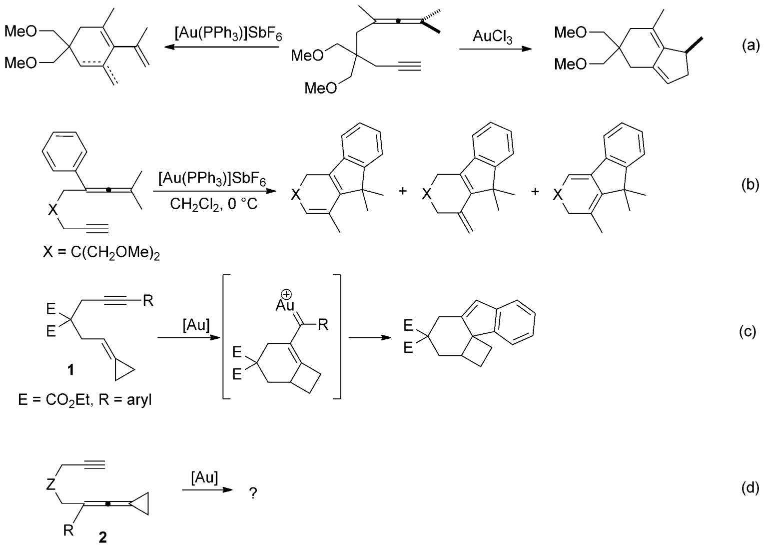
Gold Catalysis

Gold-Catalyzed Cycloisomerization of Yne-Vinylidenecyclopropanes: A Three-Carbon Synthon for [3+2] Cycloadditions

Wei Yuan, Xiangying Tang, Yin Wei,* and Min Shi*[a]

Abstract: A novel type of yne-vinylidenecyclopropanes (VDCPs) has been synthesized and applied in gold-catalyzed cycloisomerization reactions. It was found that these compounds can undergo an intramolecular cycloisomerization and perform as a three-carbon synthon for [3+2] cycloaddition under gold catalysis to give fused [4.3.0] and [5.3.0] bicyclic derivatives and VDCP rearranged products in moderated to good yields under mild conditions. The substrate scope of these novel transformations has been explored and plausible reaction mechanisms have been presented on the basis of deuterium labeling experiments and DFT calculations.

Introduction



Scheme 1. Cycloisomerization of alleneynes, yne-alkylidecyclopropanes **1**, and yne-VPCPs **2** catalyzed by gold(I) complexes.

Homogeneous gold catalysis based on activating alkenes, alkynes, and allenes has witnessed significant developments in many organic transformations within the past decade.[1,2] Many of these fascinating transformations have been applied in the synthesis of intermediates or functional blocks of natural products.[3] Enynes[4,5,1i,6] and alleneynes[2,7] feature as easily available substrates that have unique versatility in reactions catalyzed by gold catalysts and have been the focus of much recent research.

Vinylidenecyclopropanes (VDCPs) bearing an allene moiety connected to a highly strained cyclopropane group are fascinating building blocks in organic synthesis and have attracted much interest from organic chemists. To date, numerous useful and unique transformations of VDCPs have been discovered by us and other research groups.[8,9] Referring to the previous work, a number of examples of gold-catalyzed reactions of allenyene substrates have been reported (Scheme 1 a and b),[10] and reactions of yne-alkylidecyclopropane substrates **1** (Scheme 1 c)[11] catalyzed by gold complexes have been extensively explored. However, yne-VDCPs **2** (Scheme 1 d) have, to the best of our knowledge, never been synthesized and, consequently, the reactivities of these novel VDCP substrates in the presence of gold catalysts have never been explored. Because VDCPs bearing an allene moiety and a highly strained cyclopropane group are rather electron-rich substrates, we envisaged that they could react with terminal alkynes activated by gold catalysts in either an intramolecular or intermolecular manner, thus providing novel transformations through further C–C bond cleavage or ring en-

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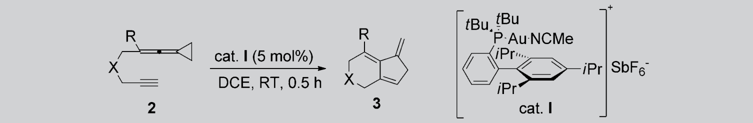
largement of cyclopropane. Recently, we discovered several unprecedented transformations of VDCPs catalyzed by gold complexes.[9d,j,m,o] Herein, we wish to present a novel cycloisomerization of newly synthesized yne-VDCPs catalyzed by an Au^I complex that efficiently affords fused [4.3.0] or [5.3.0] bicyclic derivatives as well as unexpected VDCP-rearranged products in moderate to good yields under mild conditions.

