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Gold-Catalyzed Cycloisomerization of 1,6-Diyne Carbonates and Esters to 2,4a-Dihydro-1*H*-fluorenes

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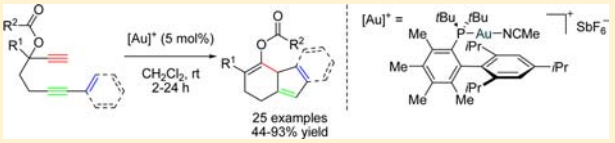
Supporting Information

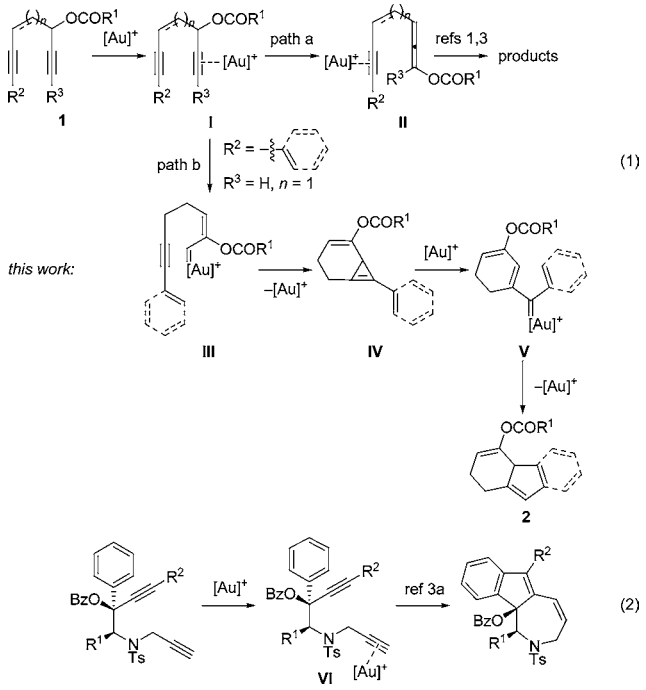
ABSTRACT: A synthetic method to prepare 2,4a-dihydro-1*H*-fluorenes efficiently from gold(I)-catalyzed 1,2-acyloxy migration/cyclopropenation/Nazarov cyclization of 1,6-diyne carbonates and esters is described. The suggested reaction pathway provides rare examples of [2,3]-sigmatropic rearrangement in this class of compounds as well as the involvement of an in situ formed cyclopropene intermediate in gold catalysis. Experimental and ONIOM(QM:QM′) [our own *n*-layered integrated molecular orbital and molecular mechanics(quantum mechanics:quantum mechanics′)] computational studies based on the proposed Au carbenoid species provide insight into this unique selectivity.



INTRODUCTION

1,*n*-Diyne cycloisomerizations catalyzed by mono- and trivalent complexes of gold have emerged as one of the most efficient and atom-economical strategies for complex molecule synthesis in a single step.[1−3] Included in this rapidly expanding field have been an increasing number of elegant methods to prepare synthetically useful cyclic compounds from 1,*n*-diyne carbonates and esters **1** shown in Scheme 1.[3] The reactions typically involve the allenyl intermediate **II** arising from the propensity of the acyloxy moiety of the gold-activated substrate **I** to undergo 1,3-migration (Scheme 1, eq 1, path a). The only notable exception to this mode of reactivity is the Au(I)-catalyzed concerted 5-endo-dig/7-endo-dig cyclization of *syn*-1,7-diyne benzoates to indeno[1,2-*c*]azepines via the gold-coordinated adduct **VI** (Scheme 1, eq 2).[3a] In contrast, the analogous transformations of 1,*n*-diyne esters initiated by a 1,2-acyloxy shift, thereby providing access to a potentially wider scope of cycloisomerization products, have so far remained unrealized. With this in mind and as part of studies examining the utility of gold catalysis in organic synthesis,[4] we became interested in the cycloisomerization chemistry of 1,6-diyne carbonates and esters **1** (Scheme 1, eq 1, path b). It was anticipated that such substrates containing a sterically less hindered terminal carbonate or estereal C≡C bond might be more prone to 1,2-acyloxy migration and subsequent trapping of the ensuing gold carbenoid adduct **III** by the remaining alkyne moiety. Cycloreversion of the resulting cyclopropene intermediate **IV**, the formation of which in gold catalysis is extremely rare, to give the gold carbenoid species **V** followed by Narazov cyclization would then be expected to provide 2,4a-dihydro-1*H*-fluorene derivatives.[5−8] Herein, we report the details of this chemistry that offers an expedient and chemoselective approach to this carbocyclic motif, present in many bioactive natural and synthetic compounds and functional materials,[9] in good to excellent yields. An ONIOM computational study on the origin of the observed selectivity was also performed by employing two different levels of quantum mechanical methods [ONIOM(QM:QM′)].[10]

