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Dual Gold Catalysis

Mechanistic Switch in Dual Gold Catalysis of Diynes: $C(sp^3)$–H Activation through Bifurcation—Vinylidene versus Carbene Pathways**

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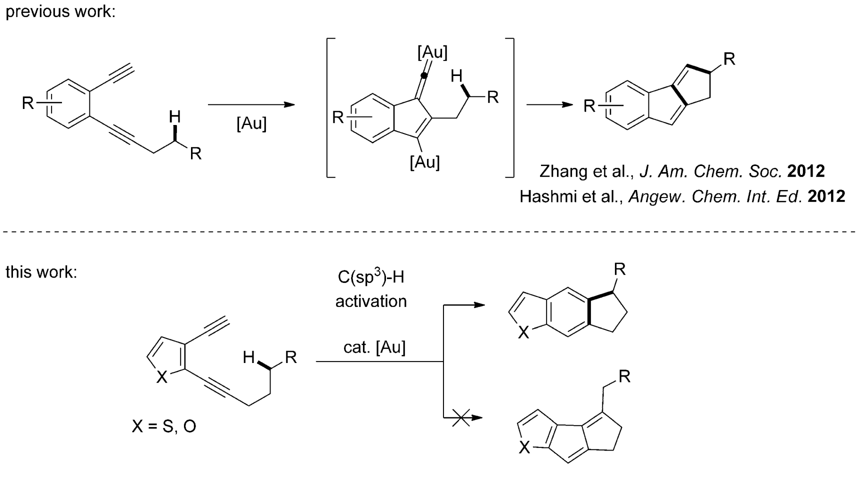
Transition-metal-catalyzed C–H activation and functionalization is an area of broad interest as it enables the rapid creation of complex molecules in an atom-economic fashion.[1] The selective formation of C–C bonds by means of C–H activation of unactivated $C(sp^3)$–H bonds without any directing groups in close proximity is still a challenging task in transition-metal catalysis and a highly active field of current research.[2]

In the last decade gold catalysis has developed into a powerful synthetic tool in organic synthesis.[3] While there are some reports on the heterolytic cleavage of $C(sp^3)$–H bonds by employing a gold-catalyzed hydride transfer, usually special electronically or structurally facilitated hydride-transfer steps are required.[4] Very recently, Zhang's group and our group could show that gold vinylidenes[5] as highly reactive intermediates can efficiently activate $C(sp^3)$–H bonds,[6] even of alkanes in an intermolecular manner.[6c]



Scheme 1. Au-catalyzed diyne cyclizations involving $C(sp^3)$–H activation.

In the intramolecular reaction of alkyl chains attached to the aromatic diyne substrates, selective activation of the β-hydrogen atom was observed, providing products with a fulvene substructure (Scheme 1, top). Based on computational results of Zhang et al., who reported on a bifurcation[7] pathway in the cyclization event of diynes,[6a] we envisioned that the use of 2,3-diethynylthiophenes as heteroaromatic precursors, which have a terminal C≡C bond, could lead to the unprecedented 6-*endo-dig* cyclization mode; the intermediate of the 5-*exo-dig* cyclization with the anellation of two five-membered rings should be less stable than the intermediate of the 6-*endo-dig* cyclization with the anellation of one five- and one six-membered ring. This would further expand the scope of the gold σ,π dual-activation chemistry.[8] Instead of the expected thiofulvene substrates, benzothiophenes should be observed (Scheme 1, bottom). The scope of this reaction and mechanistic investigations, indicating an alternative pathway besides the vinylidene chemistry, are discussed herein.