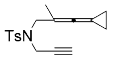
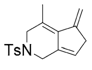
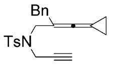
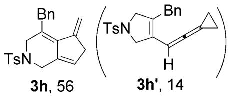
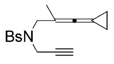
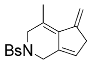
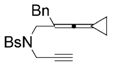
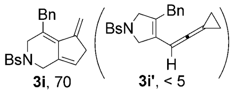
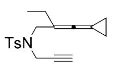
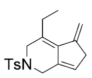
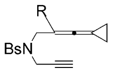
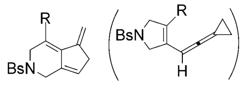
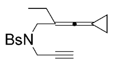
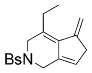
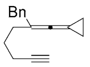
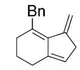
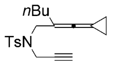
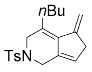
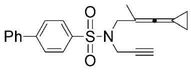
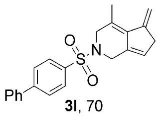
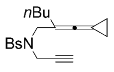
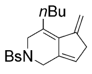
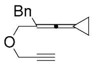
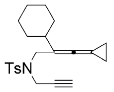
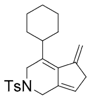
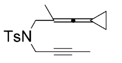
Results and Discussion

Yne-VDCP substrate **2a** was first synthesized (see the Supporting Information for details) and then reacted under gold catalysis. Through screening of the reaction conditions, it was found that the corresponding bicyclic derivative **3a**[12] could be afforded in 80% yield when 5 mol% cat. **I** was used as catalyst and the reaction was carried out at room temperature within 0.5 h in 1,2-dichloroethane (DCE) under argon (see Table SI-1 in the Supporting Information for details). Through this transformation, it is clear that the VDCP moiety can also act as a three-carbon synthon for [3+2] cycloaddition.

The substrate scope of this novel transformation was explored under the optimized reaction conditions, and the results are summarized in Table 1. For yne-VDCPs **2b–g**, in which R can be various primary or secondary alkyl groups with X as TsN (Ts = 4-methylbenzenesulfonyl) or BsN anchor (Bs = 4-bromobenzenesulfonyl), the desired products **3b–g** were obtained in moderate to good yields ranging from 43 to 85% (Table 1, entries 2–7). When yne-VDCPs **2h–j** were employed as substrates, in which R was benzyl (Bn) or 4-methylbenzyl group with X = TsN or BsN as an anchor, the corresponding products **3h–j** could also be afforded in 56–74% yield (Table 1, entries 8–10). By using yne-VDCP **2k** (X = CH_2, R = Bn) or **2l** (X = 4-phenylbenzenesulfonylamino group, R = Me) as substrate, the corresponding reaction took place smoothly, affording the desired product **3k** or **3l** in 25 or 54% yield, respectively (Table 1, entries 11 and 12). However, when yne-VPCP **2m** (X = O, R = Bn) or **2n** (X = NTs, R = Me, and the yne moiety is an internal alkyne) was used as the substrate, the reactions gave complex product mixtures (Table 1, entries 13 and 14). For substrate **2m**, the reasons for the formation of the complex product mixture are not yet clear. For substrate **2n**, the desired product could not be obtained and we believed that the reason is more related to the generation of higher energy barriers for the desired reactions when the employed alkyne is substituted. More interestingly, an unexpected VDCP rearranged product **3h′** was also isolated in 14% yield under the optimal reaction conditions when **2h** was used as substrate (Table 1, entry 8). The structure of **3h′** was unambiguously assigned by X-ray diffraction analysis, and its ORTEP drawing and the CIF data are presented in the Supporting Information.[13] Similar byproducts could be also obtained, albeit in trace amounts (< 5% yield), when **2i** or **2j** were employed as reactant, perhaps due to the electronic properties of the benzyl group.

