ChemComm

COMMUNICATION

View Article Online
View Journal

Cite this: DOI: 10.1039/d5cc06478c

Received 14th November 2025,
Accepted 16th December 2025

DOI: 10.1039/d5cc06478c

rsc.li/chemcomm

Controlled gold-catalyzed 5-*exo-dig* cyclization of 3-sulfur-substituted 1,3-dien-5-ynes for synthesizing fulvenes and the *in situ* reaction with indoles

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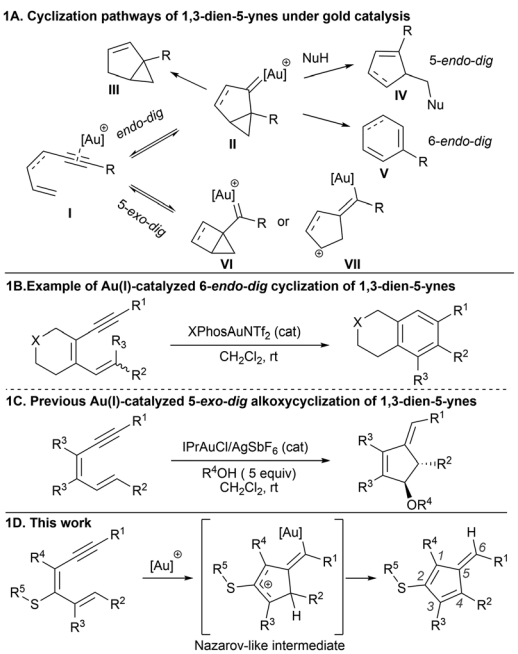
Densely substituted fulvenes have been synthesized from 1,3-dien-5-ynes by gold-catalyzed 5-*exo-dig* cyclization, determined by the S-substituent. In addition, these fulvenes interact with the gold catalyst, forming fulvenium intermediates that react with indoles in a one-pot two-step protocol to synthesize 3-(alkylidene-cyclopent-2-en-1-yl)-1*H*-indoles, by the cooperative action of gold and Brønsted acid catalysts.

1,3-Dien-5-ynes exhibit diverse and rich reactivity, allowing the construction of cyclic compounds.[1] Among the strategies used to activate these species, gold catalysis is a selective and efficient strategy for forming densely functionalized carbocyclic cores.[2] After alkyne activation by gold, 1,5-enynes almost entirely undergo *endo* cyclizations (Scheme 1A),[3] typically involving the attack of nucleophiles. Similarly, 1,3-dien-5-ynes **I** experience analogous reactions (Scheme 1A) *via* 5-*endo-dig*,[4] 6-*endo-dig* (Scheme 1B),[5] or even 7-*endo-dig* cyclizations when using 1,3,5-trien-7-ynes.[6] By contrast, the 5-*exo-dig* pathway in 1,5-enynes is significantly more challenging, as evidenced by its limited observation. This pathway has been reported as a side reaction in two pioneering works where *endo*-cyclization processes were the primary reaction.[7] Only recently, we successfully directed the reactivity exclusively toward the 5-*exo-dig* pathway in the alkoxycyclization reactions of (*E*)-1-monosubstituted 1,3-dien-5-ynes (Scheme 1C).[8] The complications in achieving the 5-*exo* cyclization have been attributed to the nature of the intermediate cyclopropyl gold carbene.[9] The favorable formation of bicyclo[3.1.0]hexane-type intermediates **II** leads the cyclization to *endo*-type processes (**III–V**), as opposed to the elusive alternative bicyclo[2.1.0]pentane-type intermediates **VI** required for *exo* processes. DFT calculations[10] have suggested that these gold intermediates display both notable cyclopropyl (**VI**) character and a marked cationic behavior (**VII**), which is particularly pronounced in the case of 1,3-dien-5-ynes, allowing the irreversible trapping of these intermediates by primary alcohols.[8]

In the absence of the external nucleophile, 1,3-dien-5-ynes exclusively evolve through *endo* pathways. In this context, dienynes adequately substituted with electron-rich groups could stabilize key intermediates. We hypothesized that a thioether at the C3 position of the 1,3-dien-5-ynes, which are easily accessible from the corresponding 1-halo-2-thio-1,3-dienes, could provide exclusively 5-*exo-dig* cyclization modes through a thio-Nazarov[11] pathway (Scheme 1D).