Heteroaromatic backbones were of particular interest for us as, apart from the electronic effect, the widening of the alkyne–alkyne angle from 60° to 70° should have a strong effect on the chemoselectivity.[9] Our initial experiment addressed the transformation of 2,3-diethynylthiophene **1a** with $IPrAuNTf_2$ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, Tf = trifluoromethylsulfonyl) as the catalyst (Scheme 2, top). To our delight, instead of a thiofulvene that would arise from the 5-*endo*-pathway (the analogue of the product formed from the corresponding benzene derivative), indanothiophene **2a** was obtained as the exclusive product in moderate yield. Shifting the alkyl substituent from the C≡C bond at the 3-position of the thiophene unit to the C≡C bond at the 2-position (**1b**) resulted in the clean formation of regioisomer **2b** in significantly higher yield. As in the reaction with **1a**, not even traces of the five-membered pentalene product were observed (Scheme 2). So far reports on the transition-metal-catalyzed cyclization of enediynes with five-

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[+] Crystallographic investigation.

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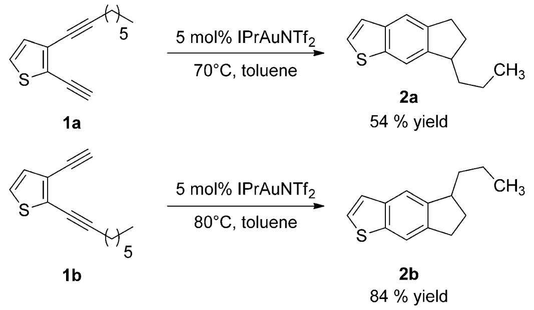
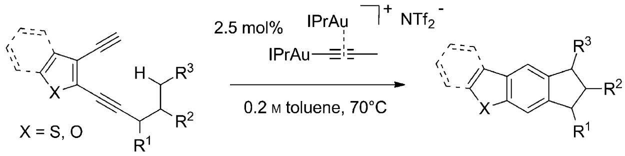
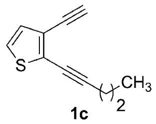
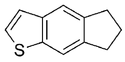
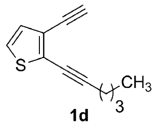
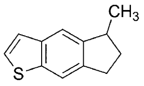
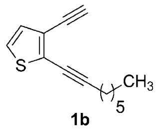
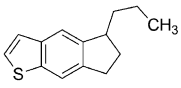
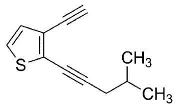
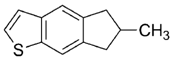
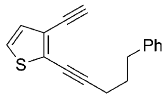
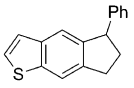
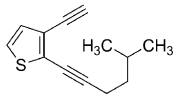
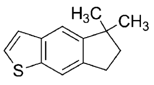
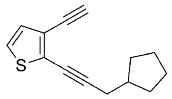
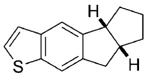
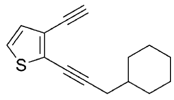
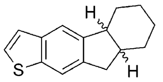
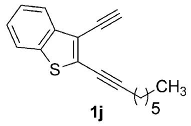
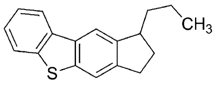
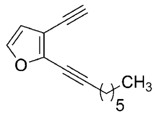
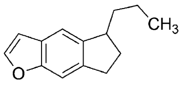


Scheme 2. Au-catalyzed synthesis of indanothiophenes: role of the position of the terminal alkyne.

Table 1: Au-catalyzed synthesis of indanothiophenes, dibenzothiophenes, and benzofurans.[a]



Entry	Substrate **1**	Product **2**	*t* [h]	Yield [%]
1	 **1c**	 **2c**	1.5	81
2	 **1d**	 **2d**	2	90
3	 **1b**	 **2b**	2	87
4	 **1e**	 **2e**	2.5	50
5	 **1f**	 **2f**	2	74
6	 **1g**	 **2g**	1.5	73
7	 **1h**	 **2h**	2.5	61[b]
8	 **1i**	 **2i**	6	56[c]
9	 **1j**	 **2j**	2	81
10	 **1k**	 **2k**	6.5	56

[a] Reactions were performed on a 0.2 mmol scale in toluene (0.2 M) at 70 °C. All yields refer to isolated product. [b] Single diastereomer. [c] d.r. = 1:3.

