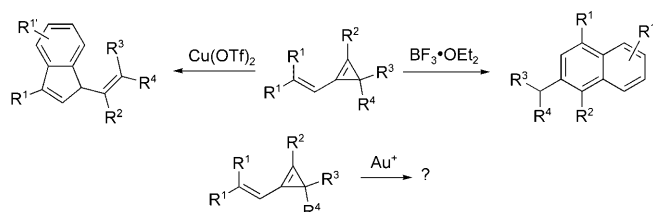


Gold(I)-Catalyzed Cycloisomerization of Arylvinylcyclopropenes: An Efficient Synthetic Protocol for the Construction of Indene Skeletons

Zhi-Bin Zhu^[a] and Min Shi^{*[a, b]}

As the smallest of cycloolefins, the cyclopropenes^[1] are highly strained^[2] but readily accessible substances, which have been serving as useful building blocks in many organic reactions.^[3] It can be seen that during the last several decades, thermal and photochemical skeleton rearrangements as well as metal-catalyzed/-mediated reactions of cyclopropene-containing compounds have attracted much attention from both synthetic and mechanistic viewpoints and numerous interesting transformations have been disclosed.^[4] For example, we recently have explored a new type of arylvinylcyclopropenes from the corresponding arylvinylidenecyclopropanes under basic conditions and have reported that the choice of Lewis acid catalyst can result in dramatic differences in the chemoselectivity of the rearrangement reactions of these vinylcyclopropenes, leading to naphthalene and indene derivatives (Scheme 1).^[5a] This is because that different Lewis acids can form the key carbon cationic intermediates at the different positions of cyclopropane. In fact, trace of water in these systems plays a very important role to release H⁺ as the real catalyst if using BF₃·OEt₂ as the catalyst.^[5b] Gold, which has emerged as the most efficient catalyst for the activation of alkynes, allenes and alkenes, has recently been a rising star of transition-metal catalysts.^[6] Since there is the similarity on the chemical behavior between LAu⁺ and H⁺,^[7] we envisaged that intramolecular rearrangement may take place in an interesting manner in the presence of gold(I) under mild conditions. In this communication, we wish to report an efficient gold(I)-catalyzed intra-

molecular cycloisomerization of arylvinylcyclopropenes to produce indene derivatives in good to excellent yields.^[8] To the best of our knowledge, this is the first example of gold-catalyzed intramolecular reaction of cyclopropenes.



Scheme 1. Lewis acid promoted rearrangement of arylvinylcyclopropenes.

Using (2-(3,3-dimethyl-2-phenylcycloprop-1-enyl)ethene-1,1-diyl)dibenzene (**1a**) as the substrate, we examined the reaction in the presence of Au⁺ (5 mol %). We found that 2-(2,2-diphenylvinyl)-1,1-dimethyl-1*H*-indene (**2a**), which was unambiguously determined by X-ray diffraction (Figure 1),^[9] and 1-(2-methyl-1-phenylprop-1-enyl)-3-phenyl-1*H*-indene (**3a**) were obtained in excellent yield and moderate selectivity (**2a/3a** 75:25) at 50 °C in 1,2-dichloroethane (DCE) (Table 1, entry 1). Interestingly, indene derivative **3a** was formed as the minor product in this reaction, but it could be obtained as the sole product in the presence of Cu(OTf)₂.^[5a]

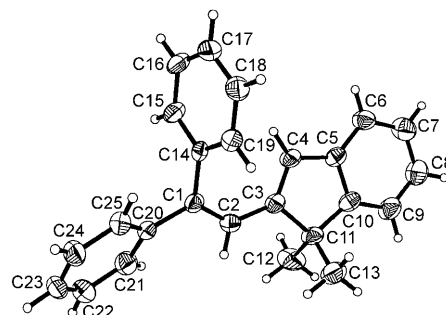


Figure 1. ORTEP drawing of compound **2a**.

