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Gold(I)-Catalyzed Asymmetric Cyclopropenation of Internal Alkynes

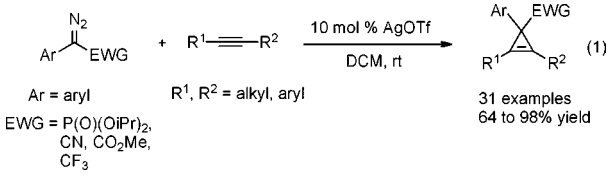
John F. Briones and Huw M. L. Davies*

Department of Chemistry, Emory University, 1515 Dickey Drive, Atlanta, Georgia 30322, United States

Supporting Information

ABSTRACT: Highly enantioselective cyclopropenation of internal alkynes with aryldiazoacetates was achieved using the binuclear gold catalyst (*S*)-xylylBINAP(AuCl)$_2$, activated by silver hexafluoroantimonate.

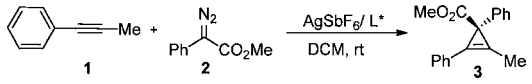
Cyclopropenes have broad utility as synthons in organic synthesis.[1] Therefore, considerable effort has been placed in developing new methods for their synthesis.[2] One of the most effective ways for their preparation in a stereoselective manner is the metal-catalyzed cyclopropenation of alkynes by diazo compounds.[3] The enantioselective cyclopropenation of terminal alkynes with dirhodium(II) catalysts is well established[4] and good results were recently obtained with chiral Co(II) and Ir(II) catalysts.[5] Despite these notable advances, extending asymmetric cyclopropenation reactions to internal alkynes has been challenging.[6] Only one report on the enantioselective cyclopropenation of internal alkynes has been published and the observed levels of enantioinduction were low (below 20% ee).[4a] Recently, our group reported an effective method for the synthesis of racemic, highly substituted cyclopropenes from the reaction of internal alkynes using silver triflate (AgOTf) as a catalyst (eq 1).[7] Aryldiazoacetates



are the optimum carbenoid precursors for this chemistry. The resulting silver-bound donor/acceptor carbenoids offer complementary reactivity to the established rhodium carbenoids in that they display increased electrophilicity and are less sterically demanding than their rhodium counterparts.[8] Given the recent demonstrations that the silver carbenoids of donor/acceptor-substituted diazo compounds have broad synthetic potential,[7,8] we have initiated a program to identify enantioselective variants of this chemistry. In this paper we describe our studies, which led to the discovery that chiral digold catalysts display similar reactivity to the achiral silver catalysts, leading to the highly enantioselective cyclopropenation of internal alkynes by donor/acceptor carbenoids.

Our exploratory studies began using 1-phenyl-1-propyne **1** and methyl phenyldiazoacetate **2** as suitable test substrates. We initially examined different chiral ligands generally employed with silver(I) catalysts in Lewis acid mediated C−C bond forming reactions.[9] Oxazoline-based ligands **4** and **5** (entries 1−3) gave poor levels of enantioinduction (up to 18% ee with Ag(I)/PHOX complex) (Table 1).[10,11] When the PyBOX ligand **6** was used, diazo decomposition did not occur. The phosphoramidite ligand MonoPhos (**7**) provided the cyclopropene product in good yield and 7% ee (entry 4).[12] Silver hexafluoroantimonate/brucine complex also provided the cyclopropene in good yield but no asymmetric induction (entry 5).[13] We then used chiral phosphine-based ligands **8** and **9** for the cyclopropenation reaction (entries 6−7). These ligands are one of the more generally used ligands for chiral silver catalysis and have been shown to create excellent asymmetric environments around the silver center.[14] Silver(I)−phosphine chiral complexes have been shown to be effective in promoting a variety of carbon−carbon bond forming reactions such as asymmetric allylation, Mannich-type reactions, aldol reactions, hetero Diels−Alder reactions, and 1,3-dipolar cycloadditions.[15] However, poor levels of enantioinduction were obtained in the cyclopropenation using (*S*)-tolBINAP (**8**) and (*R*)-DTBM-SEGPHOS (**9**) as ligands (17% and <5% ee).

Table 1. Ag(I)-Catalyzed Cyclopropenation of 1 Using Various Chiral Ligands[a]



entry	ligand	mol % Ag	mol % L*	yield, %[b]	ee, %[c]
1	tBuBOX	13	14	74	<5
2	pyBOX	13	14	NR	—
3	PHOX	10	12	79	18
4	MonoPhos	10	41	86	7
5	Brucine	5	6	42	<5
6	(*S*)-Tol-BINAP	10	12	81	17
7	(*R*)-DTBM-SEGPHOS	10	12	70	<5

[a]Standard reaction conditions: **2** (0.5 mmol, 1.0 equiv) in degassed dichloromethane (8 mL) was added to a 2 mL dichloromethane solution of **1** (2.5 mmol, 5.0 equiv), $AgSbF_6$ and ligand at 23 °C. [b]Isolated yield of **3**. [c]Determined by chiral HPLC.

Because of the disappointing results obtained using silver catalysts, we turned our attention to the use of chiral gold catalysts. Previous reports involving gold-catalyzed reactions of diazo compounds have been limited to the use of achiral gold complexes, primarily with ethyl diazoacetate as the carbenoid source.[16,17] Our studies focused on the use of Au(I) catalysts, containing various BINAP-type ligands which have been popularized by Toste and co-workers (Figure 2).[18] These Au(I) catalysts have been found to promote effectively a variety

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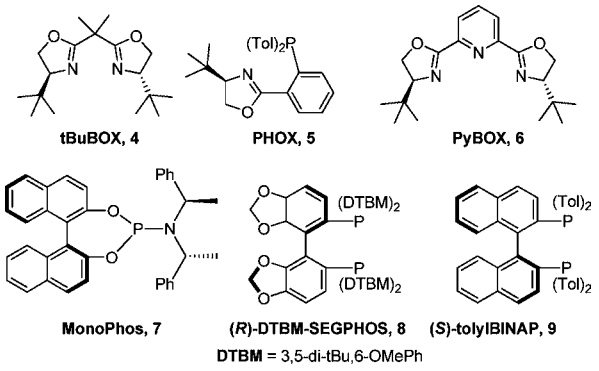


Figure 1. Chiral ligands for Ag(I)-catalyzed transformations.

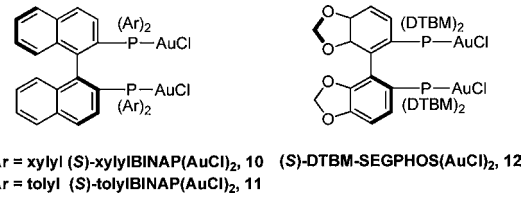
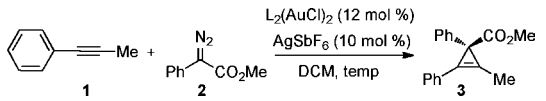


Figure 2. Structure of digold complexes.

Table 2. Cyclopropenation of 1 with 2 Using Various Au(I) Chiral Complexes[a]



entry	Au(I)	temp (°C)	% yield[b]	% ee[c]
1	(*S*)-tolBINAP(AuCl)$_2$	23	69	87
2	(*S*)-tolBINAP(AuCl)$_2$	0	74	92
3	(*S*)-xylylBINAP(AuCl)2	0	81	93
4	(*S*)-DTBMSEGPHOS(AuCl)$_2$	0	40	−91
5	(*S*)-BINAP(AuCl)$_2$	0	62	92
6	(*S*)-MONOPHOS(AuCl)	0	16	−14
7[d]	(*S*)-xylylBINAP(AuCl)$_2$	0	64	94
8[e]	(*S*)-xylylBINAP(AuCl)$_2$	23	0	0

[a]Standard reaction conditions: **2** (0.5 mmol, 1.0 equiv) in degassed dichloromethane (8 mL) was added to a 2 mL dichloromethane solution of **1** (2.5 mmol, 5.0 equiv), $AgSbF_6$ and Au(I) catalyst at specified temp (°C). [b]Isolated yield of **3**. [c]Determined by chiral HPLC. [d]Reaction was conducted under standard conditions except 1.25 mol % of $AgSbF_6$ and 1.5 mol % of Au(I) catalyst were used. [e]Reaction was conducted under standard conditions except no $AgSbF_6$ was added.