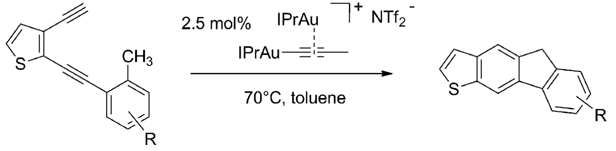
membered heteroaromatic units are not very common.[10] There are reports on the Au-catalyzed addition of external or internal nucleophiles to enediynes, which undergo cyclization after the first addition event, but these systems are not undergoing C–H bond activation and the reaction follows a very different mechanism.[11] The connectivity in the cycloisomerization product is unusual as well. With six-membered-ring substrates Pt^{II} and sometimes Ru generate products with 2,3 instead of 3,4 ring fusion; other Ru catalysts give only poor yields of products with similar connectivity.[12]

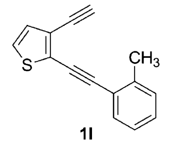
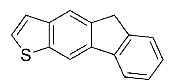
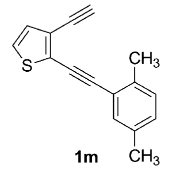
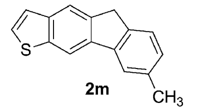
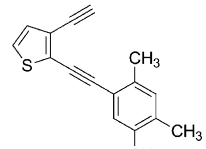
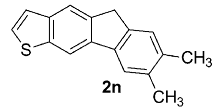
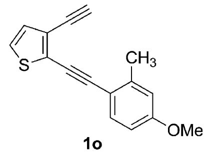
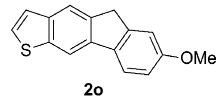
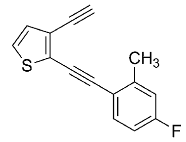
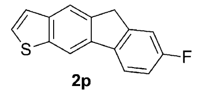
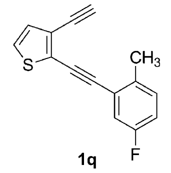
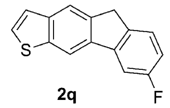
After synthesizing a small library of 2,3-diethynylthiophenes by a novel sequential one-pot tandem Sonogashira strategy,[9] we performed catalyst-screening experiments on two substrates.[9] To our delight, the dual-activation catalysts previously developed in our group[13a] turned out to be ideal catalysts. Bulky phosphane ligands such as $BrettPhosAuNTf_2$ and $XPhosAuNTf_2$ (BrettPhos = 2-(dicyclohexylphosphino)-3,6-dimethoxy-2′,4′,6′-triisopropyl-1,1′-biphenyl, XPhos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl) performed equally well in terms of selectivity, but in general longer reaction times were required. This is in accordance with a prolonged initiation phase for the generation of the gold acetylide.[5a] Simple precatalysts such as AuCl and $PtCl_2$ gave no desired product.

Next we investigated the scope of this transformation (Table 1). By choosing the appropriate alkyl chain length, it is possible to perform a $C(sp^3)$–H insertion into a methyl group, generating the unsubstituted indano[5,6-*b*]thiophene scaffold (Table 1, entry 1). Extending the alkyl chain length results in the selective activation of a methylene group, regardless of whether unactivated (Table 1, entries 2 and 3) or benzylic hydrogens (entry 5) are available. If enantiotopic methyl groups are present, it is possible to create a stereocenter in the 6-position of the indanothiophene substructure (Table 1, entry 4). It is remarkable that a methine group can also be selectively activated giving access to higher substituted products with quaternary centers (Table 1, entry 6). C–H groups in a cycloalkyl substituent can be activated as well. While the cyclopentane fragment smoothly delivered the polycyclic indanothiophene exclusively as the *cis* diastereomer (Table 1, entry 7), a mixture of diastereomers was obtained for the cyclohexane analogue (entry 8). Instead of starting with the 2,3-diethynylthiophenes, it is equally possible to employ the corresponding benzothiophenes. After the gold catalysis benzo[*b*]indano[5,6-*b*]thiophene **2j** was obtained in good yield (Table 1, entry 9). The transformation could also be extended to furans, but the yield dropped significantly (Table 1, entry 10). The assignment of the indanothiophene structure was unambiguously proven by an X-ray crystal structure analysis[9,14] of compound **2j**.