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During the further examination, we also found that **2a** could not be obtained upon treatment of **1a** with the other Lewis acids (5 mol %) or Brønsted acids (5 mol %) such as $\text{Ln}(\text{OTf})_3$ or HOTf ($\text{Tf} = \text{CF}_3\text{SO}_3$) under identical conditions. Moreover, it was found that this reaction gave **2a** in trace at room temperature (Table 1, entry 2). In the absence of AgOTf , no reaction occurred, suggesting that the in situ generated Au^+ species is the real catalyst (Table 1, entry 3). Using AgOTf as the catalyst afforded 2-isopropyl-1,4-diphenylnaphthalene as the single product. This result was very similar as that of $\text{BF}_3\cdot\text{OEt}_2$ -catalyzed result, suggesting that H^+ might be the real catalyst in this reaction (Table 1, entry 4).^[5a] Adding methanol to the reaction system did not improve the yield and selectivity (Table 1, entry 5).^[10] To clarify the influence of trace of H^+ in this reaction, we added acetic acid (50 mol %) or various bases (50 mol %) such as Et_3N , 2,4,6-tri-*tert*-butylpyridine (TTBP) and KOtBu as the additives to examine the reaction outcome. Adding acetic acid did not cause significant alteration (Table 1, entry 6). In the presence of Et_3N , most of starting materials were recovered and **2a** was obtained in 13 % yield (Table 1, entry 7).^[11] As for TTBP or KOtBu , which only can act as a base to neutralize the trace of H^+ in the reaction system, the similar result was obtained as that of $\text{PPh}_3\text{AuCl}/\text{AgOTf}$, suggesting again that Au^+ is the real catalyst in this reaction (Table 1, entries 8 and 9). To our delight, using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as an additive afforded **2a** as a single product in 97 % yield, indicating that weak coordinating amine can adjust the catalytic ability of gold(I) (Table 1, entry 10).^[11] In the presence of DBU, AgOTf did not promote the rearrangement of **1a**, suggesting clearly that H^+ is the real catalyst in entry 4 of Table 1 (Table 1, entry 11). The examination of solvent effects revealed that DCE is the best one for the reaction (Table 1, entries 12–16). Other silver salts such as AgSbF_6 and AgBF_4 could also produce **2a** in excellent yields as a sole product in the presence of DBU (Table 1, entries 17 and 18). We also examined 10 mol % and 20 mol % of DBU in this reaction and found that **2a** and **3a** were both formed in the ratios of 77:23 and 84:16, respectively (Table 1, entries 19 and 20).

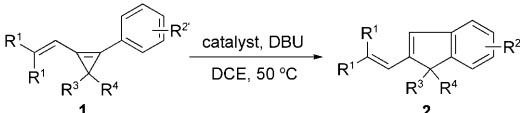
Table 1. Optimization of the reaction conditions.^[a]

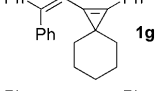
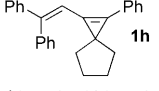
Reaction scheme: 1a (1,1-diphenyl-2-methylcyclopropene) reacts under conditions to form 2a (2-isopropyl-1,4-diphenylnaphthalene) and 3a (2-isopropyl-1,4-diphenylnaphthalene).

Entry	Catalyst	Additive	Solvent	<i>T</i> [°C]	<i>t</i> [h]	Yield [%] ^[b] (2a/3a)
1	$\text{PPh}_3\text{AuCl}/\text{AgOTf}$	–	DCE	50	24	99 (75:25)
2	$\text{PPh}_3\text{AuCl}/\text{AgOTf}$	–	DCE	20	24	trace
3	PPh_3AuCl	–	DCE	50	24	–
4	AgOTf	–	DCE	50	24	Ph-
5	$\text{PPh}_3\text{AuCl}/\text{AgOTf}$	MeOH	DCE	50	10	94 (76:24)
6	$\text{PPh}_3\text{AuCl}/\text{AgOTf}$	$\text{CH}_3\text{CO}_2\text{H}$	DCE	50	10	90 (82:18)
7 ^[c]	$\text{PPh}_3\text{AuCl}/\text{AgOTf}$	Et_3N	DCE	50	10	13 (100:0)
8	$\text{PPh}_3\text{AuCl}/\text{AgOTf}$	TTBP	DCE	50	10	90 (83:17)
9	$\text{PPh}_3\text{AuCl}/\text{AgOTf}$	<i>t</i> BuOK	DCE	50	10	90 (76:24)
10	$\text{PPh}_3\text{AuCl}/\text{AgOTf}$	DBU	DCE	50	10	97 (100:0)
11	AgOTf	DBU	DCE	50	10	–
12	$\text{PPh}_3\text{AuCl}/\text{AgOTf}$	DBU	toluene	50	10	trace of 2a
13	$\text{PPh}_3\text{AuCl}/\text{AgOTf}$	DBU	THF	50	10	–
14	$\text{PPh}_3\text{AuCl}/\text{AgOTf}$	DBU	DCM	20	24	14 (100:0)
15	$\text{PPh}_3\text{AuCl}/\text{AgOTf}$	DBU	MeOH	50	24	–
16	$\text{PPh}_3\text{AuCl}/\text{AgOTf}$	DBU	MeCN	50	24	–
17	$\text{PPh}_3\text{AuCl}/\text{AgSbF}_6$	DBU	DCE	50	10	94 (100:0)
18	$\text{PPh}_3\text{AuCl}/\text{AgBF}_4$	DBU	DCE	50	10	88 (100:0)
19	$\text{PPh}_3\text{AuCl}/\text{AgOTf}$ ^[d]	DBU	DCE	50	10	99 (77:23)
20	$\text{PPh}_3\text{AuCl}/\text{AgOTf}$ ^[e]	DBU	DCE	50	10	96 (84:16)

