Synthesis F. Hiault et al. Paper

Gold-Catalyzed Rearrangement of (Silylcyclopropenyl)methyl Ethers into (Silylmethylene)cyclopropanes

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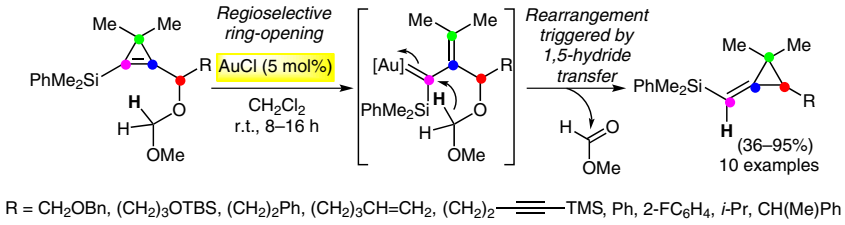

Dedicated to the memory of Professor Jean-François Normant, a remarkable mentor and scientific personality.

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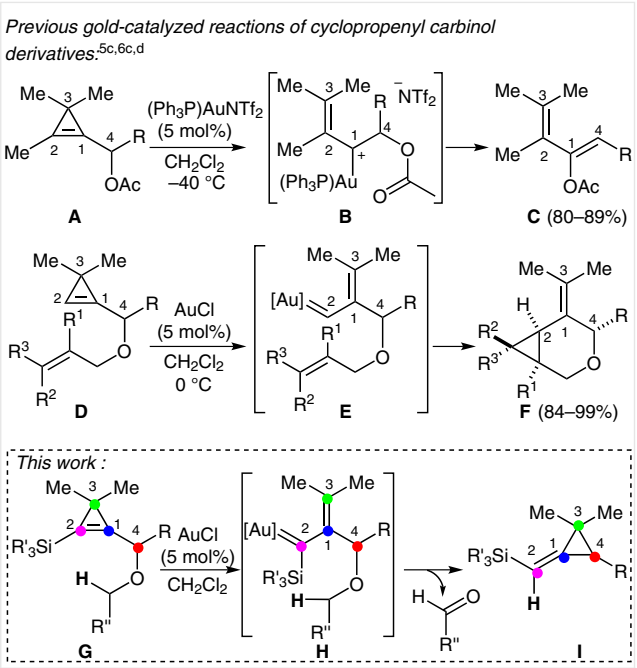
Abstract Methoxymethyl ethers derived from 2-(dimethylphenylsilyl)cycloprop-1-enyl carbinols undergo gold-catalyzed rearrangement leading to [(*Z*)-(dimethylphenylsilyl)methylene]cyclopropanes in moderate to high yields with methyl formate as a byproduct. This transformation proceeds by initial regioselective ring opening of the three-membered ring leading to an α-silyl vinyl gold carbenoid. This latter organogold species evolves by 1,5-hydride transfer, which triggers subsequent rearrangement involving loss of methyl formate, 2π-electrocyclization of the resulting allylic cation, and elimination of the metal to regenerate the catalyst.

Key words cyclopropenes, gold catalysis, strained cycles, rearrangement, hydride transfer

Transition-metal-catalyzed reactions of cyclopropenes have attracted considerable mechanistic and synthetic interest.[1,2] Indeed, transition metals are able to catalyze the addition of several reagents across the carbon–carbon double bond of cyclopropenes but also a variety of transformations accompanied by ring cleavage.[1,2] It is well known that many electrophilic metal complexes can trigger the ring opening of cyclopropenes to generate vinyl metal carbenoids that can undergo nucleophilic additions or rearrangements or be involved in cyclopropanation or C–H insertion reactions.[1,2] In 2008, the groups of Shi[3] and Lee[4] disclosed the first examples of gold(I)-catalyzed reactions of cyclopropenes. Their pioneering work and subsequent contributions demonstrated that the gold carbenoids resulting from the ring opening of cyclopropenes can participate in the inter- or intramolecular addition of nucleophiles[3–6] and in olefin cyclopropanation.[6] Cyclopropenyl carbinol derivatives, readily available by addition of cyclopropenyl organolithium reagents to aldehydes,[7] have been successfully involved in gold-catalyzed reactions. To date, Hyland, Ariafard, et al. reported the gold-catalyzed isomerization of cyclopropenylmethyl acetates **A** into 2-acetoxy-1,3-dienes that proceeds by regioselective ring opening to generate the gold carbenoid **B** at C1 followed by 1,2-acetoxy shift and elimination of the metal.[5c] Our group has shown that allyl ethers **D** derived from 3,3-dimethylcyclopropenyl carbinols underwent regioselective ring opening to generate gold carbenoids **E** at C2, which effected the highly diastereoselective intramolecular cyclopropanation of the remote olefin to afford 3-oxabicyclo[4.1.0]heptanes **F**.[6c,d] The substituents of the cyclopropene double bond in cyclopropenyl carbinol derivatives **A** and **D** were crucial to achieve regioselective ring opening. DFT calculations by Hyland, Ariafard, et al. indicated that the regioselectivity of the ring opening of a cyclopropene in the presence of a gold(I) complex is governed by the relative π-donating abilities of substituents at C1 and C2.[8,9] This study accounts well for the observed regioselectivities of the ring opening of cyclopropenes **A** and **D** because the π-donating abilities of the substituents vary in the following order Me > CH(OR) > H.[8]

Herein, we report a new gold-catalyzed rearrangement of ethers derived from silylcyclopropenyl carbinols **G**, which leads to (silylmethylene)cyclopropanes **I** and proceeds by rearrangement of α-silyl vinyl gold carbenoids **H** triggered by a 1,5-hydride transfer (Scheme 1).

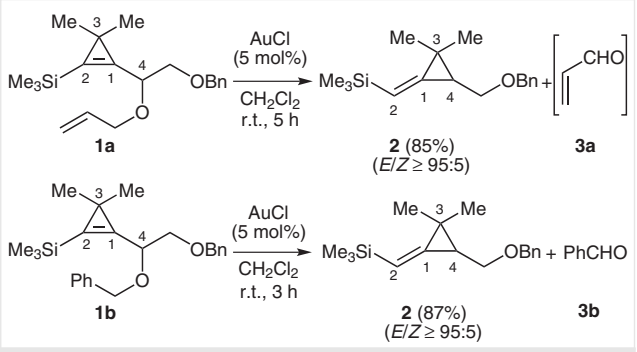
With the goal of extending the scope of the gold-catalyzed cycloisomerization of 1,6-cyclopropene-enes **D**, the reactivity of related substrates possessing a substituent at C2 was investigated. However, π-donating groups able to stabilize an adjacent positive charge would alter the regioselectivity of the ring opening and favor the formation of a regioisomeric gold carbenoid at C1.[6c] We reasoned that a silyl group should not alter the regioselectivity of the ring opening because of the β effect of silicon,[10] although DFT calculations indicated that the ring opening of (trimethylsi-



Scheme 1 Gold-catalyzed reactions of cyclopropenyl carbinol derivatives

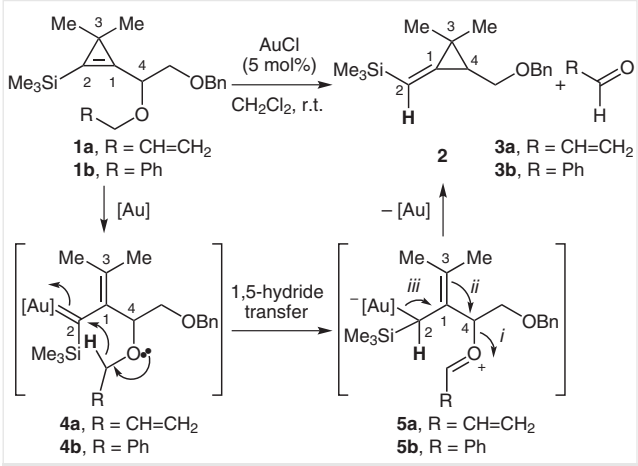
lyl)cyclopropene would produce an α-silyl vinyl gold carbenoid with a very modest preference.[8] 1,2-Silyl migration could also occur, as observed in the platinum-catalyzed isomerization of silylcyclopropenes into silylallenes.[11]

