

Synthesis of fluoranthenes by hydroarylation of alkynes catalyzed by gold(I) or gallium trichloride

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Abstract

Electrophilic gold(I) catalyst **6** competes with GaCl₃ as the catalyst of choice in the synthesis of fluoranthenes by intramolecular hydroarylation of alkynes. The potential of this catalyst for the preparation of polyarenes is illustrated by a synthesis of two functionalized decacyclenes in a one-pot transformation in which three C–C bonds are formed with high efficiency.

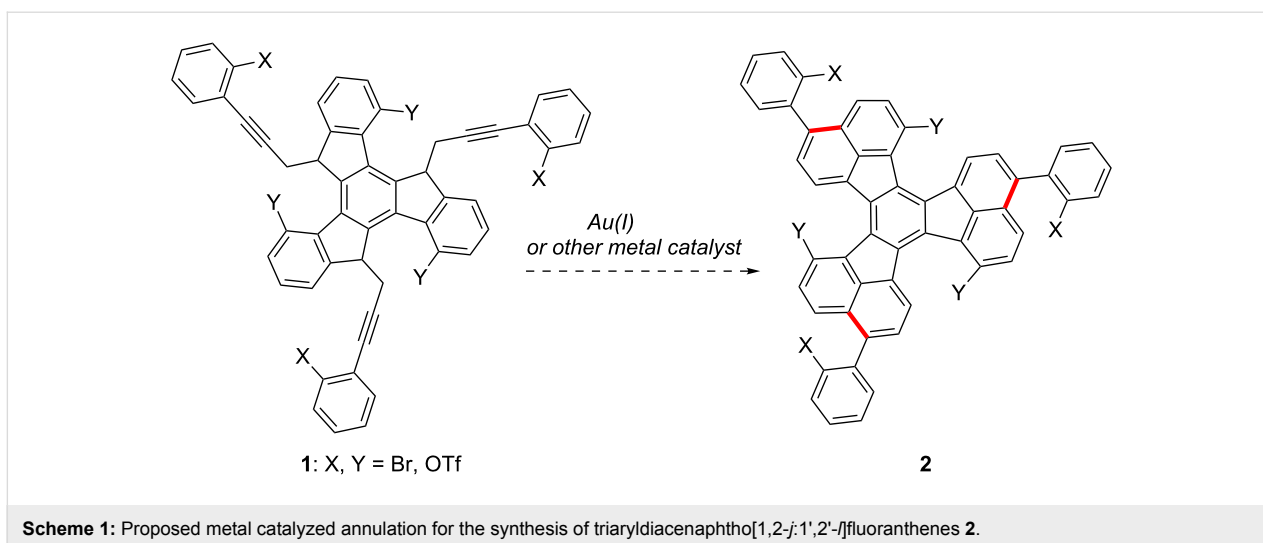
Introduction

Electrophilic activation of alkynes in functionalized substrates by gold catalysts allows for the synthesis of complex molecules under mild conditions [1-8]. Alkynes can react in gold-catalyzed Friedel–Crafts-type reactions with arenes to give products resulting from the intermolecular hydroarylation of the alkynes (or alkenylation of the arenes) [9-21]. In addition to gold, the intramolecular version of this reaction was also carried out with Ru(II) [22], Pt(II) [12,22,23], Pt(IV) [24], Ga(III) [25,26], and Hg(II) [27,28] as catalysts.

Electron-rich indoles also react with alkynes in the presence of gold catalysts to form 6–8-membered rings [29-31]. A similar

reaction can also be carried out with GaCl₃ [32] and Pt(II) [33] as catalysts. In contrast, alkynyl furans react with gold to give phenols by using Au(III), Au(I) [1,2,34-37], or Pt(II) as the catalyst [38,39].