[a] All reactions were carried out using **1** (0.2 mmol), additive (50 mol %) in the presence of catalyst (5 mol %) in various solvents (1.0 mL). [b] Isolated yield, the ratio of **2a/3a** was determined by ^1H NMR spectroscopic data. [c] 80 % of **1a** was recovered. [d] 10 mol % of DBU was added. [e] 20 mol % of DBU was added.

With these optimal conditions in hand, we next examined a variety of arylvinylcyclopropenes **1** in this reaction and the results of these experiments are shown in Table 2. When electron-rich arylvinylcyclopropenes **1b** and **1c** were used as the substrates, the corresponding products **2b** and **2c** were produced in excellent yields in the presence of $\text{PPh}_3\text{AuCl}/\text{AgOTf}$ (Table 2, entries 1 and 2). However, in the cases of arylvinylcyclopropenes **1d–f** having electron-withdrawing groups on the benzene rings, traces of **2d–f** were obtained under the standard conditions. Fortunately, if using $\text{PPh}_3\text{AuCl}/\text{AgSbF}_6$ (Table 2, entries 3–5) or $\text{PPh}_3\text{AuCl}/\text{AgBF}_4$ (Table 2, entry 6) as the catalyst, products **3d–f** could be produced in good to excellent yields. As for spiro[2.5]octene (**1g**) and spiro[2.4]heptene (**1h**) as well as (2-(2-(2-chlorophenyl)-3,3-dimethylcycloprop-1-enyl)ethene-1,1-diyl)dibenzene (**1i**) which has an *ortho*-substituted chloro atom on the aromatic ring of R^2 , the reactions could also proceed smoothly to produce indene products **2g, h** and **i** in good yields in the presence of $\text{PPh}_3\text{AuCl}/\text{AgSbF}_6$ (Table 2, entries 7–9). When there was a *meta* group on the aromatic ring of R^2 , the product mixtures of 5-chloro-2-(2,2-diphenylvinyl)-1,1-dimethyl-1*H*-indene and 7-chloro-2-(2,2-diphenylvinyl)-1,1-dimethyl-1*H*-indene were obtained in a 1:1 ratio and in excellent yields (Table 2, entry 10). Either R^3 or R^4 was hydrogen atom or both of them were hydrogen atoms,

Table 2. Scope of Au-catalyzed rearrangement of **1**.^[a]


Entry	1 (R ¹ /R ² /R ³ /R ⁴)	Catalyst	<i>t</i> [h]	Yield [%] ^[b]
1	(C ₆ H ₅ / <i>p</i> -MeC ₆ H ₄ /Me/Me), 1b	PPh ₃ AuCl/AgOTf	10	> 99, 2b
2	(<i>p</i> -MeC ₆ H ₄ /C ₆ H ₅ /Me/Me), 1c	PPh ₃ AuCl/AgOTf	12	94, 2c
3	(C ₆ H ₅ / <i>p</i> -ClC ₆ H ₄ /Me/Me), 1d	PPh ₃ AuCl/AgSbF ₆	15	89, 2d
4	(<i>p</i> -ClC ₆ H ₄ /C ₆ H ₅ /Me/Me), 1e	PPh ₃ AuCl/AgSbF ₆	15	90, 2e
5 ^[c]	(<i>p</i> -FC ₆ H ₄ /C ₆ H ₅ /Me/Me), 1f	PPh ₃ AuCl/AgSbF ₆	15	99, 2f
6	(<i>p</i> -ClC ₆ H ₄ /C ₆ H ₅ /Me/Me), 1e	PPh ₃ AuCl/AgSbF ₆	15	86, 2e
7	 1g	PPh ₃ AuCl/AgSbF ₆	10	86, 2g
8	 1h	PPh ₃ AuCl/AgSbF ₆	10	85, 2h
9	(C ₆ H ₅ / <i>o</i> -ClC ₆ H ₄ /Me/Me), 1i	PPh ₃ AuCl/AgSbF ₆	24	98, 2i
10	(C ₆ H ₅ / <i>m</i> -ClC ₆ H ₄ /Me/Me), 1j	PPh ₃ AuCl/AgSbF ₆	10	94, 2j/2j' ^[d]
11	(C ₆ H ₅ / <i>p</i> -MeC ₆ H ₄ /Me/H), 1k	PPh ₃ AuCl/AgSbF ₆	10	complex
12	(C ₆ H ₅ / <i>p</i> -MeC ₆ H ₄ /H/H), 1l	PPh ₃ AuCl/AgSbF ₆	10	complex