(Trimethylsilyl)cyclopropene **1a** was prepared and treated with a catalytic amount of AuCl (5 mol%) in CH_2Cl_2 (r.t., 2 h). A clean reaction occurred and analysis of the crude material by ^1H NMR spectroscopy indicated the formation of a new compound which was identified as [(*Z*)-(trimethylsilyl)methylene]cyclopropane **2**. This compound was formed with high stereoselectivity (*Z*/*E* ≥ 95:5)[12] and isolated in 85% yield. Interestingly, the presence of the silyl group altered the reactivity and suppressed the intramolecular olefin cyclopropanation process. At this stage, the fate of the allyloxy group of **1a**, which is not present in the rearranged product **2**, remained uncertain. This issue was solved by examination of the reactivity of the structurally related (trimethylsilyl)cyclopropene **1b** possessing a benzyl ether. The gold-catalyzed rearrangement of **1b** proceeded under equally mild conditions and also produced (silylmethylene)cyclopropane **2** (87%), but in this case benzaldehyde (**3b**) was identified as the byproduct. This finding suggested that acrolein **3a** had presumably been generated as a volatile byproduct during the gold-catalyzed rearrangement of **1a** but was lost during workup (Scheme 2).



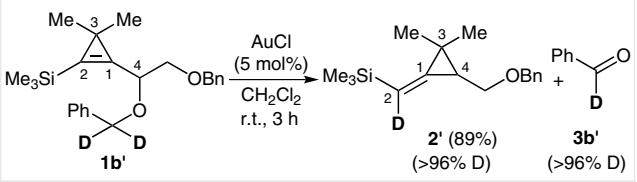
Scheme 2 Gold-catalyzed rearrangement of allyl and benzyl silylcyclopropenylmethyl ethers **1a** and **1b**

To explain the formation of alkylidenecyclopropane **2** from [(trimethylsilyl)cyclopropenyl]methyl ethers **1a** and **1b**, a plausible mechanism would involve initial regioselective ring opening of the three-membered ring to generate the corresponding α-trimethylsilyl vinyl gold carbenoids **4a** and **4b** at C2. Coordination of the gold moiety to the C1–C2 double bond with unsymmetrical binding through C2 would induce a partial charge depletion at C1,[9] stabilized by the silicon β effect.[10] The electrophilic organogold carbenoids **4a** and **4b** would then undergo 1,5-hydride transfer, assisted by the oxygen atom,[13] producing the corresponding α-silyl allyl gold complexes **5a** and **5b** with an oxonium ion leaving group at C4. The rearrangement of these latter species into (silylmethylene)cyclopropane **2** would then involve three elementary key steps: (i) ionization of the C4–O bond with elimination of acrolein or benzaldehyde,[14] (ii) a 2π-electrocyclization leading to the formation of the C3–C4 bond and hence constructing a three-membered ring, and (iii) the elimination of the gold moiety resulting in the formation of the C2=C1 alkenylsilane moiety in compound **2** (Scheme 3).



Scheme 3 Plausible mechanism accounting for the formation of (silylmethylene)cyclopropane **2** from **1a** and **1b**

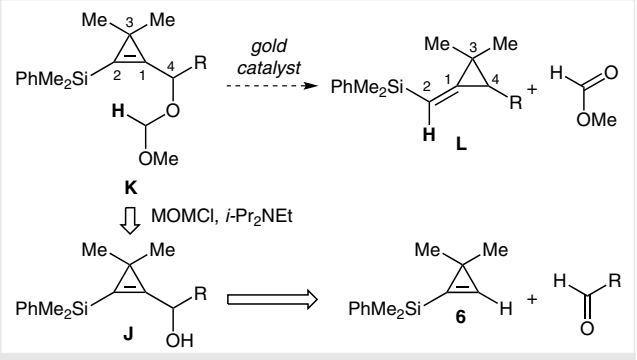
The occurrence of a 1,5-hydride transfer was confirmed by the rearrangement of the *gem*-deuterated benzyl ether **1b′** which selectively produced (silyldeuteromethylene)cyclopropane **2′** (89%) and deuterated benzaldehyde **3b′** (Scheme 4).



Scheme 4 Gold-catalyzed rearrangement of *gem*-dideuterated benzyl ether **1b′**

It is worth pointing out that the rearrangement of the cyclopropenylmethyl ether **1b** into (silylmethylene)cyclopropane **2** shares some similarities with the gold-catalyzed rearrangement of benzyl propargyl ethers into allenes, which proceeds by 1,5-hydride shift onto alkynes activated by the gold(I) complex and subsequent fragmentation with loss of benzaldehyde.[15]

Before studying the scope of this new gold-catalyzed rearrangement, our attention was drawn to the search for alternative (silylcyclopropenyl)methyl ether substrates. Indeed, a dimethylphenylsilyl substituent rather than a trimethylsilyl group would potentially offer more opportunities for further functionalization of the carbon–silicon bond.[16] Additionally, the corresponding silylated cyclopropenyl carbinol precursors **J** would be easily obtained by addition of the organolithium generated from the non-volatile and readily available 3,3-dimethyl-1-(dimethylphenylsilyl)cyclopropene (**6**)[17] to various aldehydes. However, allylation or benzylation of silylcyclopropenyl carbinols **J** cannot be conveniently achieved under the usual basic conditions (NaH or *t*-BuOK, Allyl-Br or BnBr, THF) because competitive cleavage of the C–Si bond occurred. Benzyl ethers were also not appealing substrates because the non-volatile byproduct benzaldehyde has to be separated by chromatography from the rearranged products. For these reasons, [(dimethylphenylsilyl)cyclopropenyl]methyl methoxymethyl (MOM) ethers **K** were eventually selected as substrates. Indeed, their synthesis from cyclopropenyl carbinols **J** would not require strongly basic conditions and their gold-catalyzed rearrangement into (silylmethylene)cyclopropanes **L** would produce methyl formate as a volatile byproduct (Scheme 5).