Scheme 1. Gold-Catalyzed Reactivities of 1,*n*-Diyne Carbonates and Esters



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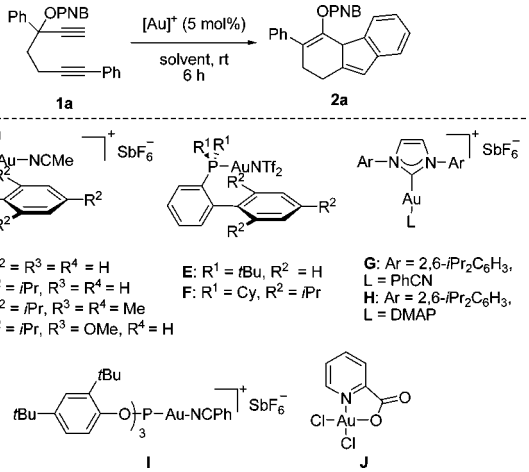
RESULTS AND DISCUSSION

We began our investigations by examining the gold-catalyzed cycloisomerizations of 1,6-diyne ester **1a** to establish the reaction conditions (Table 1).[11] This initially revealed that

Table 1. Optimization of the Reaction Conditions[a]



entry	catalyst	solvent	yield (%)[b]
1	**A**	CH_2Cl_2	71
2	**B**	CH_2Cl_2	67
3	**C**	CH_2Cl_2	78
4	**D**	CH_2Cl_2	52
5	**E**	CH_2Cl_2	12 (70)[c]
6	**F**	CH_2Cl_2	38 (50)[c]
7	Ph_3PAuCl	CH_2Cl_2	–[d]
8	AuCl	CH_2Cl_2	–[d]
9	**G**	CH_2Cl_2	62
10	**H**	CH_2Cl_2	–[d]
11	**I**	CH_2Cl_2	50
12	**J**	CH_2Cl_2	–[d]
13	**C**	PhMe	27
14	**C**	MeCN	–[d]
15	**C**	THF	–[d]

[a]All reactions were performed at the 0.2 mmol scale with catalyst:**1a** ratio = 1:20 in given solvent at room temperature for 6 h. PNB = *p*-nitrobenzoyl. [b]Isolated yield. [c]Reaction carried out at room temperature for 24 h; values in parentheses denote the yield of recovered starting material. [d]No reaction based on TLC and ^{1}H NMR analysis of the crude mixture.

treating **1a** with 5 mol % of Au(I) catalyst **A** in dichloromethane at room temperature for 6 h afforded **2a** in 71% yield (entry 1). The structure of the 2,4a-dihydro-1*H*-fluorene product was determined by NMR spectroscopic measurements and X-ray crystallography (Figure 1).[12] Our studies subsequently showed that when the reaction was repeated with the more sterically crowded gold(I) complex **C** in place of **A** as the catalyst, the product yield increased from 71 to 78% (entry 3).[13] In contrast, replacing **A** with the Au(I) phosphine complexes **B** and **D**–**F**, NHC–gold(I) (NHC = *N*-heterocyclic carbene) complex **G**, and gold(I) phosphite complex **I** as the catalyst was found to result in lower product yields of 12–67% (entries 2, 4–6, 9, and 11).[14] In the case of the reactions mediated by Au(I) phoshine complexes **E** and **F**, the substrate was also recovered in 70 and 50% yield, respectively (entries 5 and 6). With Au(I) phoshine complex **C** as the catalyst, a similar outcome was found with **2a** obtained in 27% yield on