Table 1. Substrate scope of the gold-catalyzed cycloisomerization of yne-VDCPs **2**.[a]

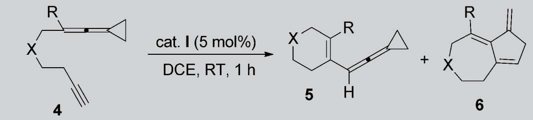


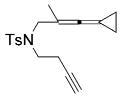
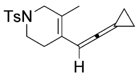
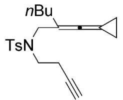
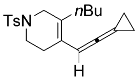
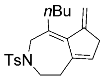
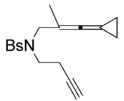
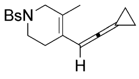
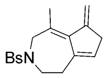
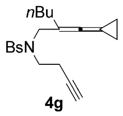
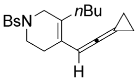
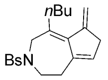
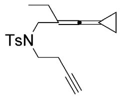
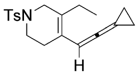
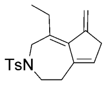
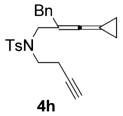
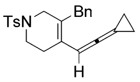
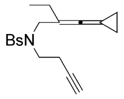
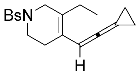
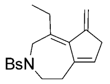
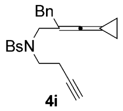
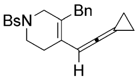
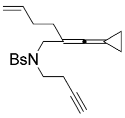
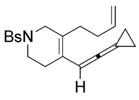
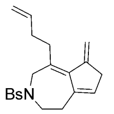
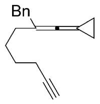
	2	3, yield [%][b]		2	3, yield [%][b]
1	 2a	 3a, 80	8[c]	 2h	 3h, 56 3h′, 14
2	 2b	 3b, 67	9	 2i	 3i, 70 3i′, < 5
3	 2c	 3c, 72	10	 2j	 3j, 74 3j′, < 5 R = $CH_2C_6H_4H_3C$-*p*
4	 2d	 3d, 55	11	 2k	 3k, 25
5	 2e	 3e, 51	12	 2l	 3l, 70
6	 2f	 3f, 43	13	 2m	complex
7	 2g	 3g, 85	14	 2n	complex

[a] Reaction conditions: **2** (0.1 mmol), gold complex **I** (5 mol%), DCE, RT, 0.5 h. [b] Isolated yield. [c] By-product **3h′** was obtained in 14% yield.

The observed formation of VDCP rearranged product **3h′** inspired us to further explore the reaction scope of this interesting transformation. We found that yne-VDCPs **4**, in which one carbon chain has been extended by a CH_2CH_2 moiety, could produce the desired VDCP rearranged product **5** in moderate yields in the presence of cat. **I** under slightly modified optimal conditions (reaction time being extended to 1 h); the results are summarized in Table 2. All the reactions proceeded smoothly to give the desired VDCP rearranged products **5** as the major species. For yne-VDCPs **4a–g**, in which R was various primary or secondary alkyl groups with X as TsN or BsN anchor, the rearranged VDCP products **5a–g** were obtained in moderate yields ranging from 28 to 56% (Table 2, entries 1–7) along with the corresponding cycloisomerization products **6b–g** in 11–25% yield (Table 2, entries 2–7). When yne-VDCP **4h** or **4i**

Table 2. Substrate scope of the gold-catalyzed cycloisomerization/rearrangement of yne-VDCPs **4**.[a]



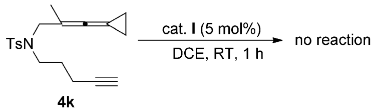
	4	Yield [%][b] 5	6		4	Yield [%][b] 5	6
1	 **4a**	 **5a**, 56	trace	6	 **4f**	 **5f**, 47	 **6f**, 25
2	 **4b**	 **5b**, 55	 **6b**, 25	7	 **4g**	 **5g**, 38	 **6g**, 24
3	 **4c**	 **5c**, 28	 **6c**, 21	8	 **4h**	 **5h**, 62	–
4	 **4d**	 **5d**, 39	 **6d**, 18	9	 **4i**	 **5i**, 58	–
5	 **4e**	 **5e**, 36	 **6e**, 11	10	 **4j**	complex	

[a] Reaction conditions: substrate **4**, cat. **I** (10 mol%), DCE (0.1 м), under argon, RT, 1 h. [b] Isolated yield.

was employed as substrate, in which R was a benzyl group with X as TsN or BsN anchor, the corresponding products **5h** or **5i** could be produced exclusively in 62 or 76% yields, respectively (Table 2, entries 8 and 9). When yne-VDCP **4k** (X = CH_2, R = Bn) was employed as substrate, the reaction only gave complex product mixtures (Table 2, entry 10). With yne-VDCP **4k** as substrate (one carbon chain being extended by a $CH_2CH_2CH_2$ moiety), no reaction occurred under the standard conditions (Scheme 2).