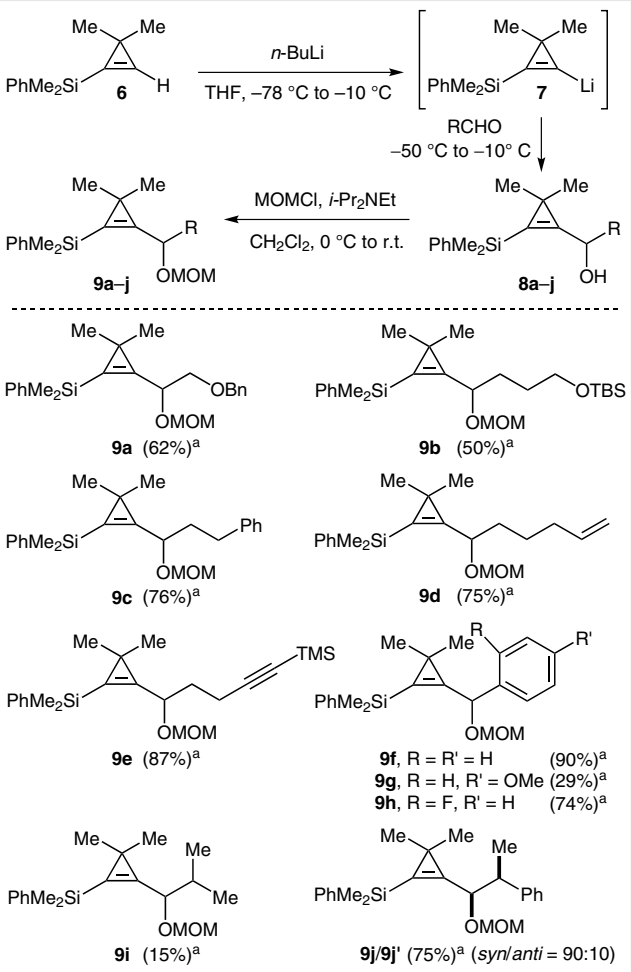
Scheme 5 Selection of [(dimethylphenylsilyl)cyclopropenyl]methyl MOM ethers **K** as substrates for gold-catalyzed rearrangement

Several [(dimethylphenylsilyl)cyclopropenyl]methyl ethers were prepared by addition of the organolithium reagent **7**, generated from silylcyclopropene **6** (*n*-BuLi, THF, –78 °C to –10 °C), to various aldehydes (–50 °C to –10 °C) followed by conversion of the resulting secondary alcohols **8a–j**/**8j′** into the corresponding MOM ethers under standard conditions (MOMCl, *i*-Pr_2NEt, CH_2Cl_2, 0 °C to r.t.). The resulting ethers **9a–j**/**9j′** were isolated in 15% to 90% overall yields (two steps from the corresponding aldehydes) without any optimization. When 2-phenylpropionaldehyde was used as the substrate, an inseparable 90:10 mixture of *syn*/*anti* diastereomers **9j**/**9j′** was obtained (75% overall yield), as a result of a Felkin–Anh addition mode of the cyclopropenyl organolithium reagent **7** (Scheme 6).[17,18]

The initial screening of the reaction conditions was carried out with substrate **9a**. As observed previously with the allyl and benzyl ethers **1a** and **1b** (Scheme 2), the rearrangement of MOM ether **9a** was efficiently catalyzed by AuCl (5 mol%) (CH_2Cl_2, r.t., 8 h), albeit a slightly longer reaction time was required. The [(*Z*)-(dimethylphenylsilyl)methylene]cyclopropane **10a** was formed as a single geometric isomer and was isolated in 86% yield.[12] Because AuCl does not lead to a well-defined catalyst in CH_2Cl_2,[19] the use of the gold(I) complexes $(Ph_3P)AuNTf_2$[20] and [Au]-**I**[21] was also attempted. Although substrate **9a** was rapidly consumed with these catalysts, the formation of **10a** was immediately accompanied by numerous side products that could not be readily separated or identified.[22] By contrast, the rearrangement of **9a** catalyzed by the gold(III) complex [Au]-**II**[23] provided **10a** in good yield (74%) (Scheme 7).

The best result was obtained with AuCl which was hence used as a catalyst for the investigation of the rearrangement of the other substrates **9b–j**/**9j′** (Table 1).

The gold-catalyzed rearrangement of ether **9b** possessing a (3-silyloxypropyl) substituent proceeded well and provided compound **10b** in 74% yield (Table 1, entry 1). The reaction is compatible with a phenyl group or a terminal alkene on the chain as shown with compounds **9c** and **9d**, respectively, which afforded the corresponding alkylidenecyclopropanes **10c** (78%) and **10d** (74%) (Table 1, entries 2 and 3). Interestingly, a (trimethylsilyl)alkyne did not interfere, as illustrated in the case of substrate **9e** which underwent an efficient chemoselective rearrangement leading to methylenecyclopropane **10e** in 86% yield (Table 1, entry 4).[24] The reactivity of arylmethyl ethers **9f–h** was next examined. The rearrangement of the phenyl-substitut-

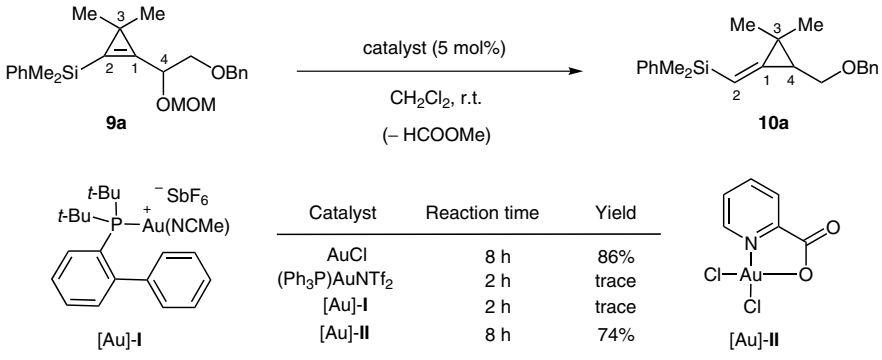


Scheme 6 Preparation of the [(dimethylphenylsilyl)cyclopropenyl]methyl MOM ether substrates **9a–9j**/**9j′**. [a] Overall yield from the corresponding aldehydes (two steps).

ed substrate **9f** led to compound **10f** albeit in moderate yield (49%) (Table 1, entry 5), because of competitive formation of unidentified byproducts. Substrate **9g** possessing an electron-rich aromatic ring decomposed under the reaction conditions (Table 1, entry 6). The rearrangement of **9h** possessing a 2-fluorophenyl group produced alkylidenecyclopropane **10h** in low yield (36%) (Table 1, entry 7). Thus, ethers derived from aryl cyclopropenyl carbinols were not viable substrates in this gold-catalyzed rearrangement. Branched alkyl groups were tolerated as illustrated by the gold-catalyzed rearrangement of cyclopropenylsilane **9i** substituted by an isopropyl group which produced alkylidenecyclopropane **10i** (90%) (Table 1, entry 8). The rearrangement of the diastereomeric mixture of **9j**/**9j′** (*syn*/*anti* 90:10) also proceeded efficiently, but provided a mixture of the corresponding alkylidenecyclopropane diastereomers **10j** and **10j′** in 65:35 ratio (81%) (Table 1, entry 9). A mixture of **9j**/**9j′** with inverted diastereomeric ratio (**9j**/**9j′** 23:77) was also prepared (by oxidation of the mixture of **9j**/**9j′** and reduction of the resulting ketone with DIBAL-H) and involved in the gold-catalyzed rearrangement. The diastereomeric alkylidenecyclopropanes **10j**/**10j′** were then formed in a 43:57 ratio (77%) (Table 1, entry 10).

The erosion of the diastereomeric ratio in the gold-catalyzed rearrangement of epimeric substrates **9j**/**9j′** seems to point toward a non-stereospecific rearrangement process. Therefore, the behavior of the enantioenriched substrate **9a** was investigated to gain further insight into the mechanism.