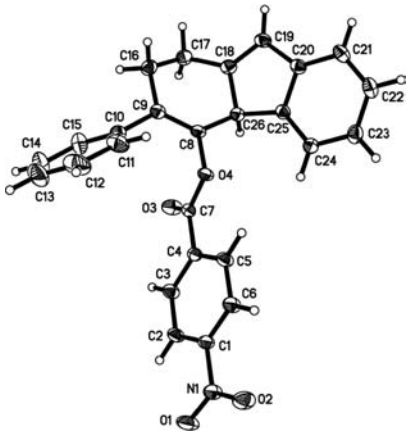


Figure 1. ORTEP drawing of **2a** with thermal ellipsoids at 50% probability levels.[12]

changing the reaction medium from dichloromethane to toluene (entry 13). In contrast, no reaction was detected in control experiments mediated by PPhAuCl, AuCl, NHC–gold(I) complex **H** or gold(III) complex **K**, or Au(I) complex **C** in polar solvents such as acetonitrile and THF (entries 7, 8, 10, 12, 14, and 15). On the basis of the above results, the reaction of **1a** in the presence of Au(I) complex **C** (5 mol %) as catalyst in dichloromethane at room temperature for 6 h provided the optimum conditions.

The scope of the present procedure was next assessed with a series of 1,6-diyne carbonates and esters, and the results are summarized in Table 2. In general, these experiments showed that with Au(I) complex **C** as catalyst, the reaction conditions proved to be broad and a variety of substituted 2,4a-dihydro-1*H*-fluorenes could be furnished in 44–93% yield from the corresponding substrates **1b**–**y**. Reactions of substrates containing a Bz (**1b**), Ac (**1c**), Cbz (**1d**), or Boc (**1e**) instead of a PNB migrating group were found to be well-tolerated under the reaction conditions and furnished **2b**–**e** in 52–80% yield. Likewise, starting 1,6-diyne esters with a pendant aryl (**1f**–**o** and **1q**–**r**), thiophene (**1p**), or cyclohexene (**1s**) functional group at the alkyne carbon center were found to proceed to give the corresponding tri-, tetra-, and pentacyclic adducts in 47–83% yield. The presence of other aryl motifs on the benzoate carbon center of the starting material (**1t**–**v**) was found to have little influence on the course of the reaction, with **2t**–**v** furnished in 53–76% yield. The reactions of substrates containing a cyclopropane ring on the benzoate carbon center (**1w** and **1x**) or methyl groups at the C5 position (**1y**) were observed to be the only exception. In these experiments, while the use of either gold(I) catalysts **C** or **G** gave similar product yields, the latter was found to form fewer impurities that were easier to remove by flash column chromatography. More notably, all the above examined cycloisomerizations also demonstrated that the ring-forming process occurs in a highly selective manner with the 1,4-diene isomer of the adduct only being furnished. Added to this, other than a number of unidentifiable decomposition products, no other cyclic adducts that could be formed from an initial 1,3-acyloxy migration step or concerted double cyclization pathway were detected by ^{1}H NMR analysis of the crude mixtures.

To provide further support as well as to gain a better understanding of the mechanistic premise put forward in Scheme 1, the following control experiments were performed (Scheme 2). In view of recent works showing the likely