Concerning the substitution requirement of the allene, we realized that a benzyl group on the allene moiety favored the formation of VDCP rearranged products, perhaps as a result of electronic effects.

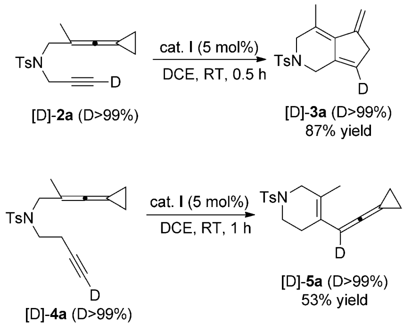
To gain more mechanistic insights into the reaction, we conducted isotope labeling experiments to examine the reaction outcome by using deuterated [D]-**2a** (D content = 99%) as the reactant under the standard conditions (Scheme 3; see the Supporting Information). It was found that product [D]-**3a** could be obtained in 87% yield and 99% D content, which clearly suggested an intramolecular cycloisomerization process. Furthermore, by using deuterated substrate [D]-**4a** (D content > 80%) in the reaction, the corresponding product [D]-**5a** was afforded in 53% yield and 80% D content under the standard conditions (Scheme 3; see the Supporting Information), which also suggests an intramolecular rearrangement process.



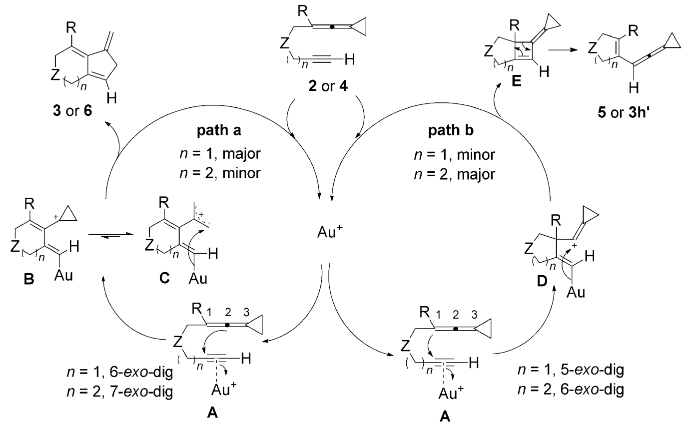
4k

Scheme 2. The cycloisomerization reaction with yne-VDCP **4k** as substrate by using catalyst **I**.

Plausible mechanisms for the cycloisomerization/rearrangement of yne-VPCPs **2** and **4** are presented in Scheme 4 on the basis of isotope labeling experiments and on previous reports.[9k,14] In path a, the coordination of terminal alkyne in VDCP **2** ($n = 1$) with Au^I catalyst initially generates gold species **A**, which cyclizes with the C-2 carbon in the tethered VDCP to give a pair of equilibrated intermediates **B** and **C** in a 6-*exo*-dig manner. Intermediate **C** then undergoes intramolecular cyclization of the nucleophilic vinylgold moiety[15,16] to produce the corresponding product **3** with release of the Au^I catalyst, which is free to engage in the next catalytic cycle. This is a main process for VDCP **2**. On the other hand, in path b, coordination of the terminal alkyne in VDCP **2** with the Au^I catalyst also initially generates gold species **A**, which cyclizes with the C-1 carbon in the tethered VDCP to give vinylgold species **D** in a 5-*exo*-dig manner. Intermediate **D** then undergoes intramolecular cyclization of the nucleophilic vinylgold moiety to produce a cyclobutene-containing bicyclic intermediate **E**. The latter intermediate produces the corresponding



