand-free, less stable gold(III)-species, typically $AuCl_3$ or K/Na/H($AuCl_4$). In contrast to the linear coordination mode of gold(I) catalysts, the ligated gold(III) complexes are square planar complexes, having four coordination sites. This may provide easier steric control, due to the proximity of the ligand to the reaction centre, which can allow for more selective reactions. Gold(III) catalyses many of the same reactions as gold(I), but may also be unreactive or exhibit quite different properties in many transformations.

Gold-catalysed cyclopropanation has emerged as a powerful method and provides complementarity to traditional metal-catalysed cyclopropanation systems. Gold vinyl carbenoids have been proposed as reactive intermediates in olefin cyclopropanations and have been generated by many methods.[4]

The propargyl ester - gold approach, based on gold-catalysed activation of propargyl esters, has been applied in a variety of cycloaddition reactions[5] (including cyclopropanation) as the easily accessible propargylic ester entity constitutes a convenient synthetic equivalent to an α-diazoketone for cyclopropanation processes. Terminal propargyl esters (**I**, Scheme 1) tend to undergo Au(I)-catalysed 1,2-acyloxy migration, analogous to Ru-catalysed[6a,b] rearrangements, affording gold vinylcarbenoid intermediates (**II**). These intermediates may undergo cyclopropanation with alkenes to give rise to vinylcyclopropyl products (**III**), normally obtained as *cis/trans* mixtures.[6]



Scheme 1. Au(I)-catalysed cyclopropanation, including a stereochemical model.[4b]

In general, reported successful gold-catalysed alkene cyclopropanations starting from propargyl esters have been performed with Au(I) complexes with e.g. phosphine or NHC ligands.[7] Some very few exceptions are known that apply Au(III) complexes, such as $AuCl_3$.[8]

Our earlier work employing propargyl esters **I** as gold vinylcarbenoid precursors in cyclopropanation reactions with alkenes (Scheme 1a,b) directly connected to a heteroatoms (X=NR,R' or OR,R')[6f,9a] provided highly functionalized vinylcyclopropyl derivatives **III** in up to 99% diastereoselectivity. Our previous cycloaddition studies of propargyl acetals,[6f,9] were based on Au(I) catalysis, as Au(III) salts mostly were shown to be unreactive.[9b-d,f,g] This is in accordance with other gold-catalysed cyclopropanation studies with varied substrates, but always performed with standard Au(I) catalysts.[6]

In light of these results, further exploration focussed on the ability of different gold catalytic species to stereoselectively afford *cis* or *trans* vinylcyclopropyl products. Our comparative studies, including the use of novel ligated gold(III) complexes, $AuCl_3$ and Pic-Au(III) as well as the JohnPhosAu(I) catalyst, are discussed below.

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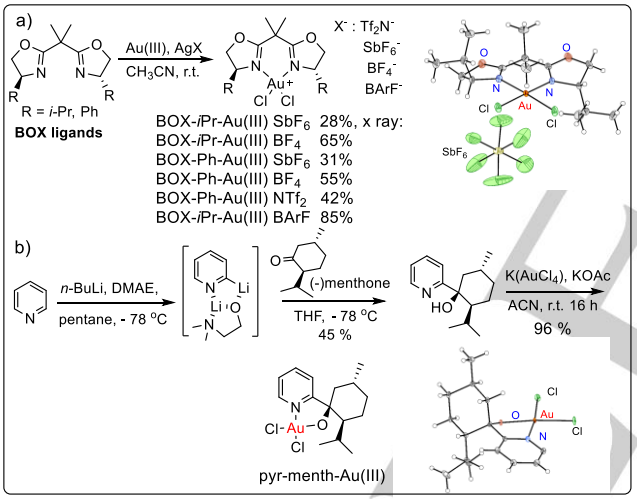
Results and Discussion

Preparation of chiral Au(III)-ligated catalysts.

Butyl-bisoxazoline-Au(III)$_2$ (BOX-*n*-Bu-Au(III))$_2$ complexes have been prepared for investigation of thermal properties of such ionic liquids.[10a] According to this method, two new chiral *i*-Pr and phenyl bisoxazoline-Au(III) complexes were prepared for application in the present study on Au(III)-catalysed cyclopropanation. The crystalline BOX-*i*-Pr-Au(III) and BOX-Ph-Au(III) complexes were obtained from the respective BOX ligands and K(AuCl$_4$) (in 28-65% yields, Scheme 2a). Different counterions, Tf_2N^-, SbF_6^-, BF_4^- and $BArF^-$ were introduced by the appropriate silver or sodium[10b] salts.

Another chiral 2-pyridyl-mentholate-Au(III) complex was prepared in 96% yield by base treatment and complexation of 2-pyridyl-menthol to K(AuCl$_4$) (Scheme 1b).[3a] The pyr-menth ligand was prepared by enantioselective addition of lithiated pyridine to (-)-menthone.[11] The bis-pyridine by-product formation was challenging, and optimization of reaction conditions (e.g. reactant equivalents, temperature, additives) allowed isolation of moderate yields of the ligand (45% from a 1:3:6:12 equiv mixture of menthone-pyridine-DMAE-BuLi).



Scheme 2. Preparation of Au(III)-ligated complexes, including single-crystal X-ray structures; a) cationic BOX-Au(III) catalysts; b) pyridine-(-)mentholate-Au(III) catalyst.

Cyclopropanation and cis-to-trans isomerization.

Most *cis/trans* ratios reported for propargyl cyclopropanation[6] are given as fixed values, characteristic for the actual product and reaction. Based on a previously postulated stereoselectivity model, dominating *cis*-selectivity is proposed to be consistent with an interaction of the olefin substituent with the ligated metal to disfavour the formation of the *trans*-cyclopropane[4b] (Scheme 1b). Thus, the steric interaction between the gold(I) ligand and the bulkier X-substituent on the vinyl substrate was suggested to preferentially give an *anti* orientation in the transition state to afford the main *cis* product. Our previous results with heteroatom-alkene cyclopropanations[6f,9a] showed that the *cis/trans* product ratios varied, depending on the bulkiness, but stereoselectivity was also clearly affected by the electronic properties of the alkenes.

Our present studies confirm the importance of the electronic nature of substrates, but also show that the properties and the catalytic activity of Au(I)/Au(III) catalysts are much more important and predominant for the steroselectivity of the reactions than the steric nature of the propargyl **1** and alkene **2** substrates. The results show that a more complex situation controls the stereochemical outcome of propargyl cyclopropanations, as particularly Au(III) catalysts may activate for in situ *cis*-to-*trans* isomerization in the course of cyclopropanation reactions. Thus, the stereoselective outcome of the reactions strongly depended on the specific performance of the applied gold catalyst. As a result, stereoselectivity could be tuned by appropriate reaction time.

A recent cyclopropanation study[12] has reported that slow *cis*-to-*trans* isomerization takes place during the progress of a similar cyclopropanation in the presence of a JohnPhosAu(I) catalyst, as shown by the moderate *cis/trans* isomerization; increasing the amount of *trans* isomer from 10% to 62 % by heating (75 ^{0}C) for nearly a week.

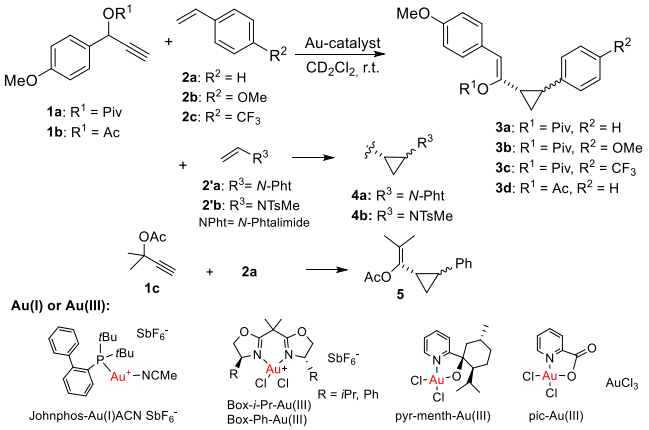
In our present study, the impact of the applied Au catalyst on the obtained stereoselectivity in cyclopropanation of terminal propargyl esters (**1a**,**b**,**c**) and alkenes **2a**-**c** and **2'a**,**b** (Table 1) was explored. The reactions were carried out as NMR experiments without stirring, affording longer reaction times than normal reactions performed in lab-scale, as shown by comparison with Table 2. The catalytic activity of the new Au(III)-complexes were compared to the simple $AuCl_3$ and the commercially available Pic-Au(III) salts, as well as the frequently used JohnPhosAu(I) catalysts. Despite the chiral nature of the new Au(III) catalysts, no enantioselectivity was observed, and racemic cyclopropyl products were obtained (HPLC).