Densely substituted pentafulvenes have exceptional electronic properties and are valuable precursors in diverse transformations.[12] A fine-tuning of their electronic properties and reactivity is easily accomplished by the nature of the substituents of the



Scheme 1 (A) Reaction patterns of 1,3-dien-ynes under Au(I) catalysis. (B) 6-*Endo-dig* cyclization of 1,3-dien-5-ynes. (C) Au(I)-catalyzed 5-*exo-dig* alkoxycyclization of 1,3-dien-5-ynes. (D) This work.

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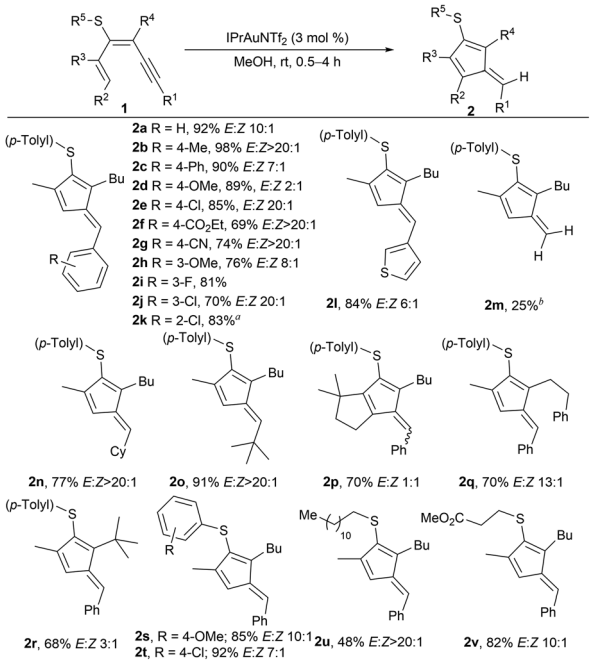
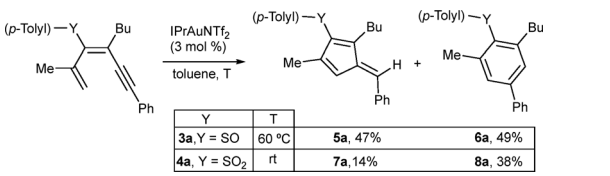
fulvene. The synthesis of polysubstituted benzofulvenes[13,14] and non-fused pentafulvenes[15] has attracted continuous interest. Metal-catalyzed protocols are practical in several cyclization reactions.[14,15] Gold complexes by alkyne activation[16] have enabled the design of elegant fulvene synthesis. In most cases, benzofulvenes were formed, and only the gold-catalyzed cycloisomerization of furan/ynes with a two-carbon tether in between the furan and the alkyne afforded enal or enone-decorated non-fused pentafulvenes *via* a cascade reaction involving 6-endo-dig cyclization followed by a furan ring-opening reaction.[17] As well, 1,5-diynes have been used for preparing benzofulvenes,[18] also pentalenes[19] and azulenes.[20] Also, benzofulvenes have been obtained from 1,6-diynes as starting materials,[21] by the 5-*endo-dig* cyclization of *o*-alkynyl styrenes,[4e] from benzophenones by addition of propargyl silanes,[22] from *o*-alkynyl benzaldehydes and diazo compounds,[23] by rearrangement of alkynyl α,β-epoxy ketones,[24] and substituted 3-propargyl indoles.[25]