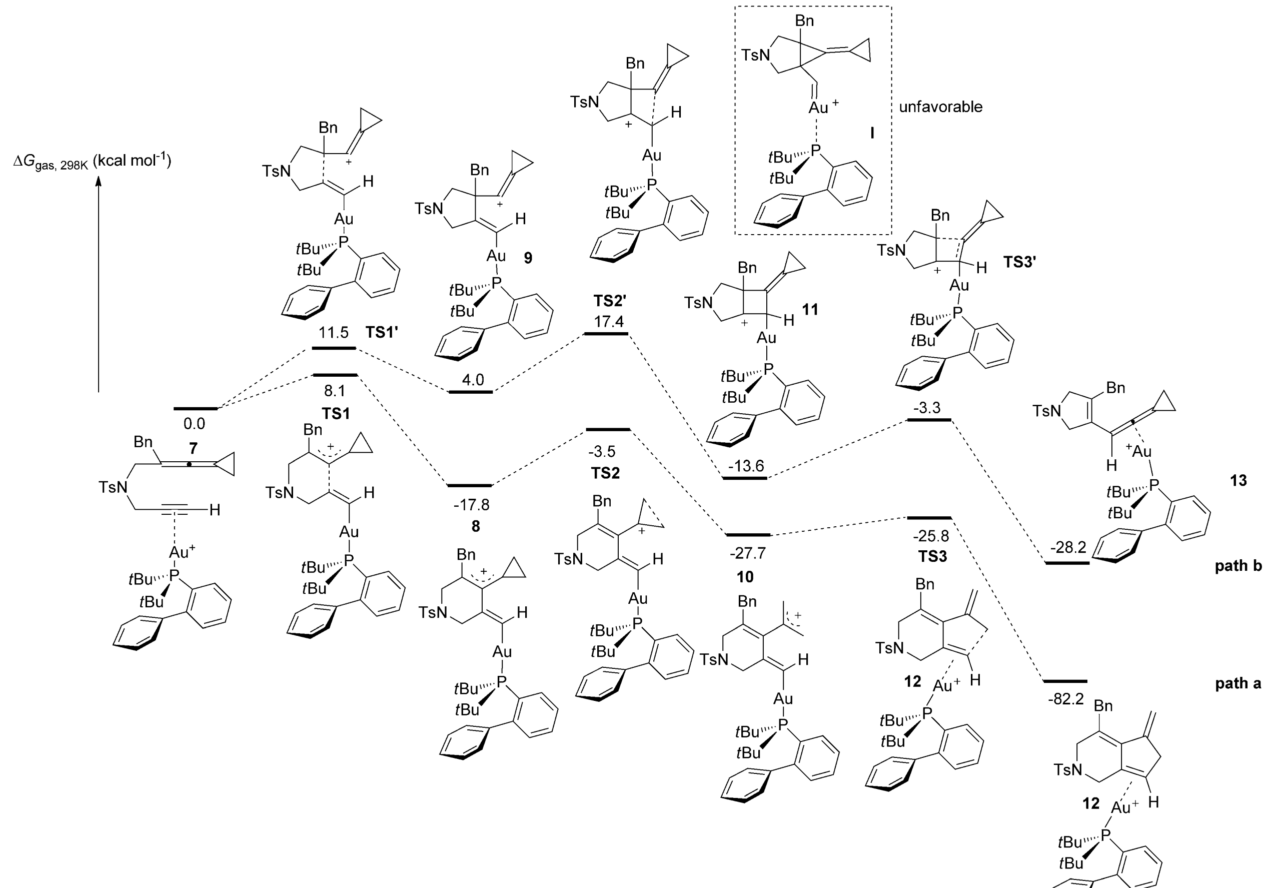
Scheme 3. Isotope-labeling experiments.



Scheme 4. Plausible mechanisms for the cycloisomerization of yne-vinylidenecyclopropanes.

product **3h′** through ring-opening of the cyclobutene together with release of the gold catalyst. This is a minor process for VDCP **2**. When VDCP **4** ($n=2$) is used as the substrate, the reaction probably also proceeds through both pathways (7-*exo*-dig and 6-*exo*-dig). In this case, path b is the main process, giving rearranged VDCP **5** as the major product and bicyclic compound **6** as the minor product. Comparing the above reaction mechanisms to those described in previous reports on alleneynes, it should be noted that the formation of VDCP rearranged products is very similar to that of cycloisomerization of alleneyne substrates catalyzed by Ga or Hg.[17] However, the formation of **3** and **6** suggests the existence of different mechanistic possibilities.