Most interestingly, the ability of BOX-Au(III) complexes to both afford fast cyclopropanation, and strongly activate for *cis*-to-*trans* isomerization was observed. Full conversion of propargyl pivaloyl ester **1a** into *cis/trans* mixtures of cyclopropyl products **3a** and **3b** was seen in the reaction with styrenes **2a**,**b** in the presence of 1-5 mol% BOX-*i*-Pr-Au(III)SbF_6 in less than 5 min (entries 1,3,7,8). With increased reaction times, a larger amount of the *trans* isomer evolved (up to 99% for **3a** in 24 h; entry 1) in the presence of 5 mol% Au(III) complex. The BOX-Ph-Au(III) catalyst afforded correspondingly 94% *trans* (entry 2). Lower catalyst loading (1 mol%) slowed down the *cis*-to-*trans* isomerization (86% *trans* **3a** in 2 d; entry 3). Propargyl acetate **1b** seemed to be slightly less reactive for both the cyclization and isomerization of product **3d** (entry 10). A marginally lower tendency for isomerization was seen for the electron-deficient *p*-CF_3 product **3c** (91% *trans* in 24 h, entry 9). A more complex situation was observed for electron-rich dimethoxy product **3b**, as shown by a competing rearrangement into cyclopentenyl products[9a] (entries 7,8). The BOX-Au(III) complexes with BF_4^- and NTf_2^- anions (Scheme 2a) gave corresponding results as the BOX-Au(III) SbF_6^- complexes (Table 1).

The pyr-menth-Au(III) complex inefficiently afforded cyclopropanation (2 h, entry 4) and isomerization (16% *trans*-**3a**

in 24 h), while the JohnPhos-Au(I) catalyst (5 mol%) gave fast cyclopropanation, but was less effective for isomerization (70% *trans* in 2d, entry 5). The $AuCl_3$ salt activated for a fast cyclization into a *cis/trans* mixture of product **3a**. However, the disadvantage with $AuCl_3$ is the low reproducibility and instability, as shown by the immediate formation of a dark gold precipitate, but generally, no subsequent isomerization took place (entry 6).

Table 1. Studies on stereoselective cyclopropanation.[a]



Entry	Substrates	Au cat (mol%)	Prod	Rx-time	*cis* : *trans* ratio
1	**1a + 2a**	BOX-*i*-Pr-Au(III)SbF_6 (5)	**3a**	< 5 min [b] 30 min 24 h	50 : 50 25 : 75 1 : 99
2	**1a + 2a**	BOX-Ph-Au(III)SbF_6 (5)	**3a**	< 15min[b] 24h	53 :47 6 : 94
3	**1a + 2a**	BOX-*i*-Pr-Au(III)SbF_6 (1)	**3a**	< 5 min[b] 19 h 2 d	88 : 12 65 : 35 14 : 86
4	**1a + 2a**	pyr-menth-Au(III) (5)	**3a**	2 h [b] 24 h	88 : 12 84 : 16
5	**1a + 2a**	JohnPhos-Au(I)ACN (5)	**3a**	< 5 min [b] 9 h 2d	95 : 5 67 : 23 30 : 70
6	**1a + 2a**	$AuCl_3$ (5)	**3a**	30 min[b] 24 h	55 : 45 55 : 45
7	**1a + 2b**	BOX-*i*-Pr-Au(III)SbF_6 (5)	**3b**	< 5 min [b] 30 min 24 h	45 : 55 27 : 73 17 : 83[c]
8	**1a + 2b**	BOX-*i*-Pr-Au(III)SbF_6 (1)	**3b**	< 5 min [b] 24 h	50 : 50 44 : 56 [c]
9	**1a + 2c**	BOX-*i*-Pr-Au(III)SbF_6 (5)	**3c**	< 5 min [b] 24 h	76 : 24 9 : 91
10	**1b + 2a**	BOX-Ph-Au(III)SbF_6 (5)	**3d**	10 min [b] 24 h	92 : 18 10 : 90
11	**1a + 2'a**	BOX-*i*-Pr-Au(III)SbF_6 (5)	**4a**	12 h[b] 24 h	86 : 14 82 : 18
12	**1a + 2'b**	BOX-*i*-Pr-Au(III)SbF_6 (5)	**4b**	< 5 min[b]	1 : 99
13	**1a + 2'b**	BOX-*i*-Pr-Au(III)SbF_6 (1)	**4b**	15 min[b]	1 : 99
14	**1a + 2'b**	JohnPhos-Au(I)ACN (5)	**4b**	< 5 min [b]	1 : 99
15	**1c + 2a**	BOX-*i*-Pr-Au(III)SbF_6 (5)	**5**	1h [b] 24 h	85 : 15 85 : 15
16	**1c + 2a**	pyr-menth-Au(III) (5	**5**	1h [b] 24 h	90 : 10 90 : 10
17	**1c + 2a**	JohnPhos-Au(I)ACN (5)	**5**	5 min [b] 24 h	95 : 5 95 : 5

[a] The general reactions were performed in NMR tubes; **1a,b** (5 mg, 1 equiv.) and vinyl substrate **2a-c** (4 equiv.) in *d*-DCM (0.6 mL) added Au catalyst (1 or 5 mol-%) in *d*-DCM and monitored by ^{1}H NMR; [b] full conversion of propargyl substrate; [c] rearranged cyclopentenyl product[9a] was also formed.

Alkenes connected to N-heteroatom functionalities were tested as well. The electron-deficient *N*-phtalimide-alkene **2'a** slowly afforded cyclization product **4a**, but no further isomerization took place in the presence of BOX-*i*-Pr-Au(III) (12-24 h, 18% *trans* entry 11). In contrast, the NTsMe-alkene **2'b** is activated for immediate cyclization into product **4b** with both Au(I) and Au(III) catalysts (1-5 mol%, entries 12-14). This reaction does not appear to be controlled by the *cis*-stereoselective model[4b] (Scheme 1b). In contrary to all the alkenes above, the reaction of NTsMe-alkene **2'b** seems to follow a selective direct *trans*-cyclization pathway, as no traces of the *cis* isomer were observed.

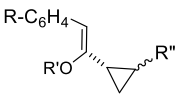
The dimethylpropargyl substrate **1c** readily afforded 85 – 95% *cis*-cyclopropylpropenyl product **5** (5 min - 1h, entries 15-17), but no further isomerization took place in the presence of any gold catalyst.

Selective preparation of cis and trans cyclopropyl products

As shown above, the appropriate choice of gold(I) or gold(III) complexes allows for the highly stereoselective formation of *cis* or *trans* products (up to 99% dr). To demonstrate the potential of the selective methods, a number of *cis* and *trans* isomers of cyclopropyl products **3** and **4** were prepared in high yields (in general 63-92%) from the appropriate propargyl esters and alkenes by applying the JohnPhosAu(I)(MeCN)SbF_6 and BOX-Au(III) catalysts, respectively (Table 2). Due to stirring, most reactions, even for *trans* preparation, were faster than the NMR experiments shown in Table 1.

Samples of >99% purity of *cis* isomers were further prepared to be used in *cis*-to-*trans* isomerization studies below (Table 3).

Table 2. Stereoselective preparation of *cis* or *trans* cyclopropyl products from appropriate substrates, according to Table 1.[a], [b]



3a: R = 4-OMe; R'= Piv; R" = Ph
3b: R = 4-OMe R' = Piv, R" = 4-OMe-C_6H_4
3c: R = 4-OMe R' = Piv, R" = 4-CF_3-C_6H_4
3d: R = 4-OMe R' = Ac, R" = Ph
3f: R = 4-CF_3 R' = Piv, R" = Ph
4a: R = 4-OMe, R' = Piv, R" = *N*-Pht
4b: R = 4-OMe, R' = Piv, R" = *N*TsMe

	cis isomer[a]		*trans* isomer[b]	
product	*cis*:*trans* ratio	yield	*cis*:*trans* ratio	yield
3a	96:4	64 %	>99 % *trans*	76 %
3b	98:2	79 %		
3c	98:2	72 %		
3d	90:10	79 %	10 : 90[c]	63%
3f	>99 % *cis*	14 %	15 :85	98%
4a	>99 % *cis*[d]	92%		
4b			>99 % *trans*	75 %

[a] Approx. 0.1 mmol substrates and JohnPhosAu(I)(MeCN)SbF_6 (5 mol%) in DCM; stirred at r.t. 3-15 min; [b] Approx. 0.1 mmol substrates and BOX-Au(III) (5 mol%) in DCM; stirred at r.t. 15-60 min; [c] 24 h reaction time; [d] 1 h reaction time.

Cis-to-*trans isomerization*

The gold-catalysed isomerizations of pure *cis* products **3a-d** and **4a** (Table 2) into the corresponding *trans* diastereomers were monitored by ^{1}H NMR (Table 3). For all substances **3a** (entries 1-4), **3b** (entry 10), **3c** (entry 14) and **3d** (entries 19-20), the BOX catalysts afforded faster isomerization (5 min - 5h) than the other tested catalysts.

Table 3. *Cis*-to-*trans* isomerization studies.[a]

Entry	Cis compound[a],[b]	Au catalyst (5 mol%)	time	*cis:trans* ratio
1	**3a**	BOX-*i*-Pr-Au(III)-SbF_6	2h	**1:99**
2	**3a**	BOX-*i*-Pr-Au(III)-SbF_6 (1mol%)	3 h	**3 : 97**
3	**3a**	BOX-Ph -Au(III)-SbF_6	2 h	**5 : 95**
4	**3a**	BOX-Ph -Au(III)-SbF_6 (1 mol%)	5 h	**5 : 95**
5	**3a**	$AuCl_3$	1 d	35 :65
6	**3a**	$AuCl_3$ (1 mol%)	1 d	11 : 89
7	**3a**	pyr-menth-Au(III)	8 h	15 : 85
8	**3a**	Pic-Au(III)	5 h	**4 : 96**
9	**3a**	JohnPhos-Au(I)	24 h	**4 : 96**
10	**3b**	BOX-*i*-Pr-Au(III)-SbF_6	5 min	**4 :96** [c]
11	**3b**	pyr-menth-Au(III)	5 min	**4:96**[c]
12	**3b**	$AuCl_3$	17 h	78:22
13	**3b**	JohnPhos-Au(I)	5 min	- [d]
14	**3c**	BOX-*i*-Pr-Au(III)-SbF_6	3 h	5 :95
15	**3c**	JohnPhos-Au(I)	4 d	**1:99**
16	**3c**	pyr-menth-Au(III)	5 h 4 d	90:10 **1:99**
17	**3c**	$AuCl_3$	3 h	**5:95**
18	**3c**	Pic-Au(III)	1 d 4 d	22:78 18:82
19	**3d**	BOX-*i*-Pr-Au(III)-SbF_6	4 h	**2:98**
20	**3d**	BOX-Ph-Au(III)-SbF_6	2 h	**5 : 95**
21	**3d**	pyr-menth-Au(III)	2 d	**5 : 95**
22	**3d**	$AuCl_3$	8 h	15 : 85
23	**3d**	JohnPhos-Au(I)	1 d	**4 : 96**
24	**4a**	BOX-*i*-Pr-Au(III)-SbF_6	2 d	67 : 33
25	**4a**	BOX-*i*-Pr-Au(III)-BArF	2 h 2 d	83 : 17 60 : 40
26	**5**[e]	BOX-*i*-Pr-Au(III)-SbF_6	1 d	95 : 5
27	**5**[e]	JohnPhos-Au(I)	1 d	95 : 5

[a] The *cis*-product (>99% purity) (5 mg, 1 equiv.) was dissolved in *d*-DCM (0.6 mL) in a NMR tube and added the gold-catalyst (1 or 5 mol%) dissolved in *d*-DCM. The reaction progress at r.t. was monitored by ^{1}H NMR; [b] Samples of >99% *cis* purity were prepared according to Table 2; [c] minor amounts of rearranged cyclopentenyl product[9a] was observed; [d] rearranged cyclopentenyl product[9a] was mainly formed; [e] Sample **5**; 95 : 5 *cis : trans*, was prepared according to Table 1, entry 17.

The pyr-menth-Au(III) and the JohnPhos-Au(I) complexes also activated for isomerization, but to a lower extent (85-96% trans-**3a**, 8-24 h, entries 7,9). Results with $AuCl_3$ were not reproducible, as discussed above (entries 5,6). Spontaneous and selective BOX-Au(III)-catalysed isomerization was seen for the electron-rich substrate **3b** (96% *trans*, 5 min, entry 10), in contrast to the rearranged cyclopentenyl product[9a] mainly afforded with JohnPhos-Au(I) (entry 13). In general, the isomerization reactions of the electron-deficient *cis* isomer of CF_3 product **3c** (entry 14-18) as well as the acetate **3d** (entry 19-23) were slower than **3a** and **3b**.

The electron-deficient N-pht product **4a** gave only partial isomerization with the BOX-*i*-Pr-Au(III)-SbF_6 complex (33% *trans*, 2d, entry 24). The BOX-*i*-Pr-Au(III)-BArF was slightly more efficient (40% *trans*, 2 d, entry 25), demonstrating the reported positive effect[10b] of counter-anion exchange with the more weakly coordinating BArF anion. Previously, JohnPhosAu(I) (10 mol%) has been reported[12] to afford slow and moderate isomerization of similar *cis* N-phtalimide- and aryl-cyclopropyl structures into 69-87% *trans* product by heating (75 °C) for 1-2 weeks. The cyclopropylpropenyl product **5**, prepared from dimethylpropargyl substrate **1c**, failed to undergo isomerization by any gold catalyst (entries 26,27).

The *cis* isomer of NTsMe product **4b** was not accessible for isomerization studies, as this isomer was not observed during cyclopropanation, explained by a possible direct *trans*-cyclization pathway.

Proposed cis-to-trans isomerization pathways.

The observed *cis*-to-*trans* isomerization of vinyl-cyclopropyl products (**III**, Scheme 3) is proposed to proceed by Au-catalysed ring-opening through intermediates i-v (Scheme 3). In the first step, the Au moiety attaches to the substrate at C1, C3 or C4, giving intermediates i/ii, iii and iv/v, respectively. Finally, the *trans*-cyclopropyl product may be formed after bond rotation and ring re-closure.

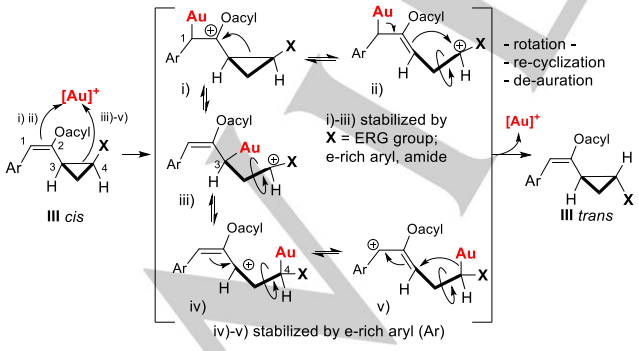
The ability of cyclopropyl moieties to undergo Au-catalysed ring opening has previously been illustrated in several studies, either as substrates or as proposed intermediates in Au-catalysed transformations.[13] Alkynylcyclopropanes are known to undergo Au-catalysed nucleophilic ring opening.[14] Ring expansions are also known to take place by C-C bond migration by Au-catalysed cyclopropyl ring opening and ring closure into larger ring systems,[6e,15] such as cyclobutane products.[16] Au-catalysed cycloisomerization of enynes may proceed through cyclopropyl-gold-carbene interemediates and ring opening by nucleophilic attack or rearrangements.[15b,17]

In contrast to our previous observations using propargyl substrates[6f] and heteroatom-alkenes, a step-wise mechanism has been suggested[15e] for ring expansion of *cis*-cyclopropyl intermediates (**III**) into cyclopentadienes. The process involves Au-vinyl activation by Au-coordination to C1, cyclopropyl ring opening (intermediates i)-ii); Scheme 3) and final ring closure to give the *trans*-product. A second mechanism for a related Au-catalysed vinylcyclopropyl (X = *N*-phtalimide or aryl) *cis-trans* isomerization has also previously been elucidated, involving intermediates iv)-v) (Scheme 3).[12]

In the present study, the total electronic properties of the *cis* product seem to control its general ability to undergo isomerization. However, our products **3**,**4** have both electron-rich and electron-deficient functionalities, some originating from the alkene substrates **2** and **2'** (X, Scheme 3). A more multifaceted situation for the *cis*-*trans* isomerization is therefore proposed for the vinylcyclopropyl derivatives **3**,**4** (**III**, Scheme 3), where the substrates can undergo isomerization through different pathways, influenced by the stabilization of the intermediate cationic Au complexes i-v. In general, the stabilities of these complexes are proposed to be dependent on the electronic natures of the substrates. Hence, the isomerization pathways may differ, as different intermediates have different stabilization capacities. This may explain the variation in ability to undergo isomerization, as different pathways are unlikely to have transition state complexes of the same stability. Consequently, one pathway will have a lower energy requirement than the others.

The presently studied aryl-vinylcyclopropyl ester products **3**, **4** (**III** in Scheme 3) contain the activating 4-OMe-phenyl-propargyl group. Such structures are proposed, to readily undergo isomerization through the stabilized allylic and benzylic carbocations (iv-v, Scheme 3), obtained by ring cleavage by Au-connection to C4. In contrast, the corresponding alkyl product **5** does not contain an analogous stabilizing group, explaining its negligible ability for isomerization (entries 26 and 27, Table 3). Electron-deficient c*is* products with additional EWG, such as **4a** (X= Npht) may also follow the iv)-v) isomerization pathway, but are overall observed to be too deactivated to undergo efficient isomerization (entries 24 and 25, Table 3).

However, c*is* products with X = ERG may favour isomerization through the alternative cationic Au intermediates i)-iii) (Scheme 3), formed by ring cleavage by allylic Au-connection to C1/C3. These intermediates are likely to be favoured due to stabilization of the positive charge by electron-rich aryl-cyclopropyl groups, as observed for **3b** (entries 10 and 11, Table 3). In particular, the X = NTsMe group would allow strong iminium stabilization of intermediates ii) and iii), which may explain the immediate cyclopropanation into the NTsMe *trans*-product **4b**, by a direct *trans* cyclization pathway (entries 12-14, Table 1).



Scheme 3. Possible intermediates in *cis*-to-*trans* vinylcyclopropyl isomerization.

Conclusions

In contrast to the established cyclopropanation stereoselectivity model,[4b] which explains the favoured *cis*-selectivity by steric interactions, we have shown that a more complex situation controls the stereochemistry of propargyl cyclopropanation reactions. The present results demonstrate that the stereoselective outcome is mostly affected by the electronic properties of substrates as well as the choice of Au(I) or Au(III) catalyst, and finally, the reaction time as well as the bulkiness of substrates.

Our studies show that BOX-Au(III) catalysts are superior to the other tested catalysts for combined fast cyclopropanation and subsequent in situ *cis*-to-*trans* vinylcyclopropyl isomerization. In the presence of BOX-Au(III) complexes, rapid and complete in situ isomerizations from initially formed *cis* (>99%) into *trans* (>99%) isomers may take place at r.t. during cyclopropanation reactions. As a consequence, the proper choice of Au(I) or Au(III) catalyst allowed highly stereoselective formation of either *cis* or *trans* products, respectively, in up to 99% dr, and facilitated isolation of pure *cis* or *trans* isomers in high yields (63-98%).

To the best of our knowledge, the present study for the first time proves the BOX-Au(III) effect on propargyl cyclopropanation, affording complete in situ *cis*-to-*trans* isomerization. The BOX-Au(III) complexes represent an interesting group of Au(III) catalysts with specific and unique properties. Further studies on comparable complexes are in progress in our laboratories.

ASSOCIATED CONTENT

Supporting Information (see footnote on the first page of this article). Characterization of compounds and copies of ^{1}H, ^{13}C NMR spectra are available free of charge at www….. Crystallographic data; Cambridge Crystallographic Data Centre; BOX-*i*Pr-Au(III)SbF_6 and pyr-menth-Au(III) complexes; CCDC ID: 1828155 and 1828159.

Experimental Section

General. Commercial grade reagents were used as received. Dry solvents were collected from a solvent-purification system. All reactions were monitored by thin-layer chromatography (TLC) using silica gel 60 F254 (0.25-mm thickness) or by ^{1}H-NMR. Flash chromatography was carried out using silica gel 60 (0.040-0.063 mm). High Throughput Flash Purification (HPFP) was performed on pre-packed cartridges. ^{1}H and ^{13}C NMR spectra were recorded using a 400 or 600 MHz spectrometer. Chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) or *d*-DCM. Coupling constants (*J*) are reported in Hertz (Hz). The attributions of the chemical shifts were determined using COSY, HSQC and HMBC NMR experiments. The identification the c*is*-/*trans*-diastereomers of products **3** was based on NOESY 2D NMR experiments. Accurate mass determination in either positive or negative mode was performed with a "Synapt G2-S" Q-TOF instrument from

Waters. Samples were ionised with an ASAP probe, and no chromatographic separation was used before the mass analysis. IR spectra were obtained using a Bruker Alpha FT-IR spectrometer using OPUS V7 software to analyze the spectra. Single crystal X-ray data was acquired using a Bruker D8 Venture diffractometer with the APEX3 suit, integrated with SAINT V9.32B, solved with XT and refined with XL using Olex2 as GUI. The cif files were edited with encipher 1.4 and molecular graphics were produced with Mercury 3.8. CCDC- ID 1828159 (BOX-Au(III)) and 1828155 (pyr-menth-Au(III)) 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. Propargyl esters **1a**[18a], **1b/1d**[18b] and **1c**[18c] were prepared according to literature procedures.

General method A for preparation of BOX-Au(III)-complexes[10a]

The *R,S*-BOX-ligand (1 equiv.) and K($AuCl_4$) (1 equiv.) were mixed in acetonitrile. A solution of the appropriate silver salt (1.5 equiv.) in acetonitrile was added. The solution was stirred in the dark for one day, before a small amount of lithium chloride was added. The solution was filtered through a short plug of celite and the solvent was removed under reduced pressure. The residue was extracted with DCM, and washed several times with water, dried over anhydrous Na_2SO_4 and filtered before the solvent was removed under reduced pressure. The gold-complexes were purified by crystallization or precipitation as described for each complex.

BOX-i-Pr-Au(III)-SbF₆ The title compound was prepared as described in Method A above from (4*S*,4'*S*)-2,2'-(propane-2,2-diyl)bis(4-isopropyl-4,5-dihydrooxazole) (38 mg, 0.143 mmol), K($AuCl_4$) (53 mg, 0.140 mmol) and $AgSbF_6$ (71 mg, 0.207 mmol) in acetonitrile (10 mL). The product was purified by precipitation from acetone in DCM over night to give the product as a pale yellow powder, 30 mg (28%, 0.039 mmol), after drying. ^{1}H NMR ($(CD_3)_2CO$, 600 MHz) δ: 5.16 (dd, J = 9.7,2.9, 2H), 5.09 (dt, J = 9.2,2.8, 2H), 4.89 (t, J = 9.4, 2H), 2.52 (dhep, J = 20.9,14.0,7.0,2.6 , 2H), 1.99 (s, 6H), 0.99 (d, J = 7.0, 6H), 0.90 (d, J = 6.9, 6H); ^{13}C NMR (CD_2Cl_2), 150 MHz) δ : 174.2 (2C), 72.0 (2C), 70.7 (2C), 42.2, 30.0 (2C), 26.0 (2C), 17.8 (2C), 13.5 (2C); HRMS (APCI/ASAP, m/z): found 529.1543 (calcd. $C_{16}H_{29}N_2O_3ClAu$, 529.1532, $[M+MeO-Cl]^+$). X-ray: CCDC ID 1828159.

BOX-i-Pr -Au(III)-BF₄ The title compound was prepared as described in Method A above from (4*S*,4'*S*)-2,2'-(propane-2,2-diyl)bis(4-isopropyl-4,5-dihydrooxazole) (36 mg, 0.135 mmol), K($AuCl_4$) (57 mg, 0.151 mmol) and $AgBF_4$ (52 mg, 0.267 mmol) in acetonitrile (10 mL). The product was purified by precipitation from DCM against *n*-pentane over night to give the product as a yellow powder, 54 mg (65%, 0.087 mmol), after drying. ^{1}H NMR (CD_2Cl_2, 400 MHz) δ: 5.03 (dt, J = 8.9,3.0, 2H), 4.86-4.77 (m, 4H), 2.62 (dp, J = 13.9,6.9,2.7, 2H), 1.86 (s, 6H), 1.00 (d, J = 7.1, 6H), 0.88 (d, J = 6.8, 6H); ^{13}C NMR (CD_2Cl_2), 100 MHz) δ: 174.4 (2C), 71.8 (2C), 70.7 (2C), 42.1, 29.9 (2C), 25.6 (2C), 17.9 (2C), 13.3 (2C); HRMS (APCI/ASAP, m/z): found 525.2030 (calcd. $C_{17}H_{32}N_2O_4Au$, 525.2028, $[M+2MeO-2Cl]^+$).

BOX-Ph -Au(III)-SbF₆ The title compound was prepared as described in Method A above from (*S,S*)-2,2'-isopropylidenebis(4-phenyl-2-oxazoline) (58 mg, 0.17 mmol), K$AuCl_4$ (65 mg, 0.17 mmol) and $AgSbF_6$ (93 mg, 0.27 mmol) in acetonitrile (20 mL). The crude product was purified by precipitation from DCM against *n*-pentane to give the product as a yellow powder, 45 mg (31%, 0.053 mmol), after drying. ^{1}H NMR (CD_2Cl_2, 400 MHz) δ: 7.18-7.45 (m, 10H), 5.18 (dd, J = 10.1,7.7, 1H), 4.87-4.92 (m, 1H), 4.67 (dd, J = 10.1,8.8, 1H), 4.48 (dd, J = 12.2,11.0, 1H), 4.38 (dd, J = 12.2,4.4, 1H), 4.19 (dd, J = 8.7,7.8, 1H), 1.59 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (CD_2Cl_2, 150 MHz) δ: 172.4, 172.12, 140.4, 133.5, 130.1 (2C), 129.6 (2C), 128.6 (2C), 127.9 (2C), 126.9 (2C), 76.3, 68.8, 66.6, 59.1, 45.1, 22.9, 22.4; HRMS (APCI/ASAP, m/z): found 531.1357 (calcd. $C_{21}H_{22}N_2O_2Au$, 531.1347, $[M-Cl2]^+$).

BOX-Ph -Au(III)-Tf₂N The title compound was prepared as described in Method A above from 2,2′-isopropylidenebis[(4*S*)-4-phenyl-2-oxazoline] (58 mg, 0.17 mmol), K$AuCl_4$ (65 mg, 0.17 mmol) and $AgTf_2N$ (110 mg, 0.28 mmol) in acetonitrile (20 mL). Removal of solvent under reduced pressure gave the product as a yellow powder, 63 mg (42%, 0.071 mmol). Recrystallization was not necessary. ^{1}H NMR (CD_2Cl_2, 400 MHz) δ: 7.45-7.12 (m, 10H), 5.18 (dd, J = 10.1,7.7, 1H), 4.92-4.86 (m, 1H), 4.67 (dd, J = 10.1,8.9, 1H), 4.48 (t, J =10.9, 1H), 4.38 (dd, J = 12.2,4.5, 1H), 4.19 (t, J = 8.5, 1H), 1.59 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (CD_2Cl_2, 150 MHz) δ: 172.4, 172.1, 140.4, 133.5, 130.1 (2C), 129.6 (2C), 128.6 (2C), 127.9 (2C), 126.9 (2C), 76.3, 68.8, 66.6, 59.1, 45.1, 22.9, 22.4; HRMS (APCI/ASAP, m/z): found 531.1357 (calcd. $C_{21}H_{22}N_2O_2Au$, 531.1347, $[M-Cl2]^+$).

BOX-Ph -Au(III)-BF₄ The title compound was prepared as described in Method A above from, 2,2′-isopropylidenebis[(4S)-4-phenyl-2-oxazoline] (54 mg, 0.16 mmol), K$AuCl_4$ (66 mg, 0.17 mmol) and $AgBF_4$ (55 mg, 0.28 mmol) in acetonitrile (20 mL). The product after extraction was a yellow oil which was crystallized by slow diffusion of *n*-pentane in a DCM solution of the product, to give 61 mg (55%, 0.089 mmol) of the product as yellow crystals. ^{1}H NMR (CD_2Cl_2, 400 MHz) δ: 7.40-7.18 (m, 10H), 5.18 (dd, J = 10.2,7.9, 1H), 4.94-4.84 (m, 1H), 4.67 (dd, J = 10.1,8.7, 1H), 4.48 (dd, J = 12.2,10.9, 1H), 4.38 (dd, J = 8.2,4.6, 1H), 4.19 (dd, J = 8.6,7.8, 1H), 1.59 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (CD_2Cl_2, 150 MHz): δ: 175.6 (2C), 129.8 (4C), 128.6 (2C), 127.9 (4C), 126.7 (2C), 80.1 (2C), 69.3 (2C), 45.1, 26.1 (2C); HRMS (APCI/ASAP, m/z): found 531.1356 (calcd. $C_{21}H_{22}N_2O_2Au$, 531.1347, $[M-Cl2]^+$)**.**

BOX-i-Pr -Au(III)-BArF The title compound was prepared based on Method A above from (4*S*,4'*S*)-2,2'-(propane-2,2-diyl)bis(4-isopropyl-4,5-dihydrooxazole) (20 mg, 0.077 mmol), $AuCl_3$ (23 mg, 0.077 mmol) and NaBArF (63 mg, 0.071 mmol) in acetonitrile (10 mL). No additional purification after extracting was necessary, yielding the product as a yellow powder, 91.3 mg (85%, 0.065 mmol), after drying. ^{1}H NMR (CD_2Cl_2, 400 MHz) δ: 7.72-7.71 (m, 8H), 5.56 (s, 4H), 5.03 (dt, J = 9.2,2.9, 2H), 4.84 (dd, J = 9.7,3.3, 2H), 4.67 (t, J = 9.5, 2H), 2.57 (dp, J = 13.9,6.9,2.6, 2H), 1.81 (s, 6H), 0.99 (d, J = 7.1, 6H), 0.80 (d, J = 7.0, 6H); ^{13}C NMR (CD_2Cl_2), 100 MHz) δ: 174.8 (2C), 162.1 (q, J = 49.5, 8C), 135.2 (8C), 129.2 (q, J = 31.5, 4C), 125.0 (q, J = 272.2, 8C), 117.9 (q, J = 4.6, 4C), 71.4 (2C), 71.1 (2C), 42.6, 30.5 (2C), 26.3 (2C), 17.9 (2C), 13.6 (2C); HRMS (APCI/ASAP, m/z): found 529.1539 (calcd. $C_{16}H_{29}N_2O_3ClAu$, 529.1532, $[M+MeO-Cl]^+$)

2-Pyridyl-mentholate-Au(III) complex

2-Pyridyl-menthol ligand; (1S,2S,5R)-2-isopropyl-5-methyl-1-(pyridin-2-yl)cyclohexan-1-ol. The pyr-menth-ligand was prepared from a 1:3:6:12 equiv. mixture of menthone:pyridine: DMAE:BuLi by optimizing a literature method.[11b] DMAE (0.98 mL, 9.72 mmol) in pentane (10 mL) was added to *n*-BuLi (10 mL, 2M, 20.0 mmol) at 0 ºC. The reaction mixture was cooled to -78 ºC before pyridine (0.39 mL, 4.82 mmol) in pentane (5 mL) was added. After stirring for 1 hour, (-)-menthone (0.28 mL, 1.61 mmol) in THF (5 mL) was added dropwise over 15 minutes. The reaction mixture was stirred for 2 hours before quenching with sat. NH_4Cl (aq., 15 ml). The water phase was extracted with diethyl ether (3 x 20 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and solvent removed *in vacuum*. The crude product was purified with silica-gel column chromatography (DCM:*n*-pentane, 1:1, R_f= 0.15) to yield the product as a colorless oil, 168 mg (45%, 0.72 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.52-8.51 (m, 1H), 7.70 (td, J = 7.6,1.7, 1H), 7.35-7.33 (m, 1H), 7.18 (ddd, J = 7.32,4.9,0.9, 1H), 5.2 (br s, 1H), 2.03-1.94 (m, 1H), 1.91-1.87 (m, 1H), 1.74-1.63 (m, 3H), 1.58-1.53 (m, 1H), 1.35 (t, J = 12.3, 1H), 1.23-1.16 (m, 1H), 1.10-1.07 (m, 1H), 0.89 (d, J = 6.6, 3H), 0.83 (d, J = 6.9, 3H), 0.67 (d, J = 7.0, 3H). The ^{1}H NMR shifts are in accordance with partly characterized product previously reported.[11b]

2-Pyridyl-mentholate-Au(III). (*1R,2R,5S*)-2-Isopropyl-5-methyl-1-(pyridin-2-yl)cyclohexan-1-ol (7 mg, 0.03 mmol) was dissolved in acetonitrile (0.8 mL) and aqueous KOAc (0.03 mL, 1M, 0.03 mmol) was added. After stirring for 15 min, $K(AuCl_4)$ (11 mg, 0.03 mmol) in water (0.8 mL) was added to the reaction mixture. The mixture was stirred over night before water (2 mL) was added and extracted with DCM (3 x 1 mL). The combined organic phases were removed *in vacuum*. The product was purified by precipitation from DCM in *n*-pentane to give the pyr-menth-Au(III) complex as an orange powder, 14 mg (96%, 0.03 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2,) δ: 9.18 (dd, J = 6.1,1.2, 1H), 8.08 (td, J = 7.7,1.5, 1H), 7.55 (ddd, J = 6.1,1.5, 1H), 7.38 (dd, J = 8.1,1.5, 1H), 2.06-1.98 (m, 2H), 1.88-1.83 (m, 1H), 1.71-1.57 (m, 4H), 1.29-1.22 (m, 1H), 1.04-1.02 (m, 1H), 1.00 (d, J = 6.7, 3H), 0.91 (d, J = 6.5, 3H), 0.81 (d, J = 6.9, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2,) δ: 146.5, 142.6, 125.3, 123.8, 96.4, 54.3, 54.0, 51.4, 35.0, 29.4, 28.3, 23.8, 22.1, 21.3, 19.5; IR (neat, cm-1): 2945, 1594, 1470, 1293, 1117, 1018, 951, 769, 743, 644; HRMS (APCI/ASAP+, m/z): found 500.0823 (calcd. $C_{15}H_{23}NOCl_2Au$, 500.0822 [M+H]$^+$). X-ray: CCDC ID 1828155.

General method for cyclopropanation and in situ cis-to-trans isomerization

The propargyl ester **1** (5 mg, 1 equiv.) and vinyl derivative **2** (4 equiv.) was dissolved in *d*-DCM (0.6 mL) and added the gold-catalyst (1 or 5 mol%) dissolved in *d*-DCM. The reaction progress was monitored by ^{1}H NMR every 2 min for the first 20 minutes, and then at 30 minutes, 1 h, 2 h, 3 h, 5 h, 8 h, 24 h. The results are presented in Table 1.

General method B for preparation of cis-isomers

The propargyl ester (1 equiv.) and the vinyl derivative (4 equiv.) was dissolved in DCM before JohnPhos Au(MeCN)SbF6 (0.05 equiv.) dissolved in DCM was added. The reaction mixture was stirred at r.t. for 5-60 min, before the reaction was quenched with triethylamine. The solvent was removed in vacuum, before the crude oil was purified directly by silica-gel column chromatography to give *cis* isomer below in 64-98% yield. Samples of >99% pure *cis* isomer were further prepared by flash chromatography for *cis*-to-*trans* isomerization studies.

***Cis-(Z)*-2-(4-methoxyphenyl)-1-(2-phenylcyclopropyl)vinyl pivalate (3a).** Compound **3a** was prepared as described in Method B above, starting with propargyl ester **1a** (28 mg, 0.114 mmol), styrene **2a** (51 mg, 0.490 mmol) and JohnPhos Au(MeCN)SbF_6 (5 mg, 0.006 mmol). The crude oil was purified by silica-gel column chromatography (*n*-pentane:EtOAc, 10:1, R_f = 0.11), affording 26 mg (64%, 0.073 mmol, 96:4 *cis*:*trans*-ratio) of **3a** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23-7.15 (m, 5H), 7.05 (d, J = 8.9, 2H), 6.73 (d, J = 8.9, 2H), 5.91 (s, 1H), 3.75 (s, 3H), 2.38-2.28 (m, 2H), 1.38-1-32 (m, 1H), 1.30-1.25 (m, 1H), 1.09 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.0, 158.4, 145.5, 138.4, 129.7 (2C), 128.2 (2C), 127.8 (2C), 126.9, 126.0, 118.4, 113.4 (2C), 55.2, 38.8, 27.0 (3C), 23.6, 23.0, 11.3; IR (neat, cm^{-1}): 2968, 2836, 1737, 1606, 1509, 1247, 1120, 1030, 825, 698; HRMS (ASAP+, m/z): found 350.1878 (calcd. $C_{23}H_{26}O_3$, 350.1882 [M*+]).

Cis-(Z)-2-(4-methoxyphenyl)-1-(2-(4-methoxyphenyl)cyclopropyl)vinyl pivalate (3b). Compound **3b** was prepared as described in Method B above, starting with propargyl ester **1a** (27 mg, 0.110 mmol), 1-methoxy-4-vinylbenzene **2b** (66 mg, 0.489 mmol) and JohnPhos Au(MeCN)SbF_6 (4 mg, 0.006 mmol). The crude oil was purified by silica-gel column chromatography (*n*-pentane:EtOAc, 10:1, R_f = 0.14). This gave the 33 mg (79%, 0.087 mmol, 98:2 *cis*:*trans*-ratio) of **3b** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.11 (d, J = 8.7, 2H), 7.06 (d, J = 8.8, 2H), 6.78 (d, J = 8.8, 2H), 6.74 (d, J = 8.9, 2H), 5.88 (s, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 2.27 (d, J = 6.2, 1H), 2.25 (d, J = 6.4, 1H), 1.34-1.28 (m, 1H), 1.19 (q, J = 6.2,5.6, 1H), 1.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.1, 158.4, 158.0, 145.7, 130.3, 129.7 (2C), 129.3 (2C), 127.0, 118.1, 113.4 (2C), 113.3 (2C), 55.3, 55.2, 38.9, 27.1 (3C), 23.1, 22.4, 11.1; IR (neat, cm^{-1}): 3334, 2947, 2899, 1396, 1181, 1144, 1118, 999, 800; HRMS (ASAP+, m/z): found 380.1988 (calcd. $C_{24}H_{28}O_4$, 380.1983 [M*+]).

***Cis- (Z)*-2-(4-methoxyphenyl)-1-(2-(4-(trifluoromethyl)phenyl)cyclopropyl)vinyl pivalate (3c).** Compound **3c** was prepared as described in Method B above, starting with propargyl ester **1a** (28 mg, 0.106 mmol), 1-(trifluoromethyl)-4-vinylbenzene **2c** (54 mg, 0.406 mmol) and JohnPhos Au(MeCN)SbF_6 (3 mg, 0.004 mmol). The crude oil was purified by silica-gel column chromatography (*n*-pentane:EtOAc, 10:1, R_f = 0.14). This gave the 32 mg (72%, 0.076 mmol, 98:2 *cis*:*trans*-ratio) of **3c** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.51 (d, J = 8.2, 2H), 7.31 (d, J = 8.2, 2H), 7.08 (d, J = 8.8, 2H), 6.78 (d, J = 8.8, 2H), 5.98 (s, 1H), 3.79 (s, 3H), 2.50-2.46 (m, 1H), 2.38-2.34 (m, 1H), 1.48-1.44 (m, 1H), 1.34 (q, J=6.1,5.9, 1H), 1.10 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 175.9, 158.7, 144.7, 143.0, 129.7 (2C), 128.3 (2C), 128.2 (q, J = 32.3), 126.5, 124.6 (q, J=3.5, 2C), 124.4 (q, J = 271.3), 119.0, 113.6 (2C), 55.2, 38.8, 27.0 (3C), 24.3, 22.8, 12.1; IR (neat, cm^{-1}): 2975, 1742, 1512, 1327,

1252, 1123, 844; HRMS (ASAP+, m/z): found 418.1756 (calcd. $C_{24}H_{25}O_3F_3$, 418.1750 [M*+]).

