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Short communication

Gold-catalyzed cyclotrimerization of arynes for the synthesis of triphenylenes

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ABSTRACT

A novel and efficient Au(I)-catalyzed cyclotrimerization of arynes, generated by fluoride-induced elimination of Kobayashi's silylaryl triflates, is described. The reactions led to the formation of triphenylenes in 45–88% yields under mild conditions. © 2015 Elsevier B.V. All rights reserved.

1. Introduction

Aryne chemistry has been of particular interest due to its high reactivity and broad applications in organic synthesis [1–4]. Recently, transition metal-catalyzed reactions involving arynes, which are generated by fluoride-induced elimination of Kobayashi's silylaryl triflate under mild conditions [5], have been well documented [6–17]. Since Guitián and co-workers [6] first reported Pd(0)-catalyzed cyclotrimerization of arynes to generate triphenylenes in 1998 (Scheme 1), a variety of important triphenylene derivatives, which demonstrated potent applications in organic materials, have been prepared under similar reaction conditions [18–25]. To our knowledge, there are many methods for triphenylene formation via arynes. For examples, the cyclotrimerization of benzyne catalyzed by Cu(I) (20 mol%) afforded triphenylene in refluxing CH_3CN (Scheme 1) [26], and triphenylenes were also isolated during attempts at obtaining a metal complex of arynes [27–30]. The efficient preparation of triphenylenes with a catalytic amount of promoters is still a demand to fulfill the modern synthesis.

Most recently, our group developed a novel Au(III)-catalyzed tetramerization of terminal electron-deficient alkynes to afford 1,2,5,6-tetrasubstituted-cyclooctatetraene (1,2,5,6-COT) [31]. We have been interested in studying gold-catalyzed cyclotrimerization of arynes (active π-components), which have seldom served as the substrate for gold catalysis [9, 26]. Herein, we report that the use of PPh_3AuCl as the catalyst for the cyclotrimerization of arynes provides a convenient and general approach to triphenylenes under mild conditions (Scheme 1).

2. Experimental

2.1. General

All reactions were carried out under an atmosphere of argon/nitrogen using oven-dried glassware and standard syringe/septa techniques. Tetrahydrofuran (THF) was distilled from sodