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gem-Digold Acetylide Complexes for Catalytic Intermolecular [4 + 2] Cycloaddition: Having Two Gold Centers Is Better for Asymmetric Catalysis

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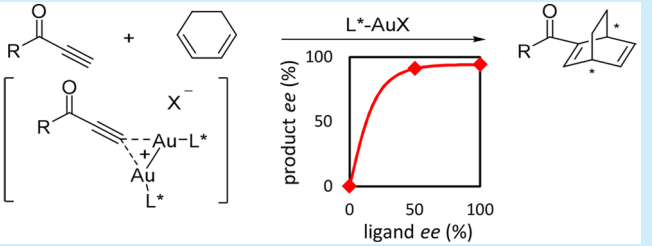
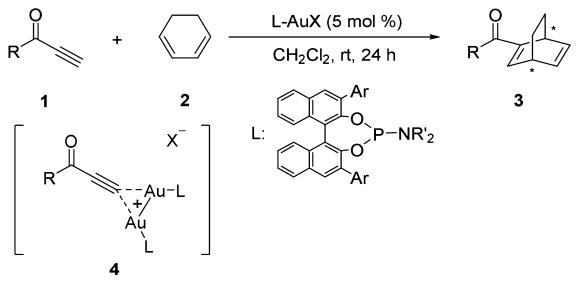
Supporting Information

ABSTRACT: Gold(I)-catalyzed highly enantioselective intermolecular [4 + 2] cycloaddition is shown with ynones and cyclohexadiene. Various bicyclo[2.2.2]octadiene derivatives are produced in high yields (up to 99%) with good enantioselectivity (up to 96% *ee*). Key to the success is generation of the *gem*-digold terminal alkyne as a catalytic on-cycle species. As proof of the *gem*-digold catalysis, a positive nonlinear effect is clarified between the *ee*'s of the ligand and the cycloadduct.



In the past decade, homogeneous gold(I) catalysts have exhibited their power for novel carbon−carbon and carbon−heteroatom bond formation by virtue of π activation of a carbon−carbon multiple bond toward nucleophilic attack in atypical catalytic pathways.[1] However, a gold(I)-catalyzed enantioselective version has been quite limited even in an intramolecular reaction.[2] Therefore, enantioselective gold(I) catalysis poses a formidable challenge because of the propensity of gold(I) to form a linear two-coordinate complex: the reacting center is distally far from the chiral ligand. For this reason, the development of gold(I)-catalyzed asymmetric reactions, especially intermolecular ones, is difficult. Recently, several intermolecular cycloadditions have been reported with highly reactive unsaturated substrates. Mascareñas described the [4 + 2] cycloaddition of allenamides,[3] and Gong reported the hetero-Diels−Alder reaction of diazenes.[4] However, an intermolecular [4 + 2] cycloaddition involving alkynes has no precedent (Scheme 1),[5] although the bicyclo[2.2.2]octadiene products **3** obtained from **1** and **2** are in synthetic demand.[6] Herein we report the asymmetric Diels−Alder cycloaddition of simple ynones **1** and cyclohexa-1,3-diene (**2**) using gold(I) catalysts containing BINOL-based phosphoramidites **L**. The *gem*-digold species **4** is found to be the key to success in the intermolecular cycloaddition[7] as a catalytic on-cycle species.

Scheme 1. Chiral Gold(I)-Catalyzed Intermolecular [4 + 2] Cycloaddition with Ynones



The Diels−Alder reaction of ynone **1a** with **2** was executed in the presence of a 5 mol % loading of the chiral phosphoramidite−gold(I) complex (*R*)-**L1**-AuOTf, and the reaction proceeded smoothly to give the desired adduct **3a** (Table 1, entry 1). Screening of solvents showed that CH_2Cl_2 was the best solvent to obtain the highest yield of the desired product **3a** (entries 1−4).

A variety of BINOL-derived phosphoramidites were then evaluated to give higher enantioselectivity. Bulky 4′-*tert*-butyl-2′,6′-dimethyl-1,1′-biphenyl (**L2**) afforded the product with lower enantioselectivity (entry 5). A ligand with a less bulky phenyl substituent (**L3**) was also ineffective for enantiocontrol (entry 6). To our delight, the ligand with Ar = 4′-*tert*-butylphenyl (**L4**) resulted in much increased enantioselectivity (entry 7). Surprisingly, however, a highly bulky substituent such as 2,4,6-triisopropylphenyl (**L5**) resulted in the formation of racemic product (entry 8). When the dimethylamino group in the phosphoramidite was replaced with a bulkier diisopropylamino substituent (**L6**; entry 9) or a chiral bis(1-phenylethyl)amino group (**L7**, entry 10), however, very low enantioselectivities were obtained. These results show that a suitable size of the amino group could exert a striking influence to give higher enantioselectivity. Thus, use of a cyclic amino group (**L8**, n = 1) afforded higher enantioselectivity up to 80% *ee* (entry 11). Incidentally, both ring-expanded piperidylamine (**L9**, n = 2; entry 12) and chiral pyrrolidylamine (**L10**, n = 1;

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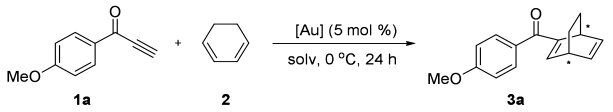
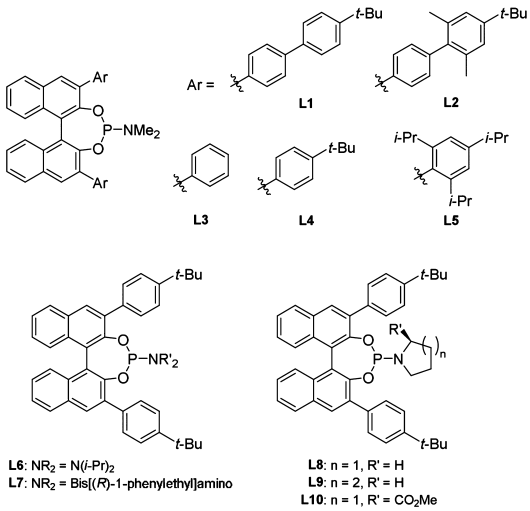
Table 1. Optimization of the Reaction Conditions[a]



entry	[Au]	solvent	yield (%)[b]	*ee* (%)[c]
1	(*R*)-**L1**-AuOTf	CH_2Cl_2	54	36
2	(*R*)-**L1**-AuOTf	THF	nr	–
3	(*R*)-**L1**-AuOTf	EtOH	nr	–
4	(*R*)-**L1**-AuOTf	toluene	trace	–
5	(*R*)-**L2**-AuOTf	CH_2Cl_2	55	4
6	(*R*)-**L3**-AuOTf	CH_2Cl_2	51	8
7	(*R*)-**L4**-AuOTf	CH_2Cl_2	55	65
8	(*R*)-**L5**-AuOTf	CH_2Cl_2	38	6
9	(*R*)-**L6**-AuOTf	CH_2Cl_2	31	1
10	(*R*,*R*,*R*)-**L7**-AuOTf	CH_2Cl_2	16	1
11	(*R*)-**L8**-AuOTf	CH_2Cl_2	41	80
12	(*R*)-**L9**-AuOTf	CH_2Cl_2	50	63
13	(*R*,*R*)-**L10**-AuOTf	CH_2Cl_2	40	63
14	(*R*)-**L8**-$AuNTf_2$	CH_2Cl_2	13	76
15	(*R*)-**L8**-$AuSbF_6$	CH_2Cl_2	17	40
16	(*R*)-**L8**-$AuBF_4$	CH_2Cl_2	23	89
17	**(*R*)-L8-AuPF$_6$**	**CH_2Cl_2**	**95**[d]	**94** (+)
18[e]	(*R*)-**L8**-$AuPF_6$	CH_2Cl_2	59	94

[a]Ynone **1a** (0.1 mmol), cyclohexadiene **2** (2 equiv), and LAuX (5 mol %) were used in 1 mL of solvent at 0 °C for 24 h. [b]Yields were determined by ^{1}H NMR analysis using tetrachloroethane as an internal standard. [c]The enantiomeric excess was determined by chiral HPLC. Remarkable enantioinversion was not observed. [d]Isolated yield. [e]The reaction time was 48 h at −10 °C.

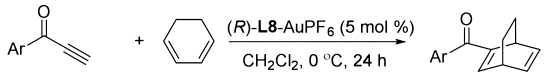


entry 13) gave lower enantioselectivity than the simple pyrrolidyl ligand **L8**.

The dramatic effects of the counteranion were then uncovered. $AuBF_4$ gave better enantioselectivity than AuOTf but a lower yield (entry 16). $AuPF_6$ was finally found to be the best: both the highest yield and the best enantioselectivity were obtained with (*R*)-**L8**-$AuPF_6$ (entry 17). When the reaction temperature was decreased to −10 °C, the cycloaddition incompletely proceeded even after 48 h but gave the same level of enantioselectivity (entry 18). For reproducibility, the optimized reaction temperature and time were set at 0 °C and 24 h, respectively.

We then explored the generality with various para substituents in aryl ynones (Table 2). Electron-donating

Table 2. Intermolecular Diels–Alder Reaction of Various Aryl Ynones[a]



entry	1	Ar	3	yield (%)[b]	*ee* (%)[c]
1	**1a**	4-MeO-C_6H_4	**3a**	95	94 (+)
2	**1b**	C_6H_5	**3b**	97	94 (+)
3	**1c**	4-Me-C_6H_4	**3c**	99	90 (+)
4	**1d**	4-Ph-C_6H_4	**3d**	99	94 (+)
5	**1e**	4-*t*-Bu-C_6H_4	**3e**	99	84 (+)
6	**1f**	4-OH-C_6H_4	**3f**	99	96 (+)
7	**1g**	4-NMe_2-C_6H_4	–	trace	–
8	**1h**	4-F-C_6H_4	**3h**	99	92 (+)
9	**1i**	4-Cl-C_6H_4	**3i**	99	87 (+)
10	**1j**	4-Br-C_6H_4	**3j**	99	90 (+)
11	**1k**	4-I-C_6H_4	**3k**	98	87 (+)
12	**1l**	4-CF_3-C_6H_4	**3l**	99	84 (+)
13	**1m**	4-CN-C_6H_4	**3m**	90	83 (+)
14	**1n**	4-MeO_2C-C_6H_4	**3n**	99	94 (+)

[a]Ynone **1** (0.1 mmol), cyclohexadiene **2** (2 equiv), and (*R*)-**L8**-$AuPF_6$ (5 mol %) were used in 1 mL of CH_2Cl_2 at 0 °C for 24 h. [b]Isolated yields. [c]The enantiomeric excess was determined by chiral HPLC.

groups on the aryl ynones, such as H (**1b**), Me (**1c**), Ph (**1d**), *t*-Bu (**1e**), and even free OH (**1f**) groups, were excellent, giving high yields and enantioselctivities (entries 2–6). However, the amino substituent (NMe_2, **1g**) gave only a trace amount of the product because it trapped the conjugate acid of the catalyst counteranion (entry 7), so protodeauration did not take place to give the product. Halide substituents (F, **1h**; Cl, **1i**; Br, **1j**; I, **1k**) afforded the corresponding products in similarly high yields and enantioselectivities (entries 8–11). The electron-withdrawing groups CF_3 (**1l**), CN (**1m**), and CO_2Me (**1n**) gave the desired bicyclooctadienes in virtually quantitative yield with high levels of stereoselectivity (entries 12–14).

The scope of this intermolecular asymmetric reactions was substantially expanded to various substituted ynones **1o–y** (Table 3). The π-conjugated 1-naphthyl (**1o**, entry 1) and 2-naphthyl (**1p**, entry 2) products were obtained in good yields with high enantioselectivities. Meta-disubstituted (**1q**, entry 3), and heterocyclic 2-furyl (**1r**, entry 4) and 2-thienyl (**1s**, entry 5) ynones effectively gave 88, 84, and 90% *ee*, respectively.