In our efforts towards the synthesis of large polyarenes [40-43], which are related to the fullerenes [44], we used the palladium-catalyzed arylation reaction as the main tool [45-48]. We decided to try the triple hydroarylation of substrates of type **1** to give 3,9,15-triaryldiacenaphtho[1,2-*j*:1',2'-*j'*]fluoranthenes **2** with X and Y substitutes at strategic positions, which could be activated by palladium in subsequent intramolecular arylations

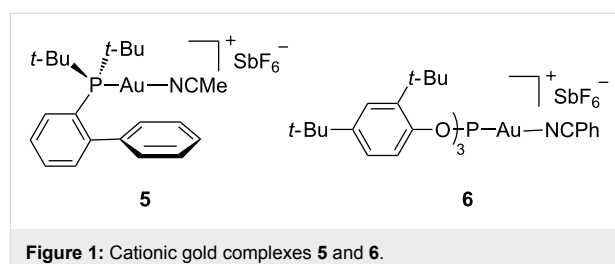


(Scheme 1). Substituted fluoranthenes are of interest since some derivatives have been shown to be useful in light-emitting devices [49-52]. Fluoranthene derivatives have already been synthesized by palladium-catalyzed arylation reactions [53,54]. Strategically halogenated decacyclenes with a substitution pattern similar to that of **2** have been used for the synthesis of circumtrindene by flash vacuum pyrolysis [55]. Here we report the results on the synthesis of large polyarenes **2** and more simple 3-arylfluoranthenes by using gold(I)- or gallium(III)-catalyzed hydroarylation reactions.

Results and Discussion

First, we examined the cyclization of **3** to give **4** or **4'** [22,24,26] (Table 1) with cationic gold(I) catalysts **5** [56] and **6** [57] (Figure 1), which have been demonstrated to be amongst the best catalysts in many gold(I)-catalyzed cyclizations [6,58]. No reaction was observed with complex **5** after heating for 5 min at 70 °C in CH₂Cl₂ under microwave irradiation (Table 1, entry 1), whereas the more electrophilic **6**, bearing a less

donating phosphite ligand, led almost quantitatively to **4'** (Table 1, entry 2). Under these conditions, AuCl₃ was not effective as a catalyst (Table 1, entry 3). As previously reported [25,26], GaCl₃ is an excellent catalyst for the cyclization of **3** to give **4'** (Table 1, entry 4). In all cases the reaction proceeds exclusively through the 6-*exo-dig* pathway.

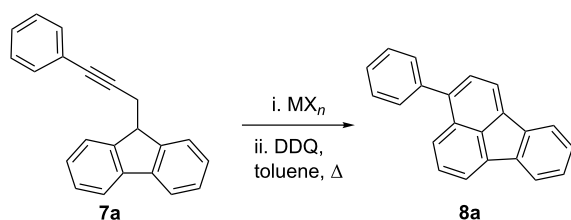


The cyclization of 9-(3-phenylprop-2-ynyl)-9*H*-fluorene (**7a**) to form 3-phenylfluoranthene (**8a**) [59] was also examined by using catalysts **5**, **6**, and GaCl₃ (Table 2). Since the initial

Table 1: Hydroarylation of **3** to give dihydronaphthalene **4'**.^a

| entry | MX _n | 4' (yield, %) |
|-------|-------------------|----------------------|
| 1 | 5 | — ^b |
| 2 | 6 | 99 |
| 3 | AuCl ₃ | — ^c |
| 4 | GaCl ₃ | 99 |

^a2 mol % catalyst, microwave irradiation, 5 min. ^b100% **3** was recovered. ^c87% **3** was recovered.