To understand in detail the mechanism for the formation of main product **3h** and side product **3h′**, we also investigated the reaction pathway theoretically. All calculations were performed at the B3LYP level with the Gaussian 09 program.[10,18,19] The SDD basis set and pseudopotential were used for the gold atom[20] and the 6-31G(d) basis set was used for other atoms. The relative energies of all intermediates and transitional states along the reaction pathways are shown in Scheme 5. Initially, coordination of terminal alkyne in VDCP **2** with Au^{I} catalyst generates gold complex **7**. In path a, the gold complex **7** undergoes a 6-*exo*-dig cyclization to give intermediate **8** via transition state **TS1** with an energy barrier of 8.1 kcal mol^{-1}. Subsequently, intermediate **8** passes through transition state **TS2** with an energy barrier of 14.3 kcal mol^{-1}, producing another carbocationic intermediate **10**. The latter intermediate undergoes intramolecular cyclization via **TS3** with an energy barrier of 1.9 kcal



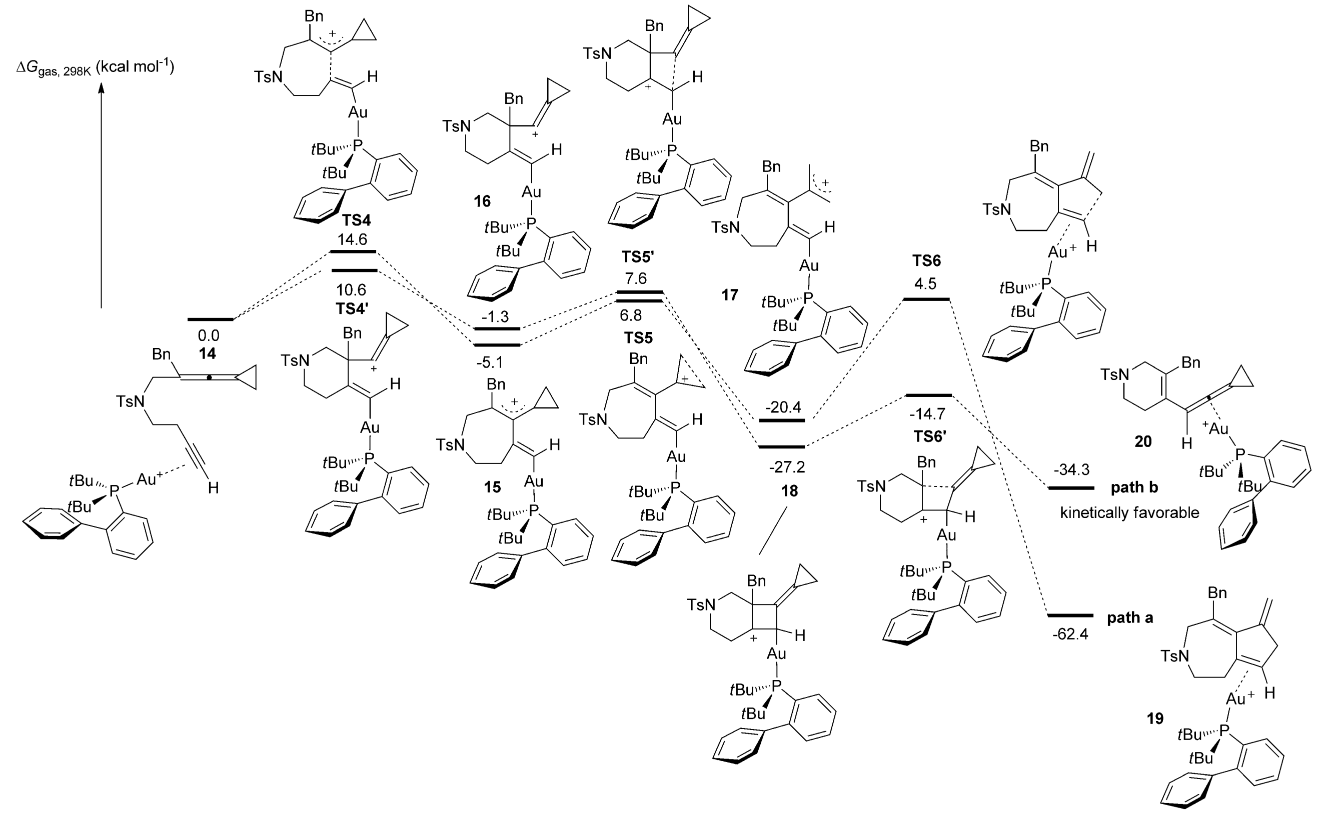
Scheme 5. Theoretical investigations on the reaction pathways for the formation of product **3**.