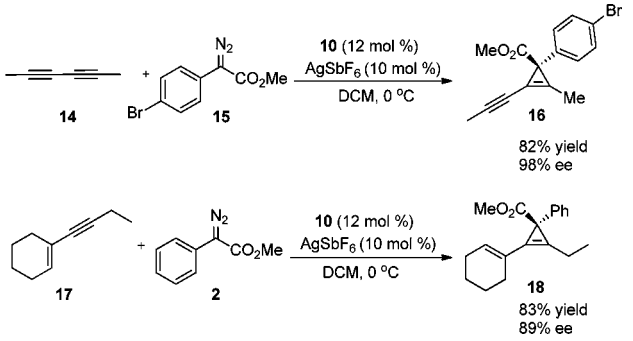
of alkyne and allene transformations.[18] However, we have seen no examples of the use of these catalysts for the reactions of diazo compounds. It became immediately apparent that digold complexes when activated by $AgSbF_6$ are excellent catalysts for asymmetric cyclopropenation with donor/acceptor carbenoids. Cyclopropenation of **1** with **2** using different Au(I) catalysts bearing the BINAP ligands provided the cyclopropene **3** with very high levels of enantioinduction (up to 93% ee with (*S*)-xylylBINAP(AuCl)$_2$ (**10**), entry 3) (Table 2). In contrast to the results with the chiral digold complexes, mononuclear Au(I) catalyst with (*S*)-MonoPhos (**7**) (entry 6) provided the cyclopropene product in very poor yield and enantioselectivity (16% yield, 14% ee). A very similar level of enantioselectivity was obtained when 1.5 mol % of the digold complex was used (entry 7). No reaction was observed in the absence of $AgSbF_6$

Table 3. Au(I)-Catalyzed Asymmetric Cyclopropenation of Disubstituted Alkynes[a]

entry	product	R_1	R_2	% yield[b]	% ee[c]
1	**13a**	H	Me	81	93
2	**13b**	H	Et	68	90
3	**13c**	H	*i*Bu	70	94
4	**13d**	H	Cy	83	86
5	**13e**	H	*n*Bu	72	90
6	**13f**	H	CH_2OTBS	62	98
7	**13g**	H	CH_2Cy	78	92
8	**13h**	H	CH_2CHCH_2	58	96
g	**13i**	*p*-Br	*n*Bu	76	89
10	**13j**	*o*-Me	*n*Bu	75	93

[a]Standard reaction conditions: Same as Table 2. [b]Isolated yield of **13a−j**. [c]Determined by chiral HPLC.

Scheme 1. Au(I)-Catalyzed Cyclopropenation of Electronically Activated Alkyl Alkynes



(entry 8). The levels of enantioselectivity does not vary over a range from 0.5 to 2.0 ratio of (*S*)-xylylBINAP(AuCl)$_2$/$AgSbF_6$ (see Supporting Information).

The scope of the cyclopropenation reaction with various disubstituted alkynes was explored using (*S*)-xylylBINAP-(AuCl)$_2$ (**10**) (12 mol %) activated by $AgSbF_6$ (10 mol %). The reaction proved to be applicable to a wide range of 1-arylalkynes and the desired cyclopropenes were obtained in moderate to good yields and with excellent levels of enantioinduction (Table 3). The absolute configuration of the cyclopropene **13a** was assigned unambiguously by X-ray crystallographic analysis.[19] The absolute configuration of the other cyclopropene products was assigned by analogy to **13a**.