As we could selectively address the γ-C(sp^3)–H bond in the presence of other C(sp^3)–H bonds, we were interested in achieving a benzylic C–H activation even in the presence of a C(sp^2)–H bond in β-position to the alkyne.[15] While the corresponding (2-ethynylphenyl)alkynes insert into the β-C(sp^2)–H bond giving access to dibenzopentalenes,[6c] fluorenothiophenes were obtained as single products for the five-membered thiophene unit (Table 2). As these compounds have a high potential for applications in material science[16] and are difficult to access otherwise, this new approach is highly interesting. The scope of this reaction is broad as well, and different substitution patterns on the aromatic ring are tolerated. Electron-rich diynes (Table 2, entries 1–4) as well as electron-poor (entries 5 and 6) substrates can be employed. It is noteworthy that with the very electron-rich substrate **1o** only a few turnovers could be achieved with the dual-activation catalyst. A possible explanation could be the formation of a highly stable *gem*-diaurated intermediate inhibiting the catalytic cycle; a similar stabilization by donor atoms was also observed by Gagné and co-workers.[17] This assumption was underlined by using catalytic amounts of *t*BuXPhosAuNTf$_2$, a catalyst with a sterically demanding ligand which should destabilize *gem*-diaurated Au compounds and therefore restore catalytic activity. Indeed with **1o** complete conversion and good yields were observed. Electron-deficient fluorinated compounds **1p** and **1q** could also be transformed into the corresponding fluorinated fluorenothiophenes in good yields (Table 2, entries 5 and 6). The X-ray crystal structure analysis of compound **2l** clearly proves the connectivity of the product.[9,14]

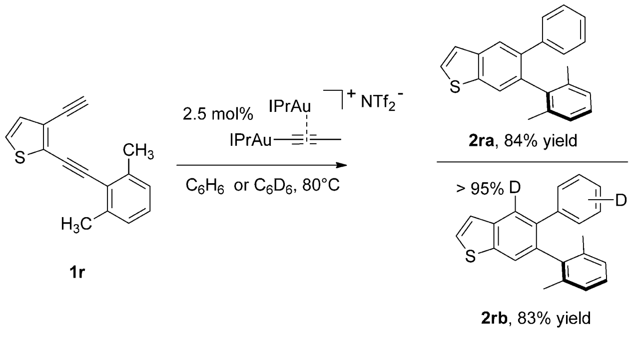
Table 2: Au-catalyzed synthesis of fluorenothiophenes.[a]



Entry	Substrate **1**	Product **2**	Yield [%]
1	 **1l**	 **2l**	77
2	 **1m**	 **2m**	74
3	 **1n**	 **2n**	82
4	 **1o**	 **2o**	84[b]
5	 **1p**	 **2p**	92
6	 **1q**	 **2q**	79

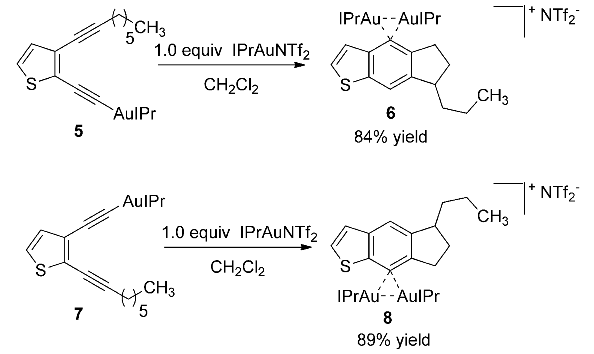
[a] Reactions were performed on a 0.2 mmol scale in toluene (0.05 M) at 70 °C. All yields refer to isolated product. [b] 5 mol% *t*BuXPhosAuNTf$_2$ was used instead.