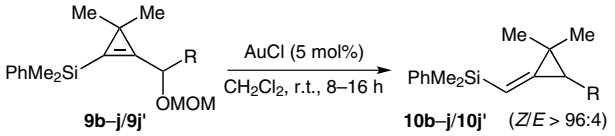
Considering the similarities between cyclopropenes and alkynes,[25] we surmised that the ruthenium(II)-catalyzed enantioselective hydrogenation transfer[26] of silylcyclopropenyl ketones could provide access to optically enriched silylcyclopropenyl carbinols. Effectively, cyclopropenyl ketone **11**, prepared by oxidation of the racemic alcohol (±)-**8a** using Dess–Martin periodinane (DMP), successfully underwent chemoselective hydrogenation transfer in isopropyl alcohol in the presence of Noyori's catalyst (*R*,*R*)-[Ru]-**I**[26] (3 × 6 mol%) (r.t. to 40 °C). Although the conditions were not optimized, the optically active silylcyclopropenyl carbinol (*R*)-**8a** was obtained in good yield (74%) and with a decent enantiomeric excess (75% ee). The absolute configuration of this latter alcohol was not determined unambiguously but assigned by analogy with the known face-



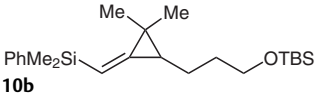
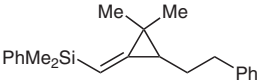
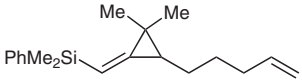
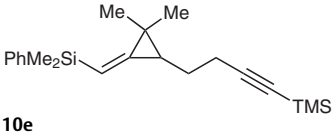
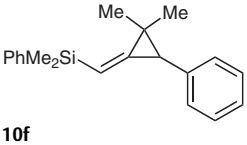
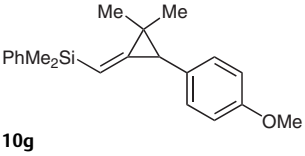
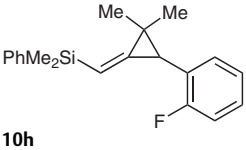
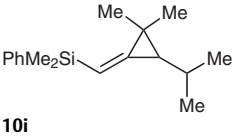
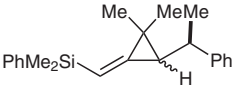
Catalyst	Reaction time	Yield
AuCl	8 h	86%
$(Ph_3P)AuNTf_2$	2 h	trace
[Au]-**I**	2 h	trace
[Au]-**II**	8 h	74%

Scheme 7 Gold-catalyzed rearrangement of MOM ether **9a**

Table 1 Gold-Catalyzed Rearrangement of Substrates **9b–j/9j'**

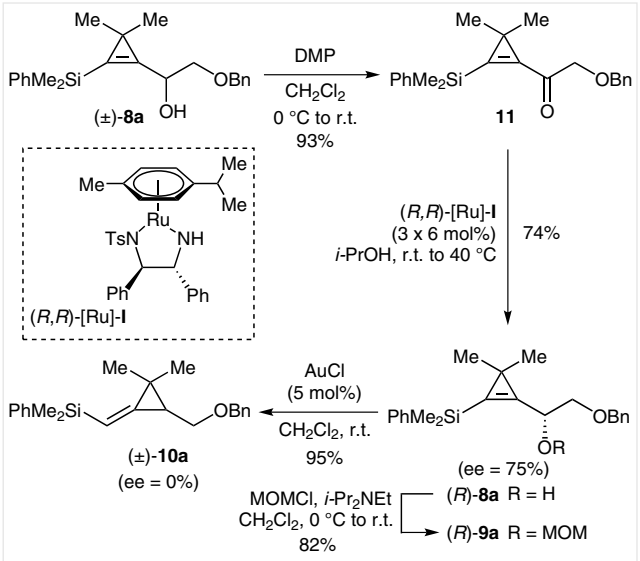


9b–j/9j' **10b–j/10j'** (*Z*/*E* > 96:4)

Entry	Substrate	Product	Yield[a] (%)
1	**9b**	 **10b**	74
2	**9c**	 **10c**	78
3	**9d**	 **10d**	74
4	**9e**	 **10e**	86
5	**9f**	 **10f**	49
6	**9g**	 **10g**	–
7	**9h**	 **10h**	36
8	**9i**	 **10i**	90
	9j/9j'		
9	**9j/9j'** (dr 90:10)	**10j/10j'** 65:35	81
10	**9j/9j'** (dr 23:77)	**10j/10j'** 43:57	77

[a] Isolated yield of analytically pure material.

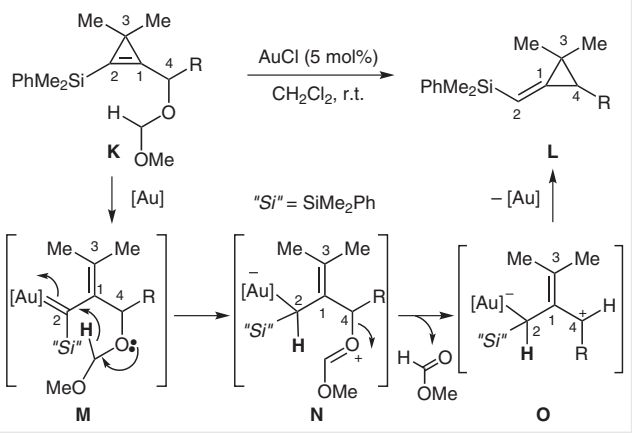
selectivity of the hydrogenation transfer of acetylenic ketones, considering the π-donating character of a cyclopropene.[27] The enantioenriched cyclopropenylmethyl ether (*R*)-**9a** was then prepared from (*R*)-**8a** and involved in the gold-catalyzed rearrangement. The formation of racemic (silylmethylene)cyclopropane (±)-**10a** (95%) confirmed the non-stereospecific character of the gold-catalyzed rearrangement (Scheme 8).



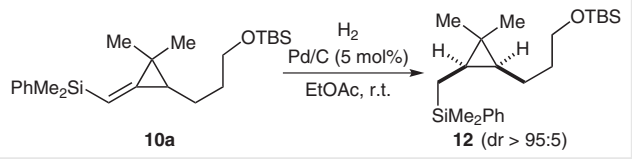
Scheme 8 Preparation and gold-catalyzed rearrangement of optically active MOM ether (*R*)-**9a**

After regioselective ring opening of cyclopropenes **K** and 1,5-hydride transfer to the α-(dimethylphenylsilyl) gold carbenoids **M**, the rearrangement of the resulting allylic organogold species **N** into (silylmethylene)cyclopropanes **L** likely involves the dissociation of the C4–O bond with elimination of methyl formate to a large extent, if not completely as in the case of substrate (*R*)-**9a** for which complete racemization occurs. The C3–C4 bond would then be created by 2π-electrocyclization of the allylic cation **O** followed by formation of the C1–C2 double bond by elimination of gold. The stereoselectivity of this latter step is difficult to explain at this stage, but the isopropylidene substituent is presumably acting as a key element for the control of the conformation around the C1–C2 and C1–C4 in the cationic intermediate **O** (Scheme 9).[28]

The reactivity of the (silylmethylene)cyclopropanes **L** produced by the gold-catalyzed rearrangement of MOM ethers **K** is still under investigation. We have shown so far that the diastereoselective hydrogenation of the exocyclic alkene could be achieved (H_2, cat. Pd/C, EtOAc, r.t.) (on the face opposite to the silyloxypropyl chain) to afford the *cis*-disubstituted cyclopropane **12** (88%) (Scheme 10).



Scheme 9 Plausible mechanism accounting for the formation of (silylmethylene)cyclopropane **2** from **1a** and **1b**



Scheme 10 Diastereoselective hydrogenation of **10a**

In summary, we have disclosed a new transition-metal-catalyzed process involving cyclopropenyl carbinol derivatives that complements the transformations in which these latter substrates have been involved so far. In the presence of gold chloride, MOM ethers derived from (dimethylphenylsilyl)cyclopropenyl carbinols undergo rearrangement to [(dimethylphenylsilyl)methylene]cyclopropanes and methyl formate. We have provided evidence that the key steps of this rearrangement involve regioselective ring opening of the cyclopropene ring leading to an α-silyl gold carbenoid and 1,5-hydride transfer, which triggers subsequent elimination of methyl formate, 2π-electrocyclization of the resulting allylic cation, and elimination of the metal. Further investigation of the scope of this transformation as well as on the reactivity of the corresponding (silylmethylene)cyclopropane products are underway.