mol^{-1}, leading to the product complex **12**, which is cleaved to give the major product **3h**. On the other hand, in path b, gold complex **7** undergoes a 5-*exo*-dig cyclization to give intermediate **9** via transition state **TS1′** with an energy barrier of 11.5 kcal mol^{-1}. Subsequently, intermediate **9** undergoes an intramolecular cyclization through transition state **TS2′** with an energy barrier of 13.4 kcal mol^{-1}, producing another carbocationic intermediate **11**. In addition, as shown in Scheme 5, a possible cyclopropyl gold carbene intermediate **I** was also investigated. However, when we looked for this intermediate, it was found to be much higher than intermediate **11** by 31.8 kcal mol^{-1}. Intermediate **11** passes through transition state **TS3′** with an energy barrier of 10.3 kcal mol^{-1}, leading to the product complex **13**, which is cleaved to give the minor product **3h′**. The results of the calculations show that all intermediates along path a are thermodynamically more stable than those along path b, and that path a is also kinetically favorable, indicating that the bicyclic product **3h** is the major product. These results are consistent with the experimental results shown in Table 1, which show that bicyclic product **3** was obtained as the major product.

We further investigated the reaction energy profiles for the reaction of yne-VDCPs **4**, which has a longer tether; the results are shown in Scheme 6. In path a, gold complex **14** undergoes 7-*exo*-dig cyclization to give intermediate **15** via transition state **TS4** with an energy barrier of 14.6 kcal mol^{-1}. Subsequently, intermediate **15** passes through transition state **TS5** with an energy barrier of 11.9 kcal mol^{-1}, producing another carbocationic intermediate **17**. The latter intermediate undergoes intramolecular cyclization via **TS6** with an energy barrier of 24.9 kcal mol^{-1}, leading to the product complex **19**, which is cleaved to give product **6**. On the other hand, in path b, gold complex **14** undergoes 6-*exo*-dig cyclization to give intermediate **16** via transition state **TS4′** with an energy barrier of 10.6 kcal mol^{-1}. Subsequently, intermediate **16** undergoes intramolecular cyclization through transition state **TS5′** with an energy barrier of 8.9 kcal mol^{-1}, producing another carbocationic intermediate **18**. The latter intermediate passes through transition state **TS6′** with an energy barrier of 12.5 kcal mol^{-1}, leading to the product complex **20**, which is cleaved to give product **5**. The energy barriers along path b are all lower than those along path a, suggesting that the formation of product **5** is kinetically favorable and that this is a kinetically controlled reaction. These results are in line with the experimental observations (Table 2), which show that **5** is obtained as the major product when yne-VDCPs **4** is used as the substrate.

Conclusion

We have reported a novel cycloisomerization/rearrangement of newly synthesized yne-VDCPs **2** or **4** catalyzed by a sterically hindered gold catalyst such as **I** under mild conditions, thereby efficiently producing the corresponding bicyclic products as well as the rearranged VDCP products in moderate to good yields. The substrate scope of these novel transformations has been investigated, and plausible reaction mechanisms have



Scheme 6. Theoretical investigations on the reaction pathways for the formation of products **5** and **6**.

been proposed on the basis of isotope labeling experiments and DFT calculations. Further investigations on the mechanistic details of the reaction as well as further explorations of other useful chemical transformations of vinylidenecyclopropanes are in progress.

Experimental Section

General procedure for the gold-catalyzed cycloisomerization of VDCPs 2

VDCPs **2** (0.1 mmol), gold catalyst **I** (5 mol %) and anhydrous DCE (1.0 mL) were added to a flame-dried tube under argon and the resulting solution was stirred at RT for 0.5 h. The reaction mixture was evaporated to dryness and the residue was purified by flash column chromatography on silica gel (PE/EtOAc 20:1) to give the desired products.

General procedure for the gold-catalyzed cycloisomerisation/rearrangement of VDCPs 4

To a flame dried tube was added VDCPs **4** (0.1 mmol), gold catalyst **I** (5 mol %) and anhydrous DCE (1.0 mL) were added to a flame-dried tube under argon and the resulting solution was stirred at RT for 1 h. The reaction mixture was evaporated to dryness and the residue was purified by flash column chromatography on silica gel (PE/EtOAc 20:1) to give the desired products.

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Keywords: alkynes · cycloaddition · gold · isomerization · rearrangement · vinylidenecyclopropanes

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