With 2,6-dimethylphenyl-substituted diyne **1r** no formation of the desired fluorenothiophene was observed; instead a solvent molecule was incorporated into the product, forming benzothiophene **2ra** (Scheme 3). This gold-catalyzed hydroarylating aromatization takes a different reaction pathway, which is in accordance with the recent discoveries in the field of Au–vinylidene chemistry.[5a] A possible reason for this reaction pathway is the steric hindrance of the two methyl groups in *ortho* position which lead to a twist of the aromatic ring out of the plane of the molecule. Instead of the intramoleculary available hydrogen atoms, which are out of reach, a solvent molecule is attacked by the electrophilic center, leading to a product of formal intermolecular C(sp^2)–H activation. (Incorporation of solvent molecules in the reactions of the substrates shown in Table 2 was never evident by GC–MS or NMR methods.) Interestingly, when deuterated benzene was employed the β-product **2rb** formed exclusively and also the deuterium was selectively transferred to only one of the two possible positions. When we used a 1:1 mixture of benzene/[D$_6$]benzene, we observed a 1:1 mixture of **2ra** and **2rb** without formation of any crossover products.

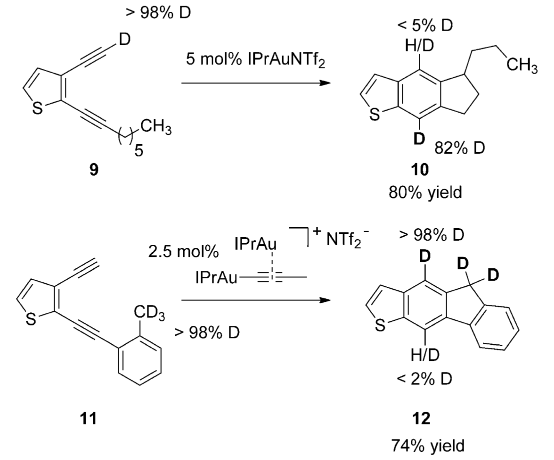


Scheme 3. Experiments with the sterically hindered substrate **1r**.

To gain further mechanistic insight, stoichiometric experiments were conducted. Treating the gold acetylide of thiophene diyne **5** with a stoichiometric amount of IPrAuNTf$_2$ resulted in the formation of the *gem*-diaurated species **6** (Scheme 4). Slow vapor diffusion of pentane into a solution of **6** in dichloromethane at −30 °C gave UV/Vis-fluorescent



Scheme 4. Stoichiometric experiments capturing arylgold intermediates as diaurated species.



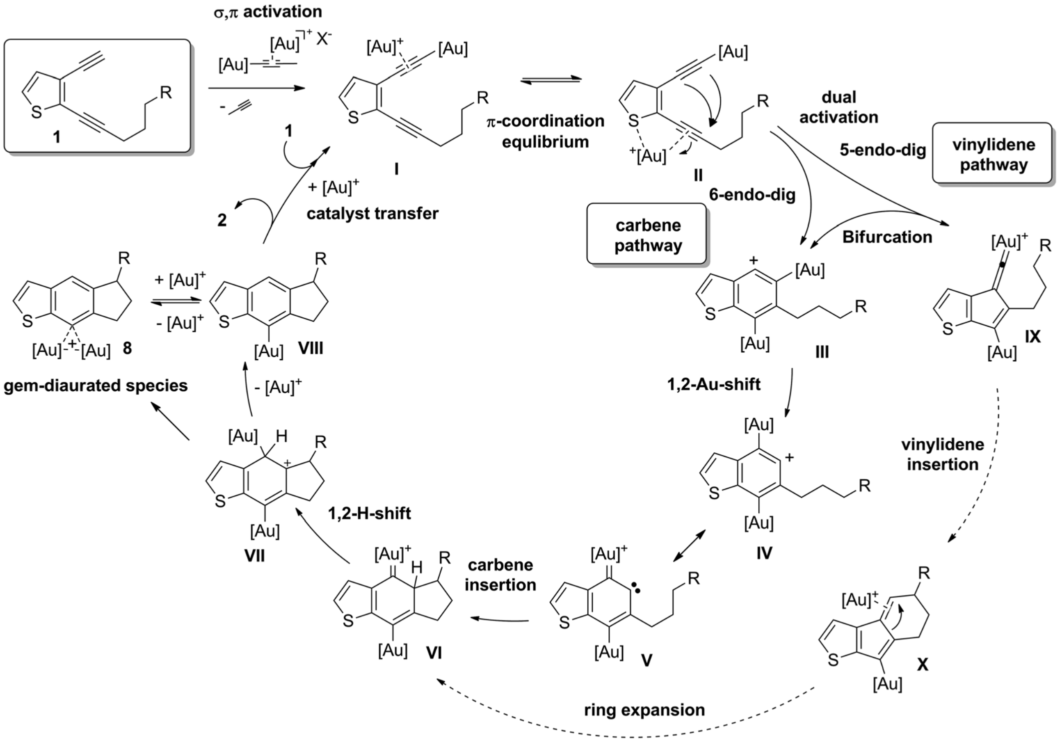
Scheme 5. Deuterium-labeling experiments.