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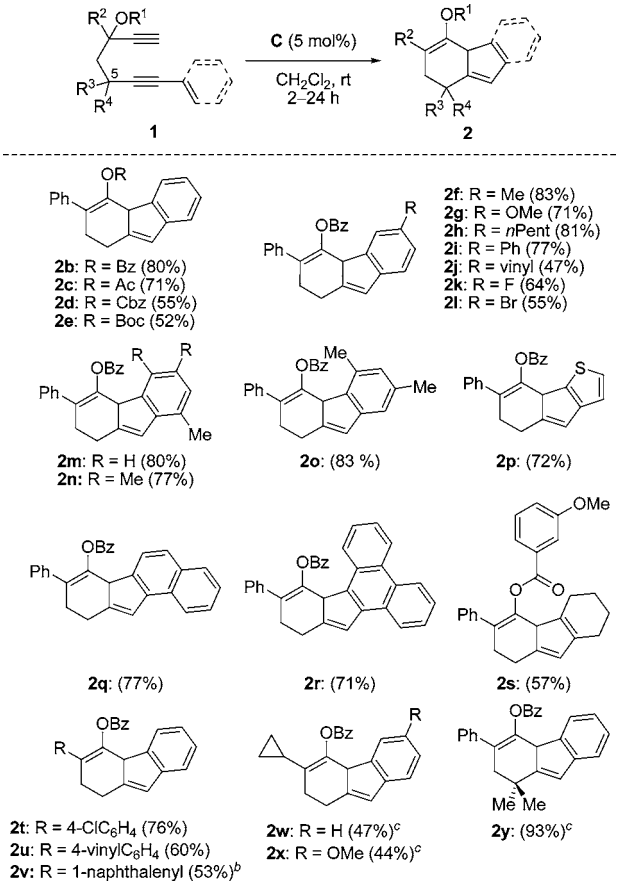
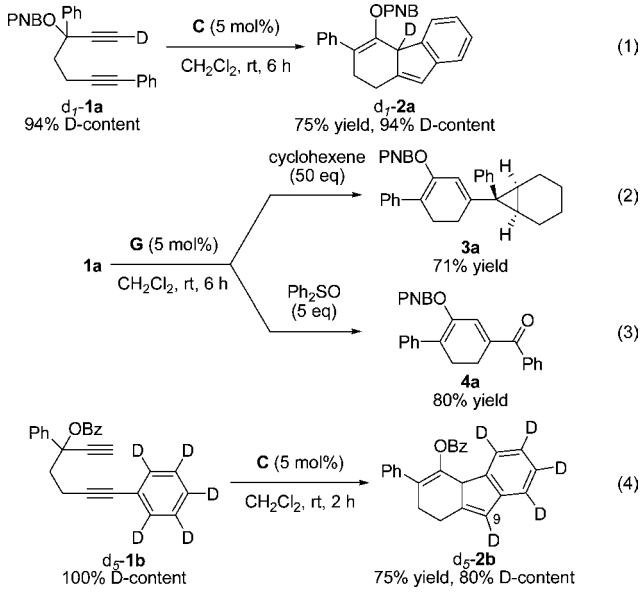
Table 2. Cycloisomerization of 1,6-Diyne Carbonates and Esters 1b–y Catalyzed by C[a]



[a]All reactions were performed at the 0.2 mmol scale with **C**:**1** ratio = 1:20 in CH_2Cl_2 at room temperature for 2–24 h. Values in parentheses denote isolated product yields. [b]Isolated as an inseparable mixture of diastereomers in a ratio = 1.1:1. [c]Reaction carried out with NHC–gold(I) complex **G** as the catalyst.

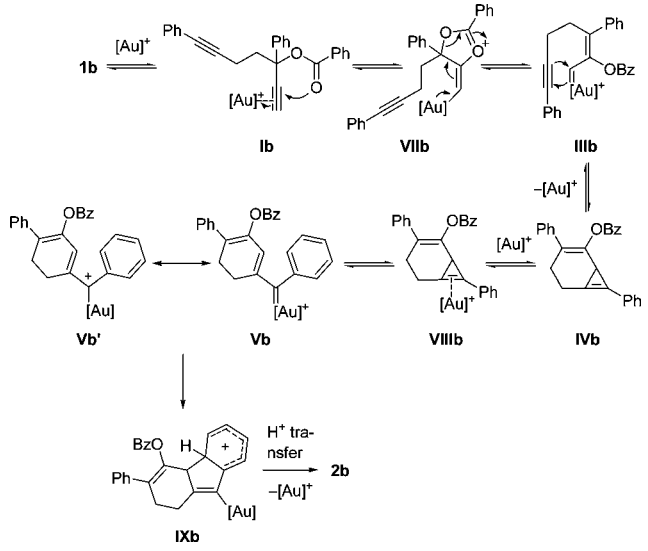
Scheme 2. Control Experiments with 1a, d_1-1a, and d_5-1b Catalyzed by C or G