In general, 1,2-dialkyl alkynes gave poor yields of the desired cyclopropene products. Electronically activated systems, however, such as in the case of diyne **14** and enyne **17**, provided the desired cyclopropene products **16** and **18**, respectively, in good yields and with excellent levels of enantioinduction (Scheme 1).

For the majority of substrates, the chiral gold(I)-complex provided similar types of products to the achiral silver(I)-catalyzed reactions, although a few exceptions were found. An unexpected result was observed in the gold-catalyzed cyclopropenation of 1,2-diaryl alkynes (Scheme 2), even though these substrates provide the desired cyclopropene products under silver catalysis.[7] The use of alkyne **19** as substrate in a gold catalyzed reaction gave a complex mixture and the major

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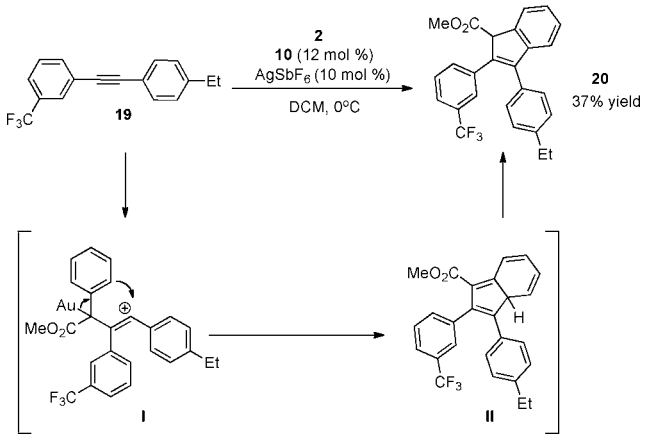
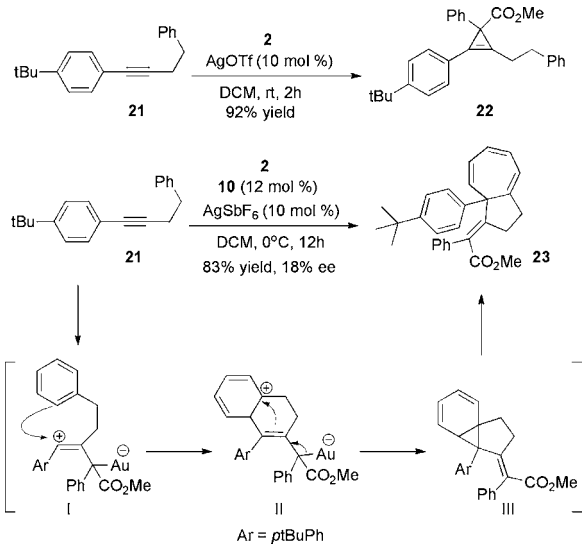
Scheme 2. Au(I)-Catalyzed Reaction of 1,2-Diarylalkyne 19



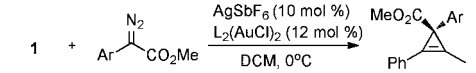
Scheme 3. Au(I)-Catalyzed Cyclopropenation of Electronically Activated Alkyl Alkynes

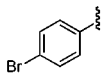
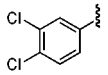
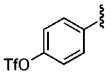
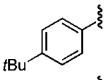
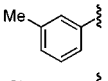
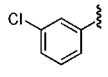
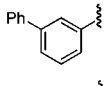
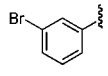


product was the indene derivative **20**, obtained in 37% yield. The structure of **20** was confirmed by X-ray crystallographic analysis.[19] This product is probably derived from the initial attack of the alkyne at the gold carbenoid leading to the cationic species **I**. Electrophilic attack of the aryl ring to the vinyl cation **I** and subsequent release of the gold catalyst leads to structure **II**. This intermediate can then undergo 1,5-sigmatropic rearrangements to afford the indene product. The formation of indenes from reaction of aryldiazoacetates and terminal alkynes has been previously observed when achiral copper catalysts were used.[20]