However, alkyl substituents at the acetylenic terminus such as cyclohexyl (**1t**, entry 6) and hexyl (**1u**, entry 7) gave low yields and enantioselectivities. Benzyl ester (**1v**, entry 8) gave a high yield but low enantioselectivity. With a silylated terminal alkyne (**1w**, entry 9), the sole product **3a** was obtained in desilylated form with good enantioselectivity. In contrast, internal alkynes **1x** (entry 10) and **1y** (entry 11) gave no products. These results imply that terminal alkyne functionality is indispensable for the progress of this reaction. The absolute configuration of the product **3b** was determined to be (1*S*,4*R*) by comparison of the specific optical rotation with that of (1*R*,4*S*)-**3b** synthesized from the known compound (1*R*,4*S*)-methyl bicyclo[2.2.2]octa-2,5-diene-2-carboxylate (see the Supporting Information). The configurations of the other products were also determined to be (1*S*,4*R*) by comparison of their specific optical rotations with that of (1*R*,4*S*)-**3b**.

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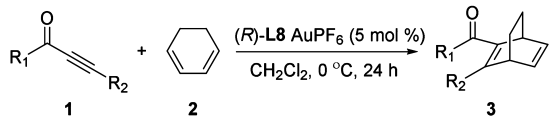
Table 3. Reaction of Various Ynones[a]



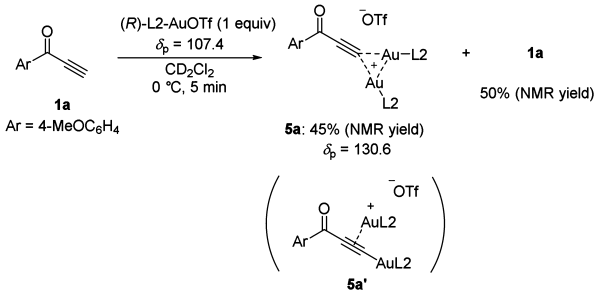
entry	1	R_1	R_2	3	yield (%)[b]	*ee* (%)[c]
1	**1o**	1-naph	H	**3o**	99	82 (+)
2	**1p**	2-naph	H	**3p**	99	82 (+)
3	**1q**	3,5-$(CH_3)_2$-C_6H_3	H	**3q**	99	88 (+)
4	**1r**	1-furyl	H	**3r**	84	84 (−)
5	**1s**	1-thienyl	H	**3s**	91	90 (+)
6	**1t**	Cy	H	**3t**	95	30 (−)
7	**1u**	C_6H_{13}	H	**3u**	98	38 (−)
8	**1v**	OBn	H	**3v**	79	7
9	**1w**	4-MeO-C_6H_4	TMS	**3a**	11[d]	92 (+)
10	**1x**	4-MeO-C_6H_4	Ph	–	nr	–
11	**1y**	4-MeO-C_6H_4	*n*-Bu	–	nr	–

[a]Ynone **1** (0.1 mmol), cyclohexadiene **2** (2 equiv), and (*R*)-**L8**-AuPF$_6$ (5 mol %) were used in 1 mL of CH_2Cl_2 at 0 °C for 24 h. [b]Isolated yields. [c]The enantiomeric excess was determined by chiral HPLC. [d]The yield was determined by ^{1}H NMR analysis using tetrachloroethane as an internal standard.

We clarified the role of digold intermediates in the catalytic cycle. Recently, Toste and co-workers proposed a possible *gem*-digold product on the basis of DFT calculations.[8a] The *ipso*-digold complexes were first discovered by Nesmeyanov et al.[9] in 1974 and play a role in gold catalysis, but off-cycle.[8b,c] However, digold catalysis on-cycle has remained uncovered.[10]

In the ^{31}P NMR spectrum, the stoichiometric reaction of **1a** with 1 equiv of (*R*)-**L2**-AuOTf showed a singlet peak for **5a** together with an equimolar amount of the remaining substrate **1a** (Scheme 2). A large downfield shift of the phosphine atom