involvement of Au(I)-activated alkynylgold(I) species in alkyne cycloisomerizations mediated by the metal catalyst,[15] we first examined the reaction of d_1-**1a** in dichloromethane with 5 mol % of gold(I) complex **C** under the conditions described in Scheme 2, eq 1. This gave d_1-**2a** in 75% yield and with a D content of 94%, based on ^{1}H NMR measurements, which led us to rule out the possible involvement of a dual activation pathway in which the alkyne terminus of **1** was activated by two molecules of the Au(I) catalyst. This was further supported by conducting the reaction again for a second time in the presence of an equimolar amount of **1l** and obtaining d_1-**2a** and **2l** as the only products in 60 and 65% yield, respectively, based on ^{1}H NMR analysis of the crude reaction mixture.[16] On the other hand, the posited participation of the gold carbenoid intermediate **V** shown in Scheme 1, eq 1, is supported by our findings when the reactions of **1a** were repeated with cyclohexene and Ph_2SO catalyzed by NHC–gold(I) complex **G** under the standard conditions (Scheme 2, eq 2 and 3).[17,18] In both test reactions, the production of the anticipated trapping products, the cyclopropane and ketone adducts **3a** and **4a**, was achieved in respective yields of 71 and 80%.[13] In a final control experiment, the origin of the proton source in the protodeauration process leading to product formation was also shown to likely come from the regeneration of aromaticity or an alkene bond in the Nazarov cyclization step.[7] Under the standard conditions depicted in Scheme 2, eq 4, subjecting d_5-**1b** to the gold(I) catalyst **C** was found to give d_5-**2b** in 75% yield and with a D content of 80% at the C9 position of the adduct, as determined by ^{1}H NMR measurements.

A tentative mechanism for the present gold(I)-catalyzed 2,4a-dihydro-1*H*-fluorene forming reaction is outlined in Scheme 3.

Scheme 3. Proposed Mechanism for Au(I)-Catalyzed Cycloisomerization of 1,6-Diyne Carbonates and Esters Represented by 1b



Using **1b** as a representative example, this might initially involve activation of the estereal alkyne moiety of the substrate by the Au(I) catalyst to give the gold(I)-coordinated complex **Ib**. This results in syn 1,2-migration of the carboxylate functional group to produce gold carbenoid adduct **IIIb** via 1,3-dioxin-1-ium intermediate **VIIb**. Trapping of this newly formed organogold species by the remaining C≡C bond may then provide the putative cyclopropene adduct **IVb**.[6] Further

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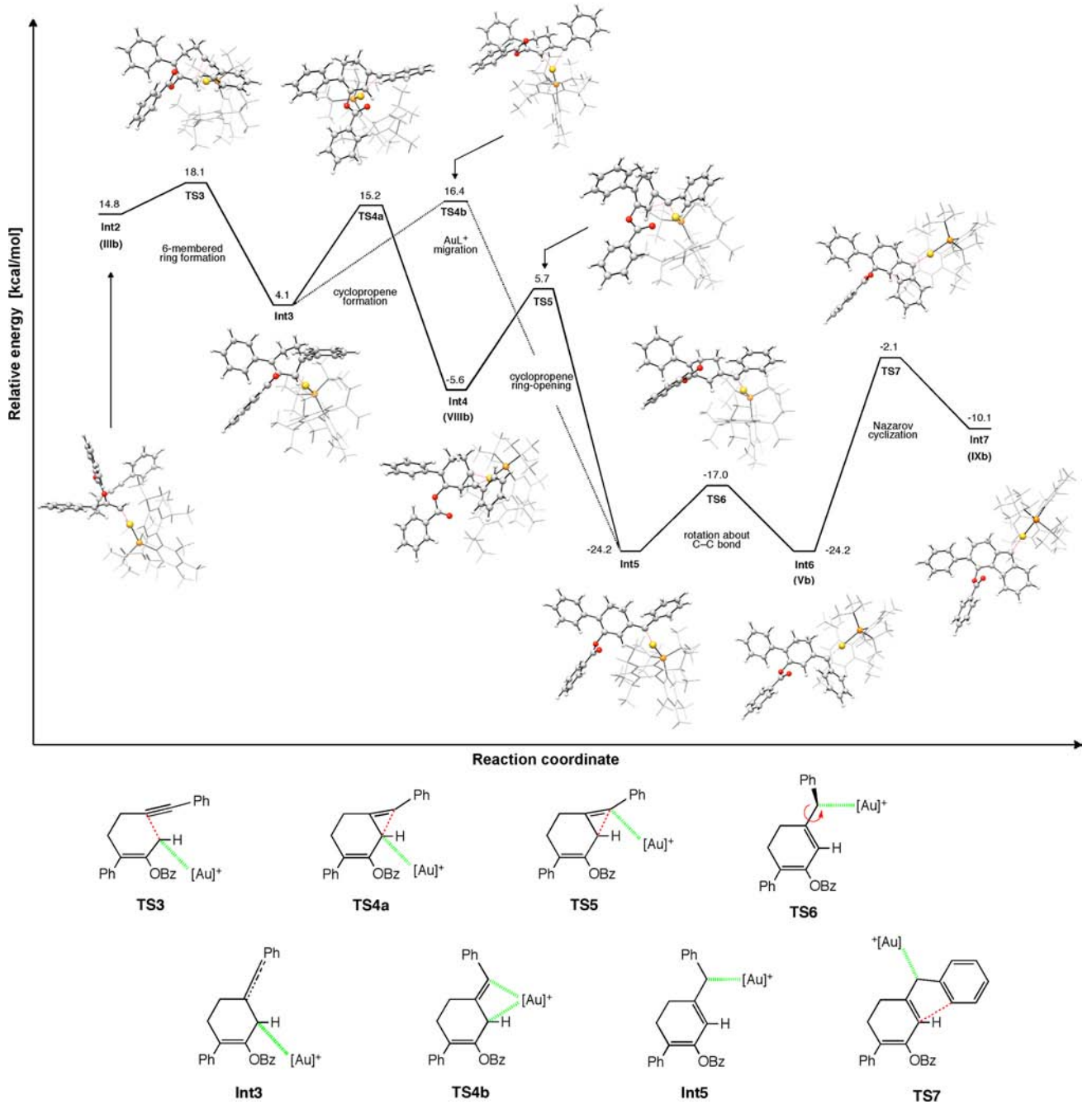