***Cis-(Z)*-2-(4-methoxyphenyl)-1-(2-phenylcyclopropyl)vinyl acetate (3d).** Compound **3d** was prepared as described in Method B above, starting with propargyl ester **1b** (30 mg, 0.147 mmol), styrene **2a** (61 mg, 0.588 mmol) and JohnPhos Au(MeCN)SbF_6 (6 mg, 0.008 mmol). The crude oil was purified by silica-gel column chromatography (*n*-pentane:EtOAc, 10:1, R_f = 0.15). This gave the 36 mg (79%, 0.117 mmol, 90:10 *cis*:*trans*-ratio) of **3d** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.24-7.19 (m, 4H), 7.17-7.15 (m, 1H), 7.07 (d, J = 8.6, 2H), 6.75 (d, J = 8.9, 2H), 5.83 (s, 1H), 3.76 (s, 3H), 2.37-2.30 (m, 2H), 3.03 (s, 3H), 1.38-1.34 (m, 1H), 1.31-1.29 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 168.7, 158.5, 145.2, 138.2, 129.5 (2C), 128.4 (2C), 127.8 (2C), 126.9, 126.0, 117.9, 113.7 (2C), 55.2, 23.7, 23.5, 21.0, 11.0; IR (neat, cm^1): 3027, 2932, 2836, 1749, 1606, 1509, 1366, 1248, 1201, 1147, 1029, 833, 699; HRMS (APCI/ASAP, m/z): found 249.1274 (calcd. $C_{18}H_{17}O$, 249.1279, [M-CH_3CO-H_2O+H].

***Cis-(Z)*-1-(2-phenylcyclopropyl)-2-(4-(trifluoromethyl)phenyl)vinyl pivalate (3f).** Compound **3f** was prepared as described in Method B above, starting with propargyl ester **1c** (19 mg, 0.07 mmol), styrene **2a** (29 mg, 0.28 mmol) and JohnPhos gold-catalyst (3 mg, 0.004 mmol). The crude product purified by silica-gel column chromatography (10:1, *n*-pentan:EtOAc, R_f = 0.14). This gave 3.8 mg (14 %, 0.01 mmol) of pure *cis*-**3f**. ^{1}H NMR (CD_2Cl_2, 600 MHz): δ = 7.45-7.17 (m, 9H), 5.95 (s, 1H), 2.43-2.31 (m, 2H), 1.42-1.34 (m, 2H), 1.09 (s, 9H); ^{13}C NMR (CD_2Cl_2, 150 MHz) δ: 175.8, 148.8, 137.8, 129.9, 128.7 (q, J = 32.2), 128.5, (2C), 128.3 (2C), 127.8 (2C), 126.8, 124.9 (q, J = 3.7, 2C), 123.7 (q, J = 272.3), 117.5, 38.9, 26.9 (3C), 23.4 (2C), 11.0; IR (neat, cm^{-1}): 2927, 2930, 1744, 1324, 1122, 1067, 699; HRMS (APCI/ASAP, m/z): found 389.1721 (calcd. $C_{23}H_{24}O_2F_3$, 389.1728, [M+H]$^+$).

***Cis-(Z)*-1-(2-(1,3-dioxoisoindolin-2-yl)cyclopropyl)-2-(4-methoxyphenyl)vinyl pivalate (4a).** Compound **4a** was prepared as described in Method B above, starting with propargyl ester **1a** (21 mg, 0.085 mmol), N-Vinylphthalimide **2'a** (48 mg, 0.277 mmol) and JohnPhos Au(MeCN)SbF_6 (5 mg, 0.006 mmol). The crude oil was purified by silica-gel column chromatography (*n*-pentane:EtOAc, 10:1, R_f = 0.06). This gave the 33 mg (92%, 0.079 mmol, 99:1 *cis*:*trans*-ratio) of **4a** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (dd, J = 5.5,3.1, 2H), 7.67 (dd, J = 5.4,3.0, 2H), 7.05 (ap. d, J = 8.9, 2H), 6.68 (ap. d, J = 8.9, 2H), 6.02 (s, 1H), 3.72 (s, 3H), 3.07-3.03 (m, 1H), 2.26-2.22 (m, 1H), 2.12-2.07 (m, 1H), 1.52-1.46 (m, 1H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.0, 168.8 (2C), 158.5, 143.2, 134.0 (2C), 131.7 (2C), 129.6 (2C), 126.6, 123.1 (2C), 118.1, 113.4 (2C), 55.1, 39.0, 28.4, 27.1 (3C), 21.2, 8.3 ; IR (neat, cm^{-1}): 2972, 1716, 1512, 1395, 1250, 1119, 723; HRMS (APCI/ASAP, m/z): found 419.1719 (calcd. $C_{25}H_{25}NO_5$, 419.1733, [M*+].

***Cis-2-methyl-1-(2-phenylcyclopropyl)prop-1-en-1-yl acetate* (5).**[4q] Compound **5** was prepared as described in Method B above, starting with propargyl ester **1c** (27 mg, 0.085 mmol), styrene **2a** (75 mg, 0.716 mmol) and JohnPhos Au(MeCN)SbF_6 (8.7 mg, 0.011 mmol). The crude oil was purified by silica-gel column chromatography (*n*-pentane:EtOAc, 10:1, R_f = 0.35). This gave 21 mg (41%, 0.091 mmol, 95:5 *cis*:*trans*-ratio) of **5** as a colorless oil. The spectroscopic data corresponds with that reported previously.[4q]

General method C for preparation of trans-isomers.

The propargyl ester (1 equiv.) and the vinyl derivative (4 equiv.) was dissolved in DCM before BOX-Au(III)-X (0.05 equiv.) dissolved in DCM was added. The reaction mixture was stirred at r.t. for 15 min - 23 h, before the solvent was removed in vacuum. The crude oil was purified directly by silica-gel column chromatography.

***Trans-(Z)*-2-(4-methoxyphenyl)-1-(2-phenylcyclopropyl)vinyl pivalate (3a).** Compound **3a** was prepared as described in Method C above, starting with propargyl ester 1a (25 mg, 0.101 mmol), styrene 2a (54 mg, 0.522 mmol) and BOX-*i*-Pr-Au(III)SbF_6 (3 mg, 0.004 mmol). The crude oil was purified by silica-gel column chromatography (n-pentane:EtOAc, 10:1, Rf = 0.13). This gave the 27 mg (76%, 0.077 mmol, 1:99 cis:trans-ratio) of 3a as a colorless oil. ^{1}H NMR (400 MHz, CDCl3) δ: 7.29-7.25 (m, 4H), 7.17 (dt, J = 7.4,1.2, 1H), 7.12-7.10 (m, 2H), 6.83-6.80 (m, 2H), 6.07 (s, 1H), 3.79 (s, 3H), 2.22 (m, 1H), 1.99-1.94 (m, 1H), 1.32-1.20 (m, 2H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, CDCl3) δ: 175.9, 158.5, 147.4, 141.6, 129.6 (2C), 128.4 (2C), 127.0, 126.1 (2C), 125.9, 115.2, 113.6 (2C), 55.2, 39.1, 27.2 (3C), 26.7, 24.0, 14.5; IR (neat, cm-1): 2968, 2836, 1737, 1606, 1509, 1247, 1120, 1030, 825, 698; HRMS (ASAP+, m/z): found 350.1875 (calcd. C23H26O3, 350.1882, [M•]+).

***Trans*-(Z)-2-(4-methoxyphenyl)-1-(2-phenylcyclopropyl)vinyl acetate (3d).** Compound **3d** was prepared as described in Method C above, starting with propargyl ester **1b** (20 mg, 0.098 mmol), styrene **2a** (41 mg, 0.392 mmol) and BOX-Ph-Au(III)BF_4 (4 mg, 0.005 mmol). The crude oil was purified by silica-gel column chromatography (*n*-pentane:EtOAc, 10:1, R_f = 0.21). This gave the 19 mg (63%, 0.062 mmol, 6:94 *cis*:*trans*-ratio) of **3d** as a colorless oil.^{1}H NMR (CD_2Cl_2, 600 MHz) δ: 7.22 (d, J = 8.6, 2H) , 7.17 (d, J = 7.8, 2H), 7.09-7.06 (m, 1H) , 7.03 (ap. d, J = 7.9, 2H), 6.75 (d, J = 7.1 Hz, 2H) , 5.93 (s, 1H) , 3.70 (s, 3H), 2.13-2.10 (m, 1H), 2.09 (s, 3H), 1.85-1.82 (m, 1H), 1.26-1.23 (m, 1H), 1.18-1.14 (m, 1H); ^{13}C NMR (CD_2Cl_2, 150 MHz) δ: 168.4, 158.7, 147.3, 141.7, 129.2 (2C), 128.3 (2C), 127.0 (2C), 125.9 (2C), 114.3, 113.9 (2C), 55.1, 26.8, 24.1, 20.9, 14.5; IR (neat, cm^{-1}): 3028, 2933, 2836, 1749, 1606, 1509, 1366, 1248, 1201, 1147, 1029, 833, 699. HRMS (APCI/ASAP, m/z): found 249.1275 (calcd. $C_{18}H_{17}O$, 350.1882, [M-CH_3CO-H_2O+H]).