Reactions involving air- and moisture-sensitive organometallic reagents were carried out under argon in flame-dried glassware with a magnetic stirring bar and sealed with a rubber septum. THF was distilled from Na-benzophenone. *i*-Pr_2NH, *i*-Pr_2NEt, CH_2Cl_2, and *i*-PrOH were distilled from CaH_2. Reagents were obtained from commercial suppliers and used as received without further purification. Flash column chromatography was performed on silica gel (230–400 mesh). IR spectra were recorded with a Bruker TENSOR 27 instrument (IR-FT) with attenuated total reflectance (ATR). NMR spectra were recorded with a Bruker Avance 400 instrument. ^{1}H NMR spectra were recorded at 400 MHz relative to TMS. ^{13}C NMR spectra were recorded at 100 MHz referenced to the solvent signal (δ = 77.16 for $CDCl_3$) and include carbon environment (deduced from DEPT experiments). HRMS (ESI) were obtained with an orbitrap mass analyzer. Enantiomeric purities were determined by supercritical fluid chromatography (SFC) on a Minigram Berger SFC-Mettler Toledo apparatus equipped with a chiral stationary phase.

The preparation of silylcyclopropenes **1a**, **1b**, **1b′**, **9b–j/9j′** is detailed in the Supporting Information.

Gold-Catalyzed Rearrangement of Cyclopropenes 1a, 1b, and 1b′

({(1*Z*)-3-[(Benzyloxy)methyl]-2,2-dimethylcyclopropylidene}methyl)trimethylsilane (2)

To a solution of silylcyclopropene **1a** (52 mg, 0.16 mmol) in CH_2Cl_2 (3 mL) at r.t., was added AuCl (1.8 mg, 0.0077 mmol, 5 mol%). The mixture was stirred for 5 h and then it was filtered through Celite (CH_2Cl_2). The filtrate was evaporated under reduced pressure and the crude material was analyzed by ^{1}H NMR spectroscopy, which indicated the formation of **2** with high stereoselectivity (*Z*/*E* >95:5). The crude material was purified by flash column chromatography (petroleum ether/EtOAc, 98:2 to 96:4) to give **2** (37 mg, 85%) as a yellow oil. Compound **2** (46 mg, 87%) was also obtained by the gold-catalyzed rearrangement of silylcyclopropene **1b** and in this case benzaldehyde was detected by analysis of the crude material by ^{1}H NMR spectroscopy.

IR (neat): 1730, 1454, 1365, 1246, 1090, 1075, 862, 835, 734, 695 cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6): δ = 7.43 (br d, *J* = 7.4 Hz, 2 H), 7.31–7.27 (m, 2 H), 7.20 (m, 1 H), 6.10 (d, *J* = 1.8 Hz, 1 H), 4.50 (d, AB syst, *J* = 12.2 Hz, 1 H), 4.45 (d, AB syst, *J* = 12.2 Hz, 1 H), 3.70 (dd, *J* = 10.5, 5.7 Hz, 1 H), 3.42 (dd, *J* = 10.5, 9.1 Hz, 1 H), 1.66 (ddd, *J* = 9.1, 5.7, 1.8 Hz, 1 H), 1.29 (s, 6 H), 0.25 (s, 9 H).

Signals observed at 6.13 (d, *J* = 2.3 Hz, 1 H) and 3.85 (dd, *J* = 10.3, 5.3 Hz, 1 H), 1.78 (ddd, *J* = 9.7, 5.3, 2.3 Hz, 1 H) were tentatively assigned to the *E*-geometric isomer (dr >95:5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.6 (C), 138.8 (C), 128.5 (2 CH), 127.8 (2 CH), 127.6 (CH), 116.9 (CH), 72.6 (CH_2), 69.5 (CH_2), 27.2 (CH_3), 26.5 (CH), 20.9 (C), 19.5 (CH_3), –0.5 (3 CH_3).

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{17}H_{26}ONaSi$: 297.16466; found: 297.16451.

({(1*Z*)-3-[(Benzyloxy)methyl]-2,2-dimethylcyclopropylidene}(²H)methyl}trimethylsilane (2′)

Prepared by gold-catalyzed rearrangement of **1b′** and purified by flash column chromatography (petroleum ether/EtOAc, 98:2 to 96:4) to give a colorless oil; yield: 60 mg (89%).

IR (neat): 1726, 1454, 1365, 1245, 1090, 1051, 1028, 834, 755, 734, 695 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.27 (m, 5 H), 4.56 (d, AB syst, *J* = 12.0 Hz, 1 H), 4.51 (d, AB syst, *J* = 12.0 Hz, 1 H), 3.64 (dd, *J* = 10.7, 5.6 Hz, 1 H), 3.34 (dd, *J* = 10.6, 9.2 Hz, 1 H), 1.47 (dd, *J* = 9.1, 5.6 Hz, 1 H), 1.24 (s, 3 H), 1.17 (s, 3 H), 0.09 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5 (C), 138.8 (C), 128.5 (2 CH), 127.9 (2 CH), 127.6 (CH), 116.5 (CD, t, $^1J_{C-D}$ = 21.2 Hz), 72.6 (CH_2), 69.5 (CH_2), 27.1 (CH_3), 26.5 (CH), 20.8 (C), 19.5 (CH_3), –0.5 (3 CH_3).

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{17}H_{25}DONaSi$: 298.17092; found: 298.17079.

{2-[2-(Benzyloxy)-1-(methoxymethoxy)ethyl]-3,3-dimethylcycloprop-1-en-1-yl}dimethylphenylsilane (9a); Typical Procedures

2-(Benzyloxy)-1-[2-(dimethylphenylsilyl)-3,3-dimethylcycloprop-1-en-1-yl]ethan-1-ol (8a)

To a solution of cyclopropenylsilane **6** (1.29 g, 6.39 mmol, 1.6 equiv) in THF (20 mL) at –78 °C was added dropwise 2.5 M *n*-BuLi in hexanes (2.4 mL, 6.0 mmol, 1.5 equiv). The mixture was stirred for 1 h with the temperature rising from –78 °C to –10 °C, the mixture was cooled to –50 °C and (benzyloxy)acetaldehyde (561 µL, 4.00 mmol) was added. The mixture was allowed to warm to –10 °C over 1 h, stirred for a further 1 h at this temperature and then hydrolyzed with sat. aq NH_4Cl soln. The layers were separated and the aqueous phase was extracted with Et_2O. The combined organic phases were washed with brine, dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Purification of the crude material by flash column chromatography (petroleum ether/Et_2O, 100:0 to 93:7) afforded alcohol **8a** (977 mg, 70%) as a yellow oil.

IR (neat): 3448 (br), 1777, 1454, 1428, 1363, 1248, 1113, 818, 778, 731, 697, 655 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.55 (m, 2 H), 7.40–7.27 (m, 8 H), 4.91 (m, 1 H), 4.56 (d, AB syst, *J* = 12.1 Hz, 1 H), 4.53 (d, AB syst, *J* = 12.1 Hz, 1 H), 3.63 (dd, *J* = 9.6, 3.5 Hz, 1 H), 3.49 (dd, *J* = 9.6, 6.9 Hz, 1 H), 2.24 (d, *J* = 5.1 Hz, 1 H, OH), 1.18 (s, 3 H), 1.17 (s, 3 H), 0.424 (s, 3 H), 0.419 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.0 (C), 138.1 (C), 138.0 (C), 133.8 (2 CH), 129.4 (CH), 128.6 (2 CH), 128.0 (2 CH), 127.9 (3 CH), 124.6 (C), 73.6 (CH_2), 73.2 (CH_2), 69.8 (CH), 27.93 (CH_3), 27.85 (CH_3), 22.6 (C), –1.6 (2 CH_3).