To test our hypothesis, we prepared 1,3-dien-5-yne **1a** bearing at position C3 a *p*-tolylthio substituent through the coupling of an alkyne with a sulfur-decorated halodiene,[26] available from propargyl sulfides.[27] After some optimization, evaluating different catalysts and solvents (see the SI), **1a** was efficiently converted into fulvene **2a** in high yields, using $IPrAuNTf_2$ as a catalyst in MeOH under open air (Scheme 2), achieving similar yields under an inert atmosphere. Interestingly, using toluene as the solvent also yielded fulvene **2a** to a similar extent to that of MeOH. Then, we studied the reaction scope by varying the aryl substituent at the R^1 position (Scheme 2). Various *para*-substituted arenes were successfully converted into the corresponding fulvenes with arenes substituted with an alkyl or an aryl group (**2b** and **c**), a strong electron-donating group (OMe) (**2d**), or halides (**2e**). Notably, strong electron-withdrawing groups (EWG) afforded the fulvenes **2f** and **g** almost as a single diastereoisomer. Both *meta* (**2h–j**) and *ortho*-substituted arenes (**2k**) were well-tolerated, although in this last case, the catalytic system $(t\mathrm{Bu})_3\mathrm{PAuCl}/\mathrm{AgNTf_2}$ was used. Although this phosphine and the IPr ligand bear similar buried volumes,[28] the shorter Au–C bond length (1.99 Å) relative to the Au–P bond length in phosphines (typically 2.23 Å) could cause sterically unfavorable interactions with bulkier substrates, as shown using the topographic steric maps calculated with both ligands using SambVca2 (see the SI).[29] A heteroaryl group at R^1, such as 3-thienyl, also yielded fulvene **2l**. In addition, dienynes bearing TMS (**1m**) or (cyclo)alkyl (**1n** and **o**) groups at R^1 provided the fulvenes in high yields with excellent diastereoselectivities. Interestingly, with dienyne **1m**, the C–Si bond cleavage afforded fulvene **2m**, unsubstituted at the exocyclic position. Alkyl groups at R^2, R^3, or R^4 positions afforded products **2p–r**. The bulky *tert*-butyl group provided lower diastereoselectivity. Various aryl or alkyl groups at the S-atom were well tolerated, obtaining the fulvenes in high yields and comparable diastereoselectivity (**2s–v**).

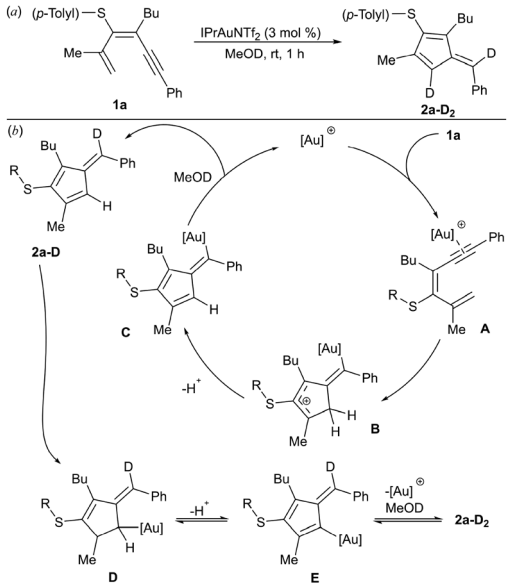
The influence of the organosulfur substituent was evaluated by subjecting 1,3-dien-5-ynes bearing sulfoxide (**3a**) or sulfone (**4a**) groups to the reaction (Scheme 3). Using MeOH as a solvent, no fulvenes were observed, and only products derived from the competitive addition of MeOH to the triple bond were detected. To avoid this path, the reaction was performed in toluene. In this case, sulfoxide **3a** gave rise to fulvene **5a** derived from the 5-*exo-dig* pathway, and a benzene derivative **6a** arising from a 6-*endo-dig* cyclization in a 1 : 1 ratio, under heating at 60 °C, to achieve full conversion of **3a**. The sulfone **4a** at rt also delivered both cyclization products, fulvene **7a** and diaryl sulfone **8a**, although in this case the ratio was more favorable to the 6-*endo-dig* product **8a**. Under these reaction conditions, no full conversion of **4a** was observed, whereas heating produced similar results. These observations support a higher stabilization of cationic intermediates by the electron-donating nature of the thioether substituent and thus favor 5-*exo-dig* cyclization. Additionally, we evaluated whether MeOH plays a more active role in the process, facilitating protodemetallation. When dienyne **1a** was subjected to the reaction in MeOD, double deuteration was observed at the exocyclic alkene position and at C4 of the cycle, affording di-deuterated **2a-D$_2$** (Scheme 4a). A plausible mechanism involves alkyne activation by the gold complex (**A**), followed by 5-*exo-dig* cyclization, affording intermediate **B** that is stabilized by the



Scheme 2 Scope of fulvenes **2** from 1,3-dien-5-ynes **1**. Yields from isolated compounds after chromatography. Reaction conditions: **1** (0.3 mmol), $IPrAuNTf_2$ (3 mol%), MeOH (3 mL) 30 min. (a) $(t\mathrm{Bu})_3\mathrm{PAuCl}/\mathrm{AgNTf_2}$ (3 mol%) was used as the catalyst. (b) Dienyne **1m**, where R^1 = TMS, was used as the substrate.