***Trans-(Z)*-1-(2-phenylcyclopropyl)-2-(4-(trifluoromethyl)phenyl)vinyl pivalate (3f).** Compound **3f** was prepared as described in Method C above, starting with propargyl ester **1d** (20 mg, 0.070 mmol), styrene **2a** (29 mg, 0.281 mmol) and BOX-Ph-Au(III)Tf_2N (3 mg, 0.004 mmol). The product was purified by silica-gel column chromatography (10:1, *n*-pentane:EtOAc, R_f = 0.15), which gave 22 mg (98 %, 0.075 mmol, 15:85 *cis*:*trans*-ratio) of product **3f.** ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.56 (d, J = 8.3, 2H), 7.45 (d, J = 8.3, 2H), 7.18-7.14 (m, 3H), 7.03-7.00 (m, 2H), 6.25 (s, 1H), 2.54-2.42 (m, 2H), 1.40-1.36 (m, 1H), 1.18 (s, 9H), 1.16-

1.12 (m, 1H); ^{13}C NMR (CD_2Cl_2, 150 MHz): δ: 176.7, 149.0, 137.7, 129.1, 128.9 (2C), 128.6 (q, J = 32.3), 127.8 (2C), 127.7 (2C), 126.0, 124.9 (q, J = 3.3, 2C), 124.3 (q, J = 272.0), 120.4, 38.9, 27.0 (3C), 25.0, 22.0, 12.3; IR (neat, cm^{-1}): 2927, 2930, 1744, 1324, 1122, 1067, 699; HRMS (APCI/ASAP, m/z): found 389.1723 (calcd. $C_{23}H_{24}O_2F_3$, 389.1728, $[M+H]^+$).

***Trans-(Z)*-1-(2-((N,4-dimethylphenyl)sulfonamido)cyclopropyl)-2-(4-methoxyphenyl)vinyl pivalate (4b).** Compound **4b** was prepared as described in Method C above starting with propargyl ester **1a** (23 mg, 0.093 mmol), N,4-dimethyl-N-vinylbenzenesulfonamide **2'b** (66 mg, 0.312 mmol) and BOX-*i*-Pr-Au(III)SbF_6 (2.5 mg, 0.003 mmol). The reaction was stirred for 5 min before the solvent was removed *in vacuum.* The crude oil was purified by silica-gel column chromatography (*n*-pentane:EtOAc, 10:1, R_f = 0.09). This gave the 38 mg (75%, 0.083 mmol, <1:>99 *cis*:*trans*-ratio) of **4b** as a colorless oil. ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 7.44 (d, J = 8.3, 2H), 7.17 (d, J = 7.8, 2H), 6.90 (ap. d, J = 8.5, 2H), 6.77 (ap. d, J = 8.7, 2H), 5.42 (q, J = 4.3,2.8, 1H), 4.59 (dt, J = 8.7,5.5, 1H), 3.89-3.87 (m, 1H), 3.79 (s, 3H), 2.88 (2, 3H), 2.54 (ddt, J = 16.7,5.4,2.5, 1H), 2.39 (s, 3H), 2.17 (ddt, J = 16.7,5.4,2.2, 1H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ: 175.7, 158.8, 150.4, 143.1, 136.6, 131.7, 129.5 (2C), 129.0 (2C), 126.9 (2C), 113.8 (2C), 112.0, 63.8, 55.2, 51.3, 38.6, 30.7, 29.0, 26.4 (3C), 21.2 ; IR (neat, cm^{-1}): 2973, 2936, 1746, 1512, 1341, 1247, 1180, 1157, 1116; HRMS (ASAP+, m/z): found 457.1924 (calcd. $C_{25}H_{31}NO_5S$ 457.1923 $[M^*+]$).

Minor amounts of pure *trans* **3b** and *trans* **3c** were purified by flash chromatography (*n*-pentane:EtOAc, 10:1) from diastereomeric mixtures for NMR and HRMS characterization:

***Trans-(Z)*-2-(4-methoxyphenyl)-1-(2-(4-methoxyphenyl)cyclopropyl)vinyl pivalate (3b**). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (ap. d, J = 8.9, 2H), 7.05 (ap. d, J = 8.5, 2H), 6.81 (dd, J = 7.9,1.7, 4H), 6.06 (s, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 2.17-2.12 (m, 1H), 1.91-1.81 (m, 1H), 1.26 (s, 9H), 1.24-1.22 (m, 1H), 1.18-1.13 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.9, 158.5, 158.0, 147.6, 133.5, 129.6 (2C), 127.2 (2C), 127.1, 114.9, 113.8 (2C), 113.6 (2C), 55.3, 55.2, 39.1, 27.2 (3C), 26.2, 23.3, 14.1; IR (neat, cm^{-1}): 3334, 2947, 2899, 1396, 1181, 1144, 1118, 999, 800; HRMS (ASAP+, m/z): found 380.1983 (calcd. $C_{24}H_{28}O_4$ 380.1988 $[M^*+]$).

***Trans-((Z)*-2-(4-methoxyphenyl)-1-(2-(4-(trifluoromethyl)phenyl)cyclopropyl)vinyl pivalate (3c).** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (d, J = 8.2, 2H), 7.28 (d, J = 8.6, 2H), 7.20 (d, J = 8.2, 2H), 6.82 (d, J = 8.8, 2H), 6.08 (s, 1H), 3.01 (s, 3H), 2.26-2.21 (m, 1H), 2.03-1.98 (m, 1H), 1.41-1.36 (m, 1H), 1.32-1.27 (m, 1H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.9, 158.7, 146.7, 145.9, 129.6 (2C), 128.2 (q, J = 32.9), 126.8, 126.2 (2C), 125.3 (q, J = 4.1, 2C), 124.3 (q, J = 271.3), 115.6, 113.7 (2C), 55.2, 39.1, 27.3, 27.2 (3C), 23.9, 15.0; IR (neat, cm^{-1}): 2975, 1742, 1512, 1327, 1252, 1123, 844; HRMS (ASAP+, m/z): found 418.1749 (calcd. $C_{24}H_{25}O_3F_3$ 418.1756 $[M^*+]$).

General procedure for separate cis-to-trans isomerization studies

Isolated *cis*-product (5 mg, 1 equiv.) was dissolved in *d*-DCM (0.6 mL) and added the gold-catalyst (1 or 5 mol%) dissolved in *d*-DCM. The reaction progress was monitored by ^{1}H NMR every 2 min for the first 20 minutes, and then at 30 minutes, 1 hour, 2 hours, 3 hours, 5 hours, 8 hours, 24 hours, 48 hours and 72 hours after the gold-catalyst was added. Some reactions were quenched earlier, dependent on the reactivity of the catalyst. The results are presented in Table 3.

Keywords: BOX-Au(III) catalysts; stereoselective propargyl cyclopropanation; *cis*-to-*trans* isomerization

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Entry for Table of Content

FULL PAPER

Gold(III)-catalysed *cis*-to-*trans* cyclopropyl isomerization

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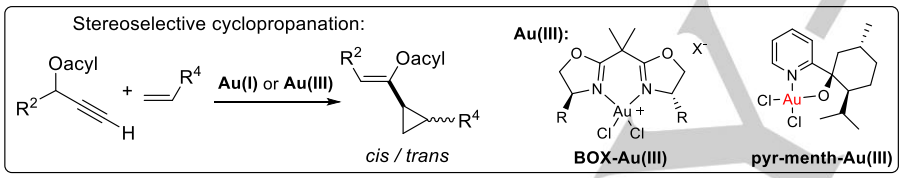

The strong ability of BOX-Au(III) catalysts for combined fast propargyl cyclopropanation and subsequent in situ *cis*-to-*trans* isomerization is reported. Au(I) or Au(III) catalysts selectively provided pure *cis* or *trans* products, respectively, and isolated *cis* isomers were shown to rapidly isomerize into *trans* products in the presence of BOX-Au(III) catalysts.

Key topic:

Au(III) catalysed cyclopropyl isomerization