Figure 2. Reaction energy diagram (in kcal/mol) for the middle stage of the reaction, as obtained at the ONIOM(B3LYP/B3:B3LYP/B1)PCM//ONIOM(B3LYP/B2:B3LYP/B1) level with zero-point energy corrections.[10] An alternative pathway between **Int3** and **Int5** via **TS4b** is indicated by a dotted line. In the 3D figures, H, C, O, P, and Au atoms are colored white, gray, red, orange, and gold, respectively. The ball-and-stick representation is used for the high-level QM layer and the stick representation is used for the rest of the system. Schematic drawings of the transition states along with **Int3** and **Int5** are also given below the energy diagram. Relative energy values are given with respect to the energy of isolated **1b** and $[AuL(NCCH_3)]^+$ from catalyst **C**.

coordination of the π-acidic metal complex to the alkene bond of the bicyclic intermediate might next provide the gold(I)-activated species **VIIIb**. Subsequent electrophilic ring-opening of the cyclopropenyl gold moiety in **VIIIb** would give the second gold carbenoid adduct **Vb** and its gold-stabilized allylic carbocation isomer **Vb′**. This is the active species that undergoes Nazarov cyclization,[7] which upon rearomatization of the ensuing Wheland-type intermediate **IXb** followed by protodeauration would regenerate the gold(I) catalyst and deliver **2b**.

To further verify our proposed mechanism shown in Scheme 3, we undertook two-layer ONIOM(QM:QM′)[10] computational studies using Gaussian 09.[19] The B3LYP functional was used for both QM layers,[20] in combination with three different basis sets, i.e., LANL2MB (B1); SDD (for Au), 6-31G* (for others) (B2); and LANL2TZ(f) (for Au), 6-311+G(d,p) (for others) (B3).[21−23] Geometry optimizations and frequency calculations were performed at the ONIOM(B3LYP/B2:B3LYP/B1) level, and single-point energy calculations were done on optimized geometries at the ONIOM(B3LYP/

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B3:B3LYP/B1) level; for the latter, the dichloromethane solvent effect was taken into account with the IEFPCM (integral equation formalism variant of the polarizable continuum model) method.[24] UCSF Chimera was used to draw the molecules.[25] The ONIOM calculations produced a number of transition states and intermediates on the reaction pathway from **1b** to **2b**. Full geometric and energetic data are summarized in the Supporting Information, and key results are presented here (Figure 2). Our calculations show that an intermediate with a six-membered ring (**Int3**) is easily formed between **IIIb** and **VIIIb** via a transition state for ring closure (**TS3**). A particularly interesting feature of our delineated mechanism is that **Int3** undergoes another ring closure to generate a unique cyclopropene adduct **Int4** (**VIIIb** in Scheme 3) via **TS4a** with an energy barrier of 11.1 kcal/mol. This is followed by a cyclopropene ring-opening process through **TS5** that has an energy barrier of 11.3 kcal/mol. As such, this implied that, despite its transient formation, the relative ease in which the cyclopropene intermediate can undergo ring-opening makes it unlikely that the putative cyclic adduct can be trapped experimentally. Our calculations further suggest that there is an alternative pathway from **Int3** to **Int5** via **TS4b** that involves gold migration, as shown in Figure 2. As can be seen from the structure of **TS4b**, this transition state features the geometry of a four-membered ring that allows efficient 1,3-migration of the gold catalyst. However, **TS4b** turns out to be slightly higher in energy than **TS4a**, and thus, this alternative Au migration pathway should be slightly less favorable than that involving cyclopropene formation via **TS4a**. During the reaction, Nazarov cyclization of **Int6** to **Int7** has the highest energy barrier (22.1 kcal/mol), suggesting that the prior intermediates [**Int5** and **Int6** (**Vb** in Scheme 3)] should be relatively long-lived. For the reaction steps after the formation of Wheland-type intermediate **Int7** (**IXb** in Scheme 3), the benzoyl group was found to play a pivotal role in assisting the 1,3-proton migration by accepting and donating the proton appropriately to yield the final product (see Figure S2 in the Supporting Information). These calculated results are also consistent with the experimentally observed preferential formation of **3a** and **4a** and the high D content found at the C9 position of d_5-**2b** as reported in Scheme 2, eq 2−4.