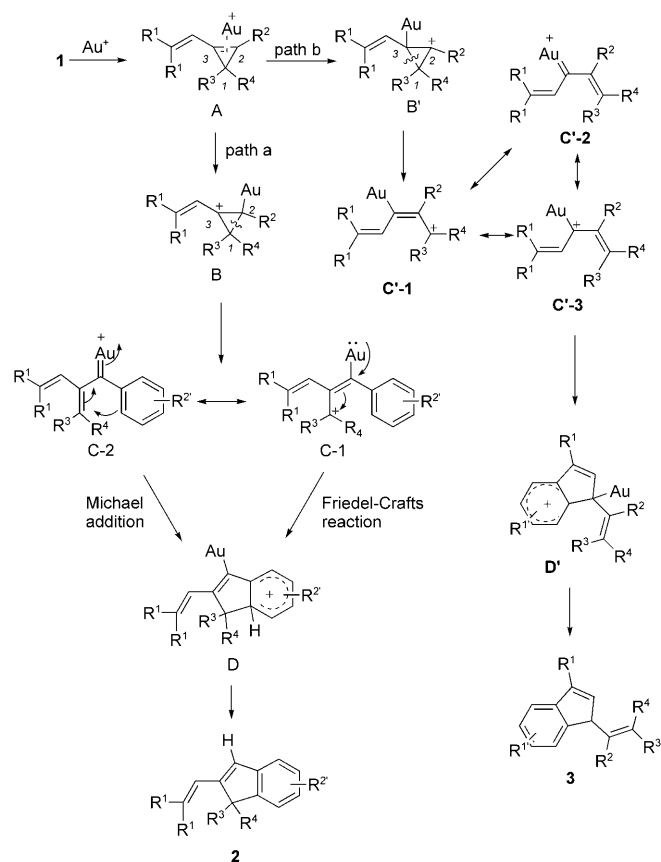
[a] All reactions were carried out using **1** (0.2 mmol) in the presence of catalyst (0.01 mmol), DBU (0.1 mmol) in DCE (1.0 mL) at 50 °C for 10 h. [b] Isolated yield. [c] The reaction was carried out at 65 °C. [d] Ratio of **2j**/**2j'** 1:1.

complex product mixtures were formed under the standard conditions (Table 2, entries 11 and 12).

A plausible mechanism for the formation of these indene derivatives is outlined in Scheme 2. Activation of cyclopropene **1a** by gold(I) forms intermediate **A**,^[12] which can produce intermediate **B** or **B'** via the addition of LAu⁺ to the double bond of cyclopropene at different position. Intermediate **B** undergoes cleavage of C₁–C₂ bond in cyclopropane cation to form π -allyl cationic intermediate **C-1** or its resonance-stabilized Au-carbene intermediate **C-2**, which produces intermediate **D** either via intramolecular Friedel–Crafts reaction of **C-1** or intramolecular Michael addition of **C-2**. Deprotonation of intermediate **D** followed by replacement of LAu⁺ with proton provides indene derivative product **2a**. On the other hand, intermediate **B'** undergoes cleavage of C₁–C₃ bond in cyclopropane cation to form π -allyl cationic intermediate **C'-1** or its resonance-stabilized cationic intermediate **C'-3** as well as Au-carbene intermediate **C'-2**. From π -allyl cationic intermediate **C'-3**, intramolecular Friedel–Crafts reaction takes place to give intermediate **D'**, which produces **3a** via deprotonation and replacement of Au⁺ with proton (Scheme 2). The mechanism on the formation of **3a** is very similar to that of Cu(OTf)₂-catalyzed rearrangement.^[5a] The addition of DBU eliminates trace of HOTf or HSbF₆, which is generated by trace water and AgOTf or AgSbF₆ and also might have weak coordination effect with gold(I) that results in perfect chemoselectivity in the addition step.^[11] If either R³ or R⁴ is hydrogen atom or both of them are hydrogen atoms, intermediate **C-1** will be a secondary or a primary carbocationic intermediate, which is not as stable as those of R³ and R⁴ are alkyl substituents and can hardly produce the rearrangement products. It is