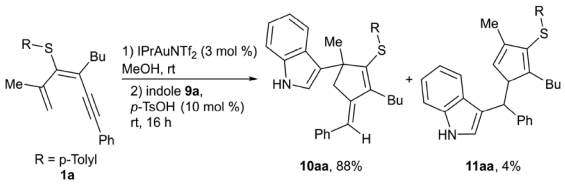


Scheme 3 The effect of the nature of the S-atom substituent on the cyclization.



Scheme 4 (a) Control experiments in MeOD. (b) Mechanism proposal.

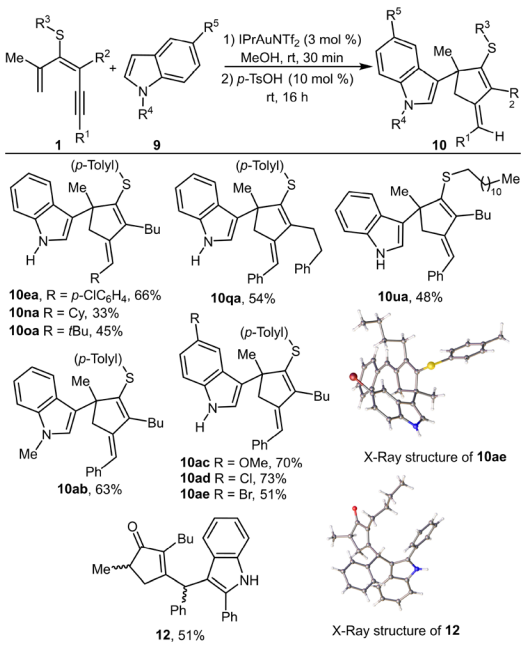
heteroatomic substituent (Scheme 4b). The loss of a proton generates an organogold intermediate **C**, which, after solvent-facilitated deutero-demetallation, releases fulvene **2a-D** and regenerates the gold catalyst. Product **2a-D** could be activated by the cationic gold complex through the more nucleophilic C1 (C4) position of the fulvene, affording a fulvenium intermediate **D** that evolves upon elimination into organogold fulvene intermediate **E**. Finally, deutero-demetallation enabled by the deuterated solvent would give rise to the doubly deuterated fulvene **2a-D$_2$**. Based on these findings, we envisioned that fulvenes **2**, upon activation by a gold catalyst, could evolve through nucleophilic addition reactions. Notably, this unconventional reactivity pattern involving the activation of fulvenes by electrophilic species has been scarcely reported, partly due to the tendency of fulvenes to experience oligomerization or polymerization processes after activation with a Brønsted acid.[30] NMR studies at low temperature under superacid conditions revealed the formation of fulvenium cations.[31] However, the reaction with an external nucleophile is challenging due to competitive oligomerization.[30] In this context, Cu(OTf)$_2$ has been reported to activate symmetric 6-mono- or 6,6-disubstituted fulvenes, followed by a reaction with indoles.[32] Inspired by these results, we envisaged that fulvenes **2** could undergo analogous reactions upon activation with the gold catalyst present in the reaction media. Moreover, the different substitution patterns at positions C2 and C3 of the fulvene could play a crucial role in achieving regiospecific nucleophilic addition to one of these positions. Based on the formation of di-deuterated fulvene **2a-D$_2$**, we hypothesized that the addition of indole **9a** (1 equiv.) to the reaction media could trigger a nucleophilic addition to the activated fulvene, achieving a one-pot two-step procedure to synthesize the 3-(alkylidene-cyclopent-2-en-1-yl)-1*H*-indole derivative **10aa** (Scheme 5). In a preliminary experiment, the expected indole **10aa** was obtained in a 54% yield directly from 1,3-dien-5-yne **1a**. Interestingly, a Brønsted acid co-catalyst such as *p*-TsOH enhanced fulvene



Scheme 5 One-pot two-step synthesis of indole functionalized alkylidene cyclopentenes **10** from dienynes **1** and indoles **9**. Reaction scale: **1** (0.3 mmol).

activation, affording compound **10aa** in 88% yield. Under these conditions, regioisomer **11aa** was also isolated in trace amounts. This by-product from a nucleophilic attack on the position C6 of the fulvene supported the participation of fulvenium ions (Scheme 5). Control experiments with isolated fulvene **2a**, catalytic amounts of *p*-TsOH, and indole **9a** (1 equiv.) in MeOH in the absence of the gold complex showed that compound **10aa** was also formed, albeit in a lower yield, suggesting that the cooperative effect between the gold and the acid enables the fulvene heterohydroarylation.

Next, we evaluated the scope of the reaction with a selection of indoles **9** and 1,3-dien-5-ynes **1** in equimolar amounts, thereby accessing indole-decorated alkylidenecyclopentenes **10** (Scheme 6). Various dienynes **1** subjected to the one-pot two-step procedure afforded 3-(alkylidene-cyclopent-2-en-1-yl)-1*H*-indole products **10** (**10ea**, **10na**, **10oa**, **10qa**, and **10ua**). More nucleophilic *N*-methyl-indole **9b** also led to the formation of compound **10ab**, although other by-products were also detected in the crude. Substituents, such as methoxy (**9c**) or halogens (**9d** and **e**), at the benzenoid ring of the indole are well-tolerated, giving rise to the 3-functionalized indoles **10ac–ae**. The structure of **10ae** was further confirmed by



Scheme 6 Scope of indole functionalized alkylidene cyclopentenes **10** from dienynes **1**. Reaction conditions: **1** (0.3 mmol), IPrAuNTf$_2$ (3 mol%), MeOH (3 mL), 30 min; then indole **9** (0.3 mmol) and p-TsOH (10 mol%) 16 h.

single-crystal X-ray analysis (CCDC 2499730). Remarkably, in all cases, compounds **10** were obtained selectively as the *E*-isomer. A switch in the regioselectivity of the nucleophile addition was achieved with more nucleophilic 2-phenylindole (**9f**), leading to a product derived from the addition at the exocyclic C6 position of the fulvene. Purification attempts yielded only hydration and cleavage of the thioorganyl moiety, yielding the 2-cyclopentenone-decorated indole **12** as a mixture of diastereoisomers (Scheme 6). Its structure was also confirmed by single-crystal X-ray analysis (CCDC 2499841).

In summary, we have described a new gold-catalyzed approach for the synthesis of densely substituted fulvenes from readily available 3-thio-1,3-dien-5-ynes. This transformation is enabled through a scarcely reported gold-catalyzed 5-*exo-dig* cyclization mode of the activated 1,3-dien-5-yne. Control experiments have demonstrated that the nature of the S-atom substituent of the dienyne is crucial in favoring the selective 5-*exo-dig* cyclization over the more commonly described *endo-dig* cyclization pathways. Additional mechanistic studies have demonstrated that these fulvenes can be activated by the gold catalyst in the reaction media, leading to fulvenium intermediates. This interaction of the pentafulvene with electrophilic π-acid catalysts enables unusual reactivity patterns on the synthesized fulvenes that involve nucleophilic addition to the C3 (C2) position of the fulvene. To the best of our knowledge, this is the first report of a gold catalyst being practical in the electrophilic activation of a fulvene, enabling subsequent reaction with nucleophiles. Also, starting dienynes have been engaged in a one-pot two-step protocol to synthesize 3-(alkylidene-cyclopent-2-en-1-yl)-1*H*-indole derivatives. This process implies a gold-catalyzed 5-*exo-dig* cyclization of the 1,3-dien-5-yne affording a fulvene intermediate that, after addition of indole and *p*-TsOH as co-catalysts, evolves through functionalization of the indole at the C3 position by a nucleophilic attack on the fulvenium ion. The combination of the gold complex and the Brønsted acid facilitates this hydroheteroarylation step, achieving higher yields. Also, the gold complex plays a dual role in the one-pot process, acting as a catalyst in both steps. We expect that ongoing studies exploring the potential synthetic applications of these compounds and their optoelectronic properties will yield diverse applications for sulfur-decorated fulvenes.

The authors acknowledge the financial support from Ministerio de Ciencia, Innovación y Universidades (PID2023-148198NB-C21/AEI/10.1039/501100011033), and Junta de Castilla y León and FEDER (BU028P23). C.M.-N. thanks Consejería de Educación (Junta de Castilla y León) for a predoctoral contract. S.S.-P. thanks Ministerio de Ciencia, Innovación y Universidades and ''NextGenerationEU''/PRTR EU for a Ramón y Cajal contract (RYC2021-031533-I).

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: experimental details and spectroscopic data. See DOI: https://doi.org/10.1039/d5cc06478c.

Data for this article, including NMR raw data, are available at Zenodo at https://doi.org/10.5281/zenodo.17519909.

CCDC 2499730 (**10ae**) and 2499841 (**12**) contain the supplementary crystallographic data for this paper.[33a,b]

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