Another interesting transformation showcasing the high electrophilic character of the Au(I) carbenoid was observed when the aryl alkyne **21** was used as substrate for the cyclopropenation reaction (Scheme 3). Instead of formation of the expected cyclopropene product **22** (which was obtained in 92% yield with AgOTf), the bicyclic product **23** was generated in 83% yield. The alkyne is considered to attack the metal carbenoid to form the ionic species **I**. The pendant aromatic ring then attacks the vinyl cation to form the bicyclic intermediate **II** which then rearranges to norcaradiene **III**. The diene undergoes a 6π electrocyclic ring-opening to afford the cycloheptatriene derivative **23**. NOE studies were

Table 4. Au(I)-Catalyzed Cyclopropenation of 1 Using Various Aryl Diazoacetates[a]



entry	Ar	$L_2(AuCl)_2$	product	% yield[b]	% ee[c]
1		**10**	**24a**	88	89
		12	**24a**	60	95
2		**10**	**24b**	88	87
		12	**24b**	79	97
3		**10**	**24c**	86	84
		12	**24c**	65	95
4		**10**	**24d**	62	85
5		**10**	**24e**	62	84
6		**10**	**24f**	71	92
7		**10**	**24g**	77	95
8		**10**	**24h**	70	95
9		**10**	**24i**	66	97

[a]Standard reaction conditions: Same as Table 2 [b]Isolated yield of **24a–i**. [c]Determined by chiral HPLC.

conducted to confirm the regiochemistry of the product. The chiral influence of the catalyst was lost during the transformation affording the product in only 18% ee.

Various aryldiazoacetates were also screened for the cyclopropenation reaction using 1-phenyl-1-propyne **1** as the representative alkyne trap (Table 4). Cyclopropene products **24a–i** were obtained in moderate to good yields with excellent levels of enantioinduction when (*S*)-xylylBINAP(AuCl)$_2$ (**10**) was used as catalyst. The reaction is compatible with aryl halides and aryl triflates. For entries 1–3, the enantioinduction can be improved further by using (*S*)-DTBM-SEGPHOS-(AuCl)$_2$ (**12**) as the catalyst. The absolute configuration of cyclopropene **24a** was confirmed by X-ray crystallographic analysis.[19]

In summary, these studies reveal that chiral digold cationic complexes are capable of high asymmetric induction in the cyclopropenation of internal alkynes by donor/acceptor carbenoids.[21] The reactivity of the gold carbenoids is similar to the silver carbenoids. Most notably, the gold carbenoids have a very different reactivity profile compared to the corresponding rhodium carbenoids, and are much less susceptible to steric interference. Therefore, we anticipate that the chiral gold catalysts will open up new synthetic opportunities for donor/acceptor carbenoids. Further studies are in progress to explore the range of the new synthetic opportunities of gold-stabilized donor/acceptor carbenoids and to determine the actual structure of the chiral catalysts involved in this chemistry.

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■ ASSOCIATED CONTENT

Supporting Information

Synthetic details and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

hmdavie@emory.edu

Notes

The authors declare no competing financial interest.

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(21) At this stage, the exact structure of the active catalyst has not been determined. It is well known that the role of combining a silver salt with a gold chloride pre-catalyst can be more significant than simply removal of the halide and generation of a gold cation catalyst. For further discussions, see: Wang, D.; Cai, R.; Sharma, S.; Jirak, J.; Thummanapelli, S. K.; Akhmedov, N. G.; Zhang, H.; Liu, X.; Petersen, J. L.; Shi, X. *J. Am. Chem. Soc.* **2012**, *134*, 9012−9019. In our case, on mixing the $P_2Au_2Cl_2$ complex with $AgSbF_6$, a persistent $P_2Au_2AgCl_2$ complex is observed by mass spectrometry, suggesting the possibility that a mixed gold−silver complex may be involved in the catalysis (see Supporting Information for details).

■ NOTE ADDED AFTER ASAP PUBLICATION

The version published ASAP July 9, 2012 contained errors in Tables 2 and 3 and Scheme 2. They were corrected and this reposted July 12, 2012.