notable that electron-withdrawing groups on the R¹ or R² aromatic ring slow down the reaction rate when AgOTf was used as the source of counter ion of gold(I), but if using AgSbF₆ as the source of counter ion, the reactions can easily take place. According to the recent DFT calculation data,^[13] PPh₃AuBF₄ or PPh₃AuSbF₆ has lower dissociation energy than that of PPh₃AuOTf. Therefore, PPh₃AuSbF₆ can more easily generate PPh₃Au⁺ to coordinate with **1a** than that of PPh₃AuOTf under identical conditions.

In summary, we have developed an efficient cycloisomerization of (2-vinylcycloprop-1-enyl)benzene **1** catalyzed by gold(I). This synthetic protocol furnishes 2-vinyl-1*H*-indene straightforwardly from simple



Scheme 2. Gold(I)-catalyzed cycloisomerization of arylvinylcyclopropenes.

starting materials in good to excellent yields under mild conditions, substantially enriching gold chemistry. A plausible mechanism has been proposed that is based on intramolecular Friedel–Crafts reaction or Michael addition reaction pathway. Clarification of the reaction mechanism and further application of this chemistry are in progress.

Experimental Section

General procedure of gold(I)-catalyzed rearrangement of arylvinylcyclopropene: Under an argon atmosphere, arylvinylcyclopropenes **1** (0.2 mmol), AgSbF₆ (0.01 mmol), PPh₃AuCl (0.01 mmol), DBU (0.1 mmol) and DCE (1.0 mL) were added into a Schlenk tube. The reaction mixture was stirred at 50 °C until the reaction completed. Then, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO₂).

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Keywords: cycloisomerization • cyclopropene • gold • homogeneous catalysis • indenenes

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- [9] CCDC 678993 (**2a**) contains 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. Empirical formula: C₂₅H₂₂; formula weight: 322.43; crystal color, habit: colorless, prismatic; crystal dimensions: 0.490 × 0.457 × 0.291 mm³; crystal system: monoclinic; lattice type: primitive; lattice parameters: *a* = 19.953(8), *b* = 10.396(4), *c* = 9.247(4) Å, *α* = 90°, *β* = 93.274(9)°, *γ* = 90°, *V* = 1914.8(14) Å³; space group: *Cc*; *Z* = 4; *ρ*_{calcd} = 1.118 g cm^{−3}; *F*₀₀₀ = 688; diffractometer: Rigaku AFC7R; residuals: *R*; *Rw*: 0.0554, 0.1005. 2-(2,2-Diphenylvinyl)-1,1-dimethyl-1-indene (**2a**): yellow solid; m.p. 87–89 °C; ¹H NMR (300 MHz, CDCl₃, TMS): *δ* = 1.37 (s, 6H, CH₃), 5.76 (s, 1H, CH), 6.65 (s, 1H, CH), 7.01–7.04 (m, 1H, Ar), 7.10–7.13 (m, 2H, Ar), 7.21–7.40 ppm (m, 11H, Ar); ¹³C NMR (75 MHz, CDCl₃, TMS): *δ* = 24.4, 50.7, 119.8, 121.1, 121.3, 124.9, 126.5, 126.7, 127.2, 127.4, 127.5, 128.2, 128.3, 128.8, 129.6, 141.1, 142.4, 142.8, 144.6, 152.5, 152.9 ppm; IR (CH₂Cl₂): *ν* = 3058, 3020, 2959, 2922, 2862, 1598, 1491, 1467, 1443, 1294, 1174, 1154, 1118, 1098, 1073, 890, 749, 699, 639 cm^{−1}; MS (EI): *m/z* (%): 322 (100) [*M*⁺], 323 (27.59), 307 (44.77), 292 (26.90), 291 (29.40), 229 (38.18), 215 (24.31), 145 (24.43); elemental analysis calcd (%) for C₂₅H₂₂: C 93.12, H 6.88; found: C 92.72, H 6.77.
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