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{22}H_{28}O_2SiNa$: 375.17508; found: 375.17532.

{2-[2-(Benzyloxy)-1-(methoxymethoxy)ethyl]-3,3-dimethylcycloprop-1-en-1-yl}dimethylphenylsilane (9a)

To a solution of alcohol **8a** (507 mg, 1.44 mmol) in CH_2Cl_2 (15 mL) at 0 °C were successively added *i*-Pr_2NEt (1.25 mL, 7.18 mmol, 5 equiv) and MOMCl (0.55 mL, 7.2 mmol, 5 equiv) dropwise. The mixture was stirred for 12 h at r.t., and then it was hydrolyzed with sat. aq NH_4Cl soln. The layers were separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude material was purified by flash column chromatography (petroleum ether/Et_2O, 90:10) to afford **9a** (508 mg, 89%) as a yellow oil.

IR (neat): 1776, 1364, 1248, 1153, 1113, 1028, 919, 817, 778, 731, 697, 655 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.53 (m, 2 H), 7.36–7.25 (m, 8 H), 4.98 (app t, *J* = 5.6 Hz, 1 H), 4.72 (d, AB syst, *J* = 6.6 Hz, 1 H), 4.61 (d, AB syst, *J* = 6.6 Hz, 1 H), 4.57 (d, AB syst, *J* = 12.0 Hz, 1 H), 4.53 (d, AB syst, *J* = 12.0 Hz, 1 H), 3.62 (d, *J* = 5.6 Hz, 2 H), 3.38 (s, 3 H), 1.153 (s, 3 H), 1.148 (s, 3 H), 0.41 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.9 (C), 138.3 (C), 137.9 (C), 133.9 (2 CH), 129.3 (CH), 128.4 (2 CH), 127.9 (3 CH), 127.7 (2 CH), 125.3 (C), 94.7 (CH_2), 73.4 (CH_2), 72.5 (CH), 72.2 (CH_2), 55.5 (CH_3), 27.92 (CH_3), 27.90 (CH_3), 21.6 (C), –1.6 (2 CH_3).

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{24}H_{32}O_3SiNa$: 419.20129; found: 419.20175.

{[(1*Z*)-3-(Benzyloxymethyl)-2,2-dimethylcyclopropylidene]methyl}dimethylphenylsilane (10a); Typical Procedure for Gold-Catalyzed Rearrangement of 9a–j/9j′

To a solution of silylcyclopropene **9a** (400 mg, 1.01 mmol) in CH_2Cl_2 at r.t., was added AuCl (11.7 mg, 0.0503 mmol, 5 mol%). The mixture was stirred for 8 h, and then it was filtered through Celite (CH_2Cl_2). The filtrate was evaporated under reduced pressure and the crude material was analyzed by ^1H NMR spectroscopy, which indicated the formation of **10a** as a single detectable geometric isomer (*Z*/*E* >96:4). After purification by flash column chromatography (petroleum ether/Et_2O, 95:5), **10a** (292 mg, 86%) was isolated as a yellow oil.

IR (neat): 1726, 1454, 1427, 1365, 1246, 1113, 1089, 1074, 840, 827, 730, 696 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.50 (m, 2 H), 7.36–7.27 (m, 8 H), 5.99 (d, *J* = 1.7 Hz, 1 H), 4.55 (d, AB syst, *J* = 12.0 Hz, 1 H), 4.50 (d, AB syst, *J* = 12.0 Hz, 1 H), 3.64 (dd, *J* = 10.6, 5.7 Hz, 1 H), 3.35 (dd, *J* = 10.6, 9.1 Hz, 1 H), 1.50 (ddd, *J* = 9.1, 5.7, 1.7 Hz, 1 H), 1.15 (s, 3 H), 1.08 (s, 3 H), 0.36 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.6 (C), 139.4 (C), 138.7 (C), 134.0 (2 CH), 129.0 (CH), 128.5 (2 CH), 127.9 (4 CH), 127.7 (CH), 115.0 (CH), 72.6 (CH_2), 69.5 (CH_2), 27.4 (CH), 26.3 (CH_3), 21.1 (C), 19.3 (CH_3), –1.8 (2 CH_3).

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{22}H_{28}OSiNa$: 359.18016.; found: 359.18051.

tert-Butyl({3-[(3*Z*)-3-[(dimethylphenylsilyl)methylidene]-2,2-dimethylcyclopropyl]}propoxy)dimethylsilane (10b)

Purified by flash column chromatography (petroleum ether/Et_2O, 98:2) to give a yellow oil; yield: 144 mg (74%).

IR (neat): 1723, 1471, 1462, 1428, 1247, 1111, 1098, 832, 773, 728, 698, 663 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.51 (m, 2 H), 7.36–7.33 (m, 3 H), 5.95 (d, *J* = 1.5 Hz, 1 H), 3.67–3.58 (m, 2 H), 1.67–1.60 (m, 2 H), 1.48–1.32 (m, 2 H), 1.10 (s, 3 H), 1.05–1.01 (m, 1 H), 1.01 (s, 3 H), 0.89 (s, 9 H), 0.35 (s, 6 H), 0.05 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.9 (C), 139.9 (C), 134.0 (2 CH), 128.9 (CH), 127.8 (2 CH), 112.9 (CH), 63.2 (CH_2), 33.3 (CH_2), 27.4 (CH_3), 26.7 (CH_3), 26.1 (3 CH_3), 24.7 (CH_2), 20.1 (C), 19.2 (CH), 18.5 (C), –1.7 (2 CH_3), –5.1 (2 CH_3).

HRMS (ESI): *m*/*z* [M + H^+] calcd for $C_{23}H_{41}OSi_2$: 389.26905; found: 389.26915.

{[(1*Z*)-2,2-Dimethyl-3-(2-phenylethyl)cyclopropylidene]methyl}dimethylphenylsilane (10c)

Purified by flash column chromatography (petroleum ether/Et_2O, 98:2) to give a colorless oil; yield: 66 mg (78%).

IR (neat): 1722, 1495, 1454, 1427, 1367, 1245, 1113, 841, 826, 788, 746, 729, 697 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.54 (m, 2 H), 7.39–7.35 (m, 3 H), 7.32–7.27 (m, 2 H), 7.23–7.18 (m, 3 H), 5.91 (br s, 1 H), 2.74 (br t, *J* = 7.5 Hz, 2 H), 1.75–1.68 (m, 2 H), 1.11 (s, 3 H), 1.11–1.07 (m, 1 H), 0.99 (s, 3 H), 0.37 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.5 (C), 142.6 (C), 139.8 (C), 134.0 (2 CH), 128.9 (CH), 128.7 (2 CH), 128.4 (2 CH), 127.8 (2 CH), 125.8 (CH), 113.1 (CH), 36.4 (CH_2), 30.6 (CH_2), 27.2 (CH), 26.6 (CH_3), 20.3 (C), 19.2 (CH_3), –1.7 (2 CH_3).

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{22}H_{28}SiNa$: 343.18525; found: 343.18531.