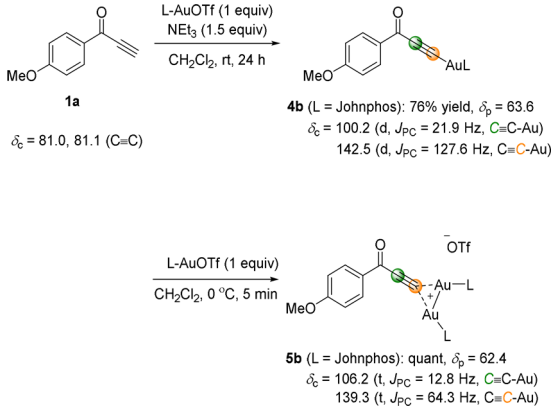
Scheme 2. Stoichiometric Reaction of Ynone 1a and (*R*)-L2-AuOTf



from δ = 107.4 ppm ((*R*)-**L2**-AuOTf) to δ = 130.6 ppm (**5a**) showed that the *gem*-digold complex **5a** was spontaneously formed rather than the σ,π complex **5a′** (Scheme 2).[11]

The "stoichiometric" reaction of **1a** with bulky Johnphos-AuOTf gave the stabilized gold acetylide complex **4b** in the presence of trimethylamine (Scheme 3). The addition of a second equivalent of Johnphos-AuOTf converted **4b** to *gem*-digold complex **5b** (two steps, 76% yield). The ^{1}H NMR spectrum of **5b** showed a single methoxy peak of **1a** and two aromatic peaks of Johnphos. The single set of peaks in a 1:2 ratio for the ynone and ligand was established by integration and hence indicative of the overall molecular composition of **5b**. The ^{31}P NMR spectrum showed only a singlet peak and upfield shifts of the phosphine atoms from δ = 63.6 ppm in **4b**

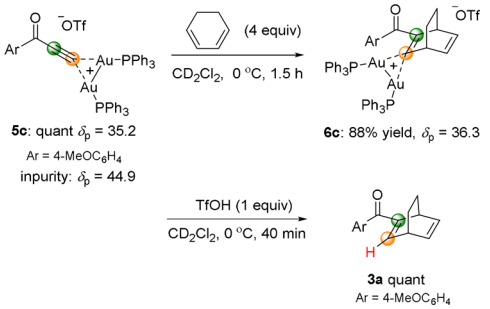
Scheme 3. Confirmation of the *gem*-Digold Acetylenic Complex



to δ = 62.4 ppm in **5b**. The ^{13}C NMR spectrum of **5b** revealed heteronuclear coupling between the acetylenic carbons and two phosphorus atoms. The signal for the aurated atom C_1 shifted from δ_C = 142.5 ppm in **4b** (d, $^2J_{PC}$ = 127.6 Hz) to δ_C = 139.3 ppm (t, $^2J_{PC}$ = 64.3 Hz) in *gem*-digold complex **5b**. The $^2J_{PC}$ coupling constant was 64.3 Hz, in good agreement with the previous report by Fürstner.[12] Another important feature in the ^{13}C NMR spectrum is the shift in the signal for the α-C atom C_2 from δ_C = 100.2 ppm in **4b** (d, $^3J_{PC}$ = 21.9 Hz) to δ_C = 106.2 ppm (t, $^3J_{PC}$ = 12.8 Hz) in *gem*-digold complex **5b**.

Addition of cyclohexadiene to *gem*-digold complex **5b** led to the stable diaurated intermediate **6b**. Unfortunately, the sterically demanding **6b** could not provide the protodeaurated product **3a** even at high temperature. With less sterically demanding triphenylphosphine as the ligand (**5c**), the reaction proceeded smoothly to generate *gem*-diaurated intermediate **6c** in 88% yield. Finally, TfOH was added to protonate **6c** and give the product **3a** in quantitative yield (Scheme 4). In

Scheme 4. Diels–Alder Reaction of *gem*-Digold Species



contrast, the addition of cyclohexadiene to monogold complex **4c** did not provide any Diels–Alder product. These results imply the importance of the *gem*-diaurated ynone as an on-cycle species in this asymmetric catalysis.