(even in the solid state)[9,18] orange crystals suitable for X-ray diffraction.[9,14] Several IR spectroscopic measurements of the X-ray sample and the bulk material proved that only this *gem*-diaurated compound is formed.[9] Interestingly, when the same procedure was employed for the regioisomer **7**, the *gem*-diauration occurred at the opposite position. In this case crystals suitable for X-ray diffraction could be obtained as well.[9,14] These structures confirm the connectivity of the products and unambiguously prove the relevance of diaurated Au compounds in these transformations. In accordance to earlier results,[5,6] these species can be seen as resting states of the dual-catalysis cycle.

Furthermore, we performed deuterium-labeling studies to gain insight into the nature of the proton transfer leading to the two benzothiophene H atoms (Scheme 5). Deuterium labeling of the terminal C≡C unit resulted in high deuterium enrichment on the arene position that was diaurated in the stoichiometric reaction. The second arene proton was unaffected. The gold-catalyzed reaction of the deuterated compound **11** resulted in exclusive deuterium enrichment at the other arene position. This clearly indicates a completely selective reaction mechanism.

Our experiments clearly indicate a gold-catalyzed dual-activation mode (Scheme 6). In order to gain further inside and to support our outlined mechanism, we performed DFT calculations at the B3LYP/cc-pVDZ level of theory on the main intermediates and transition states (Figure 1; for a complete energy profile see the Supporting Information).[9]

In line with the related transformations,[5,6] the σ,π dual-activation cycle is initiated by the precatalyst, which generates the gold-bonded thiophene acetylide **II**. According to the work of our group and others, the Au fragment coordinates



Scheme 6. Proposed catalytic cycle:6-*endo-dig* versus 5-*endo-dig* cyclization.