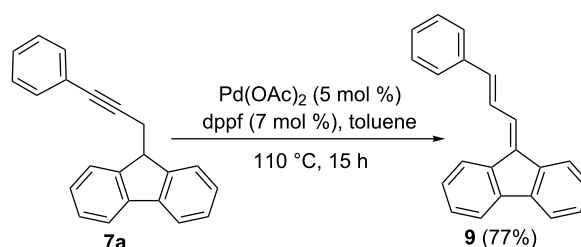
Table 2: Hydroarylation of 9-(3-phenylprop-2-ynyl)-9*H*-fluorene (**7a**) to give 3-phenylfluoranthene (**8a**).^a

| entry | MX _n (mol %) | solvent | T (°C) | t (h) | yield (%) |
|-------|---|---------------------------------|-----------------|-------|-----------------|
| 1 | 5 (2) | CH ₂ Cl ₂ | 70 ^b | 0.7 | — ^c |
| 2 | 5 (5) | toluene | 110 | 1 | — ^d |
| 3 | 6 (5) | CH ₂ Cl ₂ | r.t. | 17 | 64 |
| 4 | 6 (2) | CH ₂ Cl ₂ | r.t. | 16 | 70 |
| 5 | 6 (1) | CH ₂ Cl ₂ | r.t. | 16 | 70 |
| 6 | PtCl ₂ (5) | toluene | 110 | 17 | — ^c |
| 7 | AuCl ₃ (5) | toluene | 110 | 17 | — ^c |
| 8 | InCl ₃ (5) | toluene | 110 | 17 | — ^d |
| 9 | GaCl ₃ (2) | CH ₂ Cl ₂ | r.t. | 26 | 16 ^e |
| 10 | GaCl ₃ (2) | toluene | 70 ^b | 0.2 | 57 |
| 11 | FeCl ₃ ·6H ₂ O (10) | DCE ^f | r.t. | 40 | 36 ^e |
| 12 | FeCl ₃ ·6H ₂ O (5) | DCE ^f | 70 ^b | 0.2 | 34 ^e |

^aCrude reaction mixtures were aromatized by heating in toluene with DDQ (3 equiv) for 12 h. ^bMicrowave irradiation. ^cNo reaction. ^dProduct decomposition. ^eYield determined by ¹H NMR. ^fDCE = 1,2-dichloroethane.

gold(I)-catalyzed reaction provided a mixture of 3-phenyl-1,10b-dihydrofluoranthene, 3-phenyl-1,2,3,10b-tetrahydrofluoranthene, and **8a**, the crude mixtures were treated with excess DDQ in toluene under reflux to provide pure **8a**. No reaction or decomposition was observed when the reaction was carried out with gold(I) complex **5** (Table 2, entries 1 and 2). In contrast, the more electrophilic gold(I) complex **6** with phosphite as the ligand led to **8a** in 64–70% yield by stirring at room temperature in CH₂Cl₂ (Table 2, entries 3–5). Satisfactory results were obtained by simply using 1 mol % of **6** (Table 2, entry 5). No reaction was observed with PtCl₂ or AuCl₃ even after heating in toluene under reflux (Table 2, entries 3–5). Whereas InCl₃

led to decomposition of **7a** under these conditions (Table 2, entry 6), GaCl₃ led to **8a**, although satisfactory results were only obtained in toluene at 70 °C (Table 1, entry 10). Interestingly, FeCl₃ was also catalytically active, although fluoranthene **8a** was only obtained in moderate yields (Table 2, entries 11 and 12). The reaction of **3a** with Pd(OAc)₂ as catalyst proceeded differently to give known (*E*)-9-(3-phenylallylidene)-9*H*-fluorene (**9**) [60], presumably via the formation of the corresponding allene as an intermediate (Scheme 2).