CONCLUSIONS

In summary, we have developed a gold(I)-catalyzed strategy for the construction of highly functionalized 2,4a-dihydro-1*H*-fluorenes from the respective 1,6-diyne carbonates and esters. Our studies suggest that the tandem process was initiated by a 1,2-acyloxy migration step previously not seen in this class of substrates. It also hints at the possible involvement of an in situ formed cyclopropene intermediate, examples of which have remained conspicuously rare in gold catalysis. Exploration of the scope and synthetic applications of the present reactions are in progress and will be reported in due course.

EXPERIMENTAL SECTION

General Considerations. All reactions were performed in oven-dried glassware under an argon atmosphere. Unless specified, all reagents and starting materials were purchased from commercial sources and used as received. Compound **1** was prepared following literature procedures.[11] Gold complexes **A**−**J** were purchased from commercial sources or prepared following literature procedures.[11] Solvents were purified following standard literature procedures. Analytical thin-layer chromatography (TLC) was performed using precoated silica gel plate. Visualization was achieved by UV light (254 nm). Flash chromatography was performed using silica gel and gradient solvent system (EtOAc:*n*hexane as eluent). ^{1}H and ^{13}C NMR spectra were recorded on 300, 400, and 500 MHz spectrometers. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as s (singlet), br s (broad singlet), d (doublet), t (triplet), dd (doublet of doublets), or m (multiplet). The number of protons (*n*) for a given resonance is indicated by *n*H and coupling constants are reported as a *J* value in hertz. Infrared spectra were recorded on a FTIR spectrometer. Solid and liquid samples were examined as a thin film between NaCl salt plates. Low-resolution mass spectra were determined on a mass spectrometer and are reported in units of mass to charge ratio (*m*/*z*). High-resolution mass spectra (HRMS) were obtained on a LC/HRMS TOF spectrometer using simultaneous electrospray (ESI).

General Procedure for Gold Complex C Catalyzed Cycloisomerization of 1,6-Diyne Carbonates and Esters 1 to 2,4a-Dihydro-1*H*-fluorene Derivatives 2. To a solution of 1,6-diyne carbonate or ester **1** (0.2 mmol) in anhydrous CH_2Cl_2 (4 mL) was added gold(I) complex **C** (10 μmol). The reaction mixture was stirred at room temperature for 2−24 h until TLC analysis indicated that the reaction was complete. The reaction mixture was then concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*-hexane:EtOAc:CH_2Cl_2 = 50:1:1) to give the title compound.

General Procedure for Control Reactions of 1a with Cyclohexene and Diphenyl Sulfoxide Catalyzed by Gold Complex G. To a 2 mL CH_2Cl_2 solution containing gold(I) complex **G** (10 μmol) and cyclohexene (10 mmol) or diphenyl sulfoxide (1.0 mmol) was added a solution of **1a** (0.2 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was stirred at room temperature for 6 h until TLC analysis indicated that the reaction was complete. The reaction mixture was then concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*-hexane:EtOAc:CH_2Cl_2 = 50:1:1 or *n*-hexane:EtOAc = 7:1) to give the product **3a** or **4a**, respectively.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, crystal structure data (CIF), raw ONIOM data, XYZ coordinates, and complete ref 19. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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