{[(1*Z*)-2,2-Dimethyl-3-(pent-4-en-1-yl)cyclopropylidene]methyl}dimethylphenylsilane (10d)

Purified by flash column chromatography (petroleum ether/Et_2O, 95:5) to give a colorless oil; yield: 61 mg (74%).

IR (neat): 1722, 1641, 1428, 1368, 1246, 1113, 910, 840, 825, 787, 729, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.59–7.55 (m, 2 H), 7.39–7.35 (m, 3 H), 5.99 (d, *J* = 1.0 Hz, 1 H), 5.85 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1 H), 5.04 (dm, app br d, *J* = 17.0 Hz, 1 H), 4.97 (dm, app br d, *J* = 10.5 Hz, 1 H), 2.14–2.08 (m, 2 H), 1.58–1.33 (m, 4 H), 1.13 (s, 3 H), 1.08–1.06 (m, 1 H), 1.06 (s, 3 H), 0.39 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.0 (C), 139.9 (C), 139.2 (CH), 134.0 (2 CH), 128.9 (CH), 127.8 (2 CH), 114.5 (CH_2), 112.0 (CH), 33.8 (CH_2), 29.4 (CH_2), 28.0 (CH_2), 27.6 (CH), 26.7 (CH_3), 20.1 (C), 19.3 (CH_3), –1.7 (2 CH_3).

(4-{(3*Z*)-3-[(Dimethylphenylsilyl)methylene]-2,2-dimethylcyclopropyl}but-1-yn-1-yl)trimethylsilane (10e)

Purified by flash column chromatography (petroleum ether/Et_2O, 90:10) to give a colorless oil; yield: 73 mg (86%).

IR (neat): 2174, 1723, 1247, 1113, 1047, 838, 759, 729, 698, 638 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.53 (m, 2 H), 7.38–7.35 (m, 3 H), 6.02 (d, *J* = 1.7 Hz, 1 H), 2.36–2.32 (m, 2 H), 1.70–1.56 (m, 2 H), 1.17–1.13 (m, 1 H), 1.13 (s, 3 H), 1.05 (s, 3 H), 0.38 (s, 6 H), 0.17 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9 (C), 139.7 (C), 134.0 (2 CH), 129.0 (CH), 127.8 (2 CH), 113.6 (CH), 107.6 (C), 84.2 (C), 27.9 (CH_2), 27.0 (CH), 26.5 (CH_3), 20.5 (C), 20.5 (CH_2), 19.4 (CH_3), 0.3 (3 CH_3), –1.7 (2 CH_3).

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{21}H_{32}Si_2Na$: 363.19347; found: 363.19347.

{[(1*Z*)-2,2-Dimethyl-3-phenylcyclopropylidene]methyl}dimethylphenylsilane (10f)

Purified by flash column chromatography (toluene) to give a yellow oil; yield: 20 mg (49%).

IR (neat): 1733, 1601, 1494, 1449, 1427, 1246, 1113, 964, 839, 816, 793, 730, 697 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.62–7.59 (m, 2 H), 7.39–7.37 (m, 3 H), 7.28–7.25 (m, 2 H), 7.19–7.16 (m, 3 H), 6.29 (d, *J* = 1.6 Hz, 1 H), 2.41 (d, *J* = 1.6 Hz, 1 H), 1.28 (s, 3 H), 0.79 (s, 3 H), 0.44 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9 (C), 139.4 (C), 138.7 (C), 134.0 (2 CH), 129.13 (2 CH), 129.10 (CH), 128.1 (2 CH), 127.9 (2 CH), 125.9 (CH), 117.1 (CH), 32.6 (CH), 26.7 (CH_3), 24.5 (C), 19.1 (CH_3), –1.6 (CH_3), –1.7 (CH_3).

{[(1*Z*)-3-(2-Fluorophenyl)-2,2-dimethylcyclopropylidene]methyl}dimethylphenylsilane (10h)

Purified by flash column chromatography (petroleum ether/Et_2O, 90:10) to give a colorless oil; yield: 30 mg (36%).

IR (neat): 1732, 1581, 1489, 1454, 1246, 1220, 1234, 1113, 1098, 965, 829, 814, 789, 753, 730, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.61–7.57 (m, 2 H), 7.39–7.36 (m, 3 H), 7.18–7.13 (m, 1 H), 7.08 (m, 1 H), 7.04–6.99 (m, 2 H), 6.32 (d, *J* = 1.8 Hz, 1 H), 2.45 (m, app br s, 1 H), 1.31 (s, 3 H), 0.78 (s, 3 H), 0.43 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.2 (C, $^1J_{C\text{-}F}$ = 245.3 Hz, C_7), 155.6 (C), 139.3 (C), 134.0 (2 CH), 129.9 (CH, $^3J_{C\text{-}F}$ = 4.2 Hz), 129.1 (CH), 127.9 (2 CH), 127.5 (CH, $^3J_{C\text{-}F}$ = 7.8 Hz), 125.9 (C, ^2J = 15.8 Hz), 123.6 (CH, $^4J_{C\text{-}F}$ = 3.3 Hz), 117.8 (CH), 114.8 (CH, $^2J_{C\text{-}F}$ = 21.9 Hz), 26.2 (CH), 24.3 (C), 19.3 (2 CH_3), –1.7 (CH_3), –1.8 (CH_3).

{[(1*Z*)-2,2-Dimethyl-3-(propan-2-yl)cyclopropylidene]methyl}dimethylphenylsilane (10i)

Purified by flash column chromatography (petroleum ether) to give a colorless oil; yield: 18 mg (90%).

IR (neat): 1720, 1463, 1427, 1368, 1289, 1246, 1176, 1113, 970, 840, 822, 794, 767, 728, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.53 (m, 2 H), 7.37–7.34 (m, 3 H), 5.99 (d, *J* = 1.7 Hz, 1 H), 1.36–1.30 (m, 1 H), 1.11 (s, 3 H), 1.06 (s, 3 H), 1.02 (d, *J* = 6.6 Hz, 3 H), 0.99 (d, *J* = 6.6 Hz, 3 H), 0.81 (dd, *J* = 10.2, 1.7 Hz, 1 H), 0.36 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.9 (C), 139.9 (C), 134.0 (2 CH), 128.9 (CH), 127.8 (2 CH), 112.5 (CH), 35.6 (CH), 29.3 (CH), 26.9 (CH_3), 23.4 (CH_3), 23.1 (CH_3), 20.4 (C), 19.3 (CH_3), –1.7 (2 CH_3).

({(3*R/*S**)-(1*Z*)-2,2-Dimethyl-3-[(1*R**)-1-phenylethyl]cyclopropylidene}methyl)dimethylphenylsilane (10j/10j')**

The gold-catalyzed rearrangement of a diastereomeric mixture of **9j**/**9j'** (90:10) afforded a mixture of **10j**/**10j'** (34 mg, 81%, 65:35). Alternatively, the gold-catalyzed rearrangement of a diasteromeric mixture of **9j**/**9j'** (23:77) produced a diastereomeric mixture of **10j**/**10j'** (13 mg, 77%, 43:57).

IR (neat): 1723, 1602, 1494, 1450, 1427, 1246, 1112, 968, 841, 827, 786, 729, 697 cm^{-1}.

Diastereomer 10j

^1H NMR (400 MHz, $CDCl_3$): δ = 7.59–7.57 (m, 2 H), 7.38–7.17 (m, 8 H), 6.13 (d, *J* = 1.3 Hz, 1 H), 2.55–2.43 (m, 1 H), 1.41–1.37 (m, 1 H), 1.37 (d, *J* = 6.9 Hz, 3 H), 1.11 (s, 3 H), 0.94 (s, 3 H), 0.39 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9 (C), 147.8 (C), 139.7 (C), 134.0 (2 CH), 129.0 (CH), 128.4 (2 CH), 127.9 (2 CH), 126.8 (2 CH), 125.9 (CH), 113.3 (CH), 39.9 (CH), 33.5 (CH), 26.5 (CH_3), 23.7 (CH_3), 21.0 (C), 19.6 (CH_3), –1.7 (2 CH_3).