**Scheme 2:** Pd(OAc)₂-catalyzed isomerization of **7a** to form (*E*)-9-(3-phenylallylidene)-9*H*-fluorene (**9**).

Substrates **7b–j**, prepared by alkylation of fluorenyl lithium with the corresponding propargyl bromide or by Sonogashira couplings of 9-(prop-2-ynyl)-9*H*-fluorene [61], were cyclized by using gold(I) complex **6** or GaCl₃ as the catalyst (Table 3). Although both catalysts could be used for the synthesis of 3-arylfluoranthenes **8b–h**, better yields were obtained with GaCl₃ in toluene at 100 °C. However, in the case of 9-(3-bromoprop-2-yn-1-yl)-9*H*-fluorene (**7i**), gold(I) complex **6** gave more satisfactory results (Table 3, compare entries 10 and 11). The reaction proceeded satisfactorily with aryl-substituted substrates bearing either electron-donating (*p*-Me, *o*-OMe) or electron-withdrawing (*p*-Cl, *p*-Br, *p*-CN, *p*-NO₂) groups. However, no reaction was observed for *n*-butyl derivative **7j** with **6** or with GaCl₃ (Table 3, entries 12 and 13).

Cyclization of substrate **7k**, having an electron-rich aryl group at the alkyne, with catalyst **6** gave 1,10b-dihydrofluoranthene **9** cleanly in quantitative yield (Scheme 3).

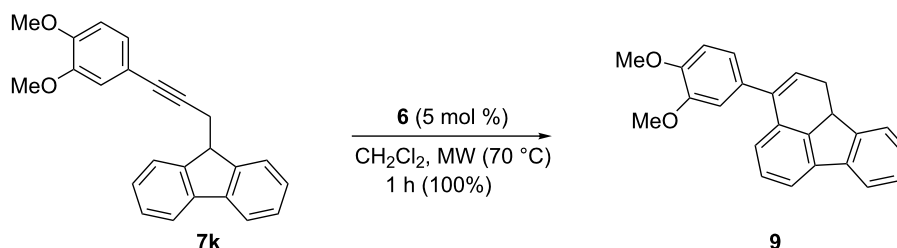
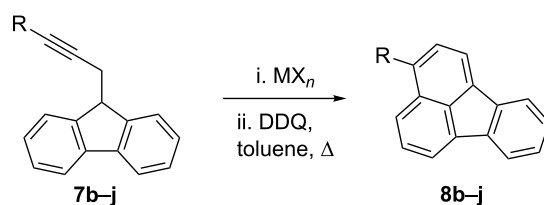
**Scheme 3:** Gold(I)-catalyzed hydroarylation of **7k** to give 1,10b-dihydrofluoranthene **9**.

Table 3: Hydroarylation of **7b–j** to give 3-substituted fluoranthenes **8b–i**.^a

| entry | fluorene | R | MX _n (mol %) | solvent | T (°C) | t (h) | yield (%) |
|-------|-----------|---|-------------------------|---------------------------------|------------------|-------|----------------|
| 1 | 7b | <i>p</i> -Tol | GaCl ₃ (5) | toluene | 100 ^b | 0.2 | 45 |
| 2 | 7b | <i>p</i> -Tol | 6 (5) | CH ₂ Cl ₂ | r.t. | 17 | 28 |
| 3 | 7c | <i>p</i> -ClC ₆ H ₄ | GaCl ₃ (5) | toluene | 100 ^b | 0.2 | 71 |
| 4 | 7d | <i>p</i> -NCC ₆ H ₄ | GaCl ₃ (2) | toluene | 100 ^b | 0.2 | 88 |
| 5 | 7e | <i>p</i> -O ₂ NC ₆ H ₄ | GaCl ₃ (2) | toluene | 70 ^b | 0.2 | 92 |
| 6 | 7f | <i>o</i> -MeOC ₆ H ₄ | 6 (5) | CH ₂ Cl ₂ | r.t. | 17 | 17 |
| 7 | 7f | <i>o</i> -MeOC ₆ H ₄ | GaCl ₃ (5) | toluene | 100 ^b | 0.2 | 57 |
| 8 | 7g | <i>o</i> -BrC ₆ H ₄ | GaCl ₃ (5) | toluene | 100 ^b | 0.2 | 44 |
| 9 | 7h | C ₆ F ₅ | GaCl ₃ (5) | toluene | 100 ^b | 2 | 74 |
| 10 | 7i | Br | 6 (5) | CH ₂ Cl ₂ | r.t. | 20 | 44 |
| 11 | 7i | Br | GaCl ₃ (5) | toluene | 100 ^b | 0.2 | 21 |
| 12 | 7j | <i>n</i> -Bu | 6 (5) | CH ₂ Cl ₂ | r.t. | 7 | — ^c |
| 13 | 7j | <i>n</i> -Bu | GaCl ₃ (2) | toluene | 70 ^b | 0.2 | — ^c |