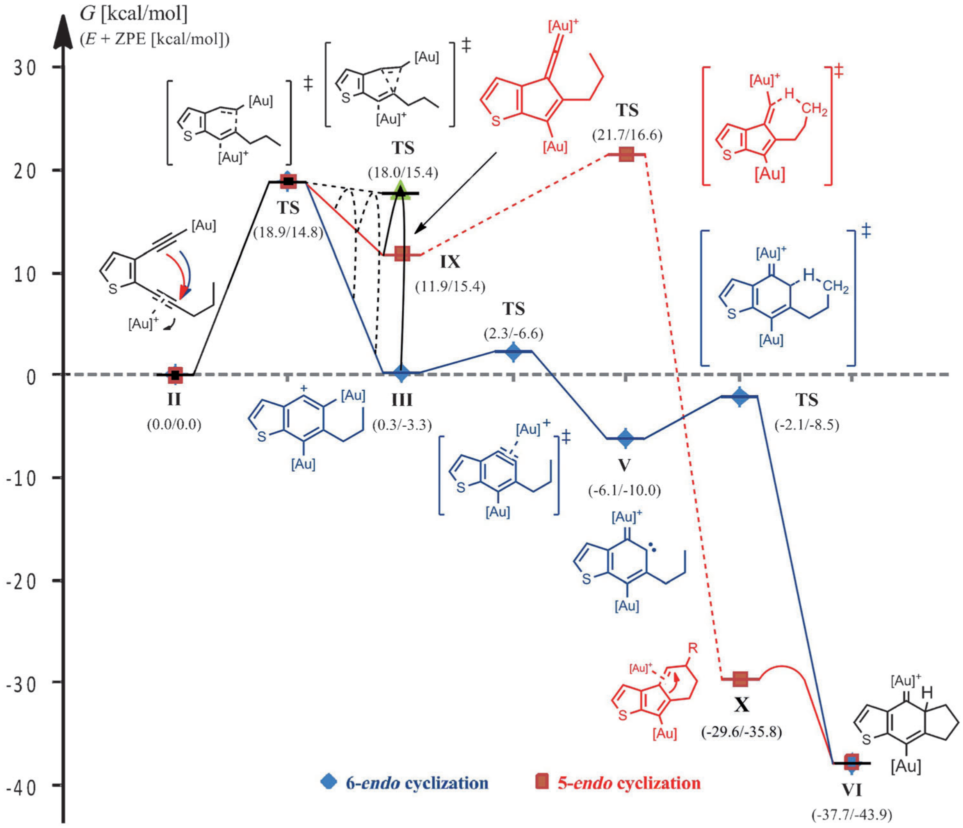


Figure 1. Calculated energy profile for the Au-catalyzed diyne cycloisomerization. TS = transition state, E + ZPE = electronic energy + zero point energy.

preferentially to the Au acetylide as shown in **I**.[13,19] An additional coordination to the sulfur atom of the thiophene potentially shifts the equilibrium to **II** (which also would explain the higher reactivity of substrates bearing the alkyl-substituted alkyne in the 2-position of the thiophene). For the generation of product **2** two potential pathways must be considered: a 6-*endo-dig* cyclization leading to intermediate **III** and a 5-*endo-dig* cyclization generating the gold–vinylidene **IX**. Until now, six-membered aromatic products were never observed to form when C–H bonds were available for an intramolecular reaction. The experiments described here indicate a switch in the bifurcation pathway by a slight change of the aromatic backbone.[20] Indeed, we could locate a transition state connecting the 6-*endo* cyclization product **III** and the 5-*endo* cyclization product **IX** typical for a ridge–valley situation which would be in accordance with the work of Zhang et al.[6a] We assume that the two cyclization products equilibrate via this transition state and that the selectivity is controlled by the subsequent reaction step.[21] As the C–H insertion event of the Au–vinylidene is calculated to be higher in energy than the equilibration over the ridge–pathway connecting **IV** and **IX**, this equilibration seems to be reasonable. The 6-*endo* cyclization product **III**, which is energetically preferred by about 10 kcal mol^{-1} with regard to the 5-*endo* cyclization product **IX**, undergoes a fast and exothermic 1,2-Au migration to form carbene **IV** via an Au^{+}–aryne-type transition state.[22] C–H insertion of **IV** and a 1,2-hydride shift lead to the final diaurated compound **8** (this is also in accord with the labeling experiments).

Alternatively, we cannot rule out a 5-*endo-dig* cyclization forming the gold(I)–vinylidene **IX**, which after selective insertion into the δ-C(sp^3)–H bond (**X**) and subsequent ring expansion would lead to the same intermediate **VI.** Based on our computational results this pathway is energetically disfavored.[9]

In summary, we report a gold-catalyzed cycloisomerization of 2,3-diethynylthiophenes with a terminal C≡C bond affording indanothiophenes and fluorenothiophenes. Variation of the backbone of the diyne system opens up a new pathway for the intramolecular C(sp^3)–H activation event. Based on theoretical work we postulate a switch in selectivity along a bifurcation pathway, for the first time leading to products through σ,π dual activation and a 6-*endo* diyne cyclization. Deuterium-labeling studies together with the capture and characterization of *gem*-diaurated gold intermediates, which serve as a potential resting state in the catalytic cycle, are in agreement with the new reactivity of the dual gold catalysis.

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[22] The optimized structure of carbene **IV** shows a high degree of distortion towards a bent Au–allene, which is stabilized through the *para*-digold substitution, and this distorsion acts as driving force.