Diastereomer 10j'

^1H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.48 (m, 2 H), 7.38–7.17 (m, 8 H), 5.70 (br s, 1 H), 2.54–2.43 (m, 1 H), 1.36 (d, *J* = 6.9 Hz, 3 H), 1.28 (m, 1 H), 1.17 (s, 6 H), 0.334 (s, 3 H), 0.329 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1 (C), 147.1 (C), 139.8 (C), 134.0 (2 CH), 128.9 (CH), 128.4 (2 CH), 127.8 (2 CH), 127.3 (2 CH), 125.9 (CH), 113.4 (CH), 39.8 (CH), 34.3 (CH), 26.9 (CH_3), 22.5 (CH_3), 20.4 (C), 19.3 (CH_3), –1.7 (2 CH_3).

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{22}H_{28}SiNa$: 343.18525; found: 343.18529.

Preparation and Gold-Catalyzed Rearrangement of (*R*)-9a

2-(Benzyloxy)-1-[2-(dimethylphenylsilyl)-3,3-dimethylcycloprop-1-en-1-yl]ethanone (11)

To a solution of (±)-**8a** (56.9 mg, 0.161 mmol) in CH_2Cl_2 (2 mL) at 0 °C, was added Dess–Martin periodinane (82.2 mg, 0.194 mmol, 1.2 equiv). After 10 min at 0 °C, the mixture was warmed to r.t., stirred for further 10 min and then hydrolyzed with sat. aq $NaHCO_3$ soln. The re-

sulting mixture was extracted with Et_2O and the combined organic phases were washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude material was purified by flash column chromatography (petroleum ether/Et_2O, 80:20) to afford **11** (52.7 mg, 93%) as a yellow oil.

IR (neat): 1736, 1687, 1250, 1113, 1078, 835, 817, 780, 733, 697, 655 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.52 (m, 2 H), 7.41–7.30 (m, 8 H), 4.55 (s, 2 H), 4.18 (s, 2 H), 1.25 (s, 6 H), 0.49 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.1 (C), 148.0 (C), 143.4 (C), 137.4 (C), 135.8 (C), 133.8 (2 CH), 130.0 (CH), 128.6 (2 CH), 128.3 (2 CH), 128.2 (2 CH), 128.1 (CH), 74.2 (CH_2), 73.3 (CH_2), 27.2 (2 CH_3), 24.8 (C), –2.4 (2 CH_3).

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{22}H_{26}OSiNa$: 373.15943; found: 373.15948.

(*R*)-2-(Benzyloxy)-1-[2-(dimethylphenylsilyl)-3,3-dimethylcycloprop-1-en-1-yl]ethan-1-ol [(*R*)-8a]

To a solution of ketone **11** (51.4 mg, 0.147 mmol) in *i*-PrOH (3 mL) at r.t., was added catalyst (*R*,*R*)-[Ru]-**I**[26] (50 µL, 0.17 M stock solution in CH_2Cl_2, 0.0085 mmol, 6 mol%). After 15 h at r.t., more catalyst (*R*,*R*)-[Ru]-**I** (6 mol%) was added. After 4 h at r.t., the reaction was still incomplete and another portion of catalyst (*R*,*R*)-[Ru]-**I** (6 mol%) was added. The mixture was heated at 40 °C for 2 h, then cooled to r.t. and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/Et_2O, 80:20) to afford optically active alcohol (*R*)-**8a** (38.4 mg, 74%) as a colorless oil.

$[\alpha]_D^{20}$ –7.2 (*c* 0.25, $CHCl_3$).

The enantiomeric excess of (*R*)-**8a** (75% ee) was determined by SFC [Daicel Chiralpak OD-H, 100 bar, sc CO_2/MeOH (97:3), flow rate 5.0 mL/min, λ = 210 nm] after calibration with racemic sample: t_R = 5.38 (minor), 5.74 min (major), see Supporting Information.

(*R*)-{2-[2-(Benzyloxy)-1-(methoxymethoxy)ethyl]-3,3-dimethylcycloprop-1-en-1-yl}dimethylphenylsilane [(*R*)-9a]

Alcohol (*R*)-**8a** (75% ee) was converted into the MOM ether (*R*)-**9a**, as described for the preparation of the racemic compound.

$[\alpha]_D^{20}$ +16.0 (*c* 0.5, $CHCl_3$).

Gold-Catalyzed Rearrangement of (*R*)-9a

The rearrangement of optically active (*R*)-**9a** (75% ee) catalyzed by AuCl (5 mol%) (CH_2Cl_2, r.t., 8 h) provided (silylmethylene)cyclopropane **10a** (23 mg, 95%) as a racemate (0% ee).

The enantiomeric excess of this latter product was determined by SFC [Daicel Chiralpak OJ-H, 100 bar, sc CO_2/MeOH (95:5), 5.0 mL/min, λ = 220 nm] after calibration with an authentic sample of (±)-**10a** arising from the gold-catalyzed rearrangement of (±)-**9a**: t_R = 2.99, 3.85 min, see Supporting Information.

{(1*R**,3*S**)-3-[3-(*tert*-Butyldimethylsiloxy)propyl]-2,2-dimethylcyclopropylmethyl}dimethylphenylsilane (12)

To a solution of **10a** (30 mg, 0.077 mmol) in EtOAc (1.5 mL) was added 5% Pd/C (4 mg, 0.004 mmol, 5 mol%). After 1 h stirring under an atmospheric pressure of H_2, the mixture was filtered through Celite (EtOAc) and the filtrate was evaporated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/EtOAc, 90:10) to provide **12** (27 mg, 88%, dr > 95:5) as a colorless oil. The relative configuration of **12** was assigned on the basis of the coupling constant value between the two cyclopropyl protons (*J* = 8.6 Hz).

IR (neat): 1471, 1462, 1249, 1111, 1098, 833, 773, 726, 698, 661 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.55–5.51 (m, 2 H), 7.37–7.35 (m, 3 H), 3.60 (t, *J* = 6.7 Hz, 2 H), 1.59–1.50 (m, 2 H), 1.26–1.15 (m, 2 H), 0.98 (s, 3 H), 0.90 (s, 9 H), 0.80 (s, 3 H), 0.72 (dd, *J* = 14.8, 5.0 Hz, 1 H), 0.57 (dd, *J* = 14.8, 8.6 Hz, 1 H), 0.47 (app td, *J* = 8.6, 5.0 Hz, 1 H), 0.36 (ddd, *J* = 8.6, 7.7, 6.5 Hz, 1 H), 0.302 (s, 3 H), 0.298 (s, 3 H), 0.06 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.8 (C), 133.8 (2 CH), 128.9 (CH), 127.8 (2 CH), 63.5 (CH_2), 33.4 (CH_2), 29.4 (CH_3), 26.8 (CH), 26.1 (3 CH_3), 21.9 (CH), 20.8 (CH_2), 18.5 (C), 17.2 (C), 15.0 (CH_3), 9.9 (CH_2), –2.8 (CH_3), –2.9 (CH_3), –5.1 (2 CH_3).

HRMS (ESI): *m*/*z* [M + H^+] calcd for $C_{23}H_{43}OSi_2$: 391.28470; found: 391.28444.

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Supporting Information

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