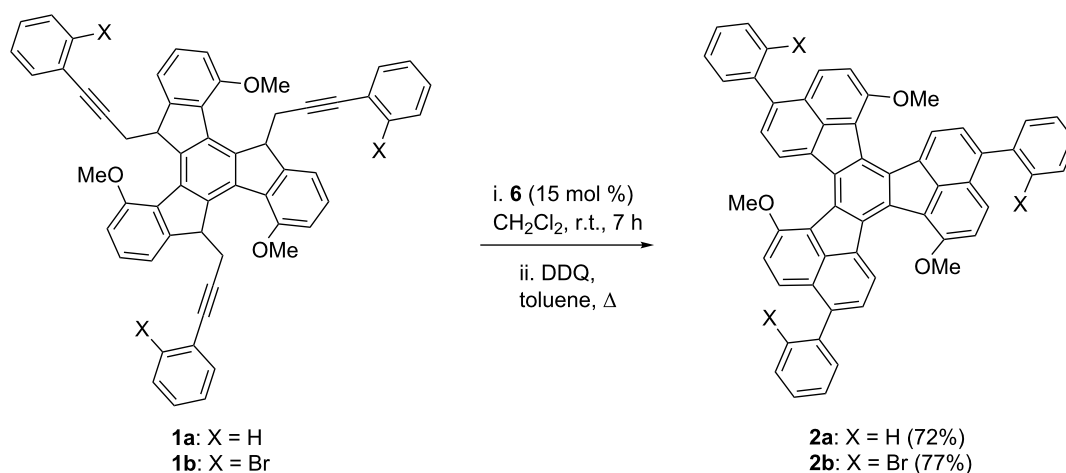
^aCrude reaction mixtures were aromatized by heating in toluene with DDQ (3 equiv) for 12 h. ^bMicrowave irradiation. ^cNo reaction.

Derivatives **1a** and **1b** were readily prepared by the triple alkylation of the lithium anion of 4,9,14-trimethoxytruxene (Scheme 4) [41,62]. The cyclization reaction was carried out efficiently with gold(I) catalyst **6** (15 mol %) at room temperature in CH₂Cl₂ to give triaryl substituted diacenaphtho[1,2-*j*:1',2'-*l*]fluoranthenes (decacyclenes) **2a** and **2b** in very good overall yields after aromatization of the crude products with DDQ. Remarkably, this triple hydroarylation occurs efficiently

with an average yield per C–C bond formation that is greater than 90%.

Conclusion

Highly electrophilic gold(I) catalyst **6** with a bulky phosphite ligand competes with GaCl₃ as the catalyst of choice for the hydroarylation of alkynes. The synthetic potential of this catalyst is illustrated by the synthesis of functionalized triarylated

**Scheme 4:** Gold(I)-catalyzed triple hydroarylation of **1a,b** to give **2a,b**.

decacyclenes in which three C–C bonds are formed with high efficiency in a one-pot transformation. The reaction is totally compatible with aryl bromides, which do not undergo subsequent arylation reaction due to the inertness of gold(I) catalysts towards oxidative addition reactions under homogeneous conditions [63,64].

Supporting Information

Supporting Information features experimental details and characterization data for new compounds.

Supporting Information File 1

Experimental details

[<http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-7-178-S1.pdf>]

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