As proof of the *gem*-digold catalysis, an asymmetric amplification, namely, a positive nonlinear effect ((+)-NLE) was validated between the *ee*'s of ligand **L8** and cycloadduct **3a** (Figure 1).[13] A convex deviation from the linear relationship was indeed observed through a wide range of *ee* values of the catalyst (*R*)-**L8**-AuPF$_6$ to give highly enantioselective cycloadduct **3a** (**L8**-Au: 0, 50, and 100% *ee*; **3a**: 0, 90, and 94% *ee*, respectively). This significant (+)-NLE clearly proved the

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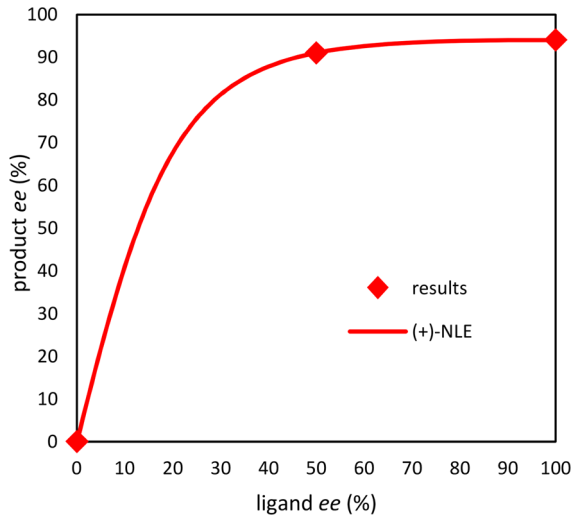
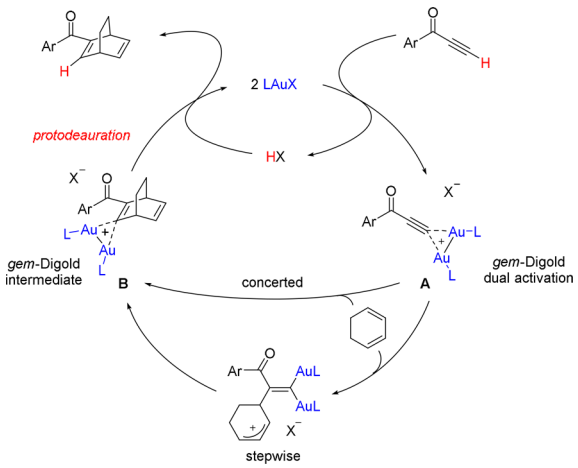


Figure 1. Positive nonlinear effect between the *ee*'s of the cycloadduct **3a** and the catalyst (*R*)-**L8**-AuPF$_6$.

intervention of the *gem*-digold-activated terminal alkyne as a triggering species.

The catalytic cycle was thus clarified (Scheme 5). The cationic gold complex and ynone form *gem*-digold complex **A**

Scheme 5. *gem*-Digold Catalytic Cycle



along with liberation of the conjugate acid HX. The Diels–Alder reaction of the *gem*-digold complex with the cyclohexadiene takes place more efficiently to give *gem*-digold product **B** via a stepwise or concerted process. At the last catalytic stage, the conjugate acid HX protonates **B** to release the chiral bicyclo[2.2.2]octadiene product and regenerate the cationic gold catalyst via protodeauration.

In conclusion, we have developed a chiral-digold-catalyzed intermolecular Diels–Alder cycloaddition of ynones and dienes to give bicyclo[2.2.2]octadienes of synthetic importance in up to 99% yield with 96% *ee*. Furthermore, the reaction mechanism was clarified to involve *gem*-digold complexes as catalytic on-cycle species in highly enantioselective catalysis of the intermolecular reaction. This *gem*-digold catalytic method is general and can be applied for intramolecular Diels–Alder cycloaddition, which is now under investigation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02263.

Experimental procedures and compound characterization data (DOCX)

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Notes

The authors declare no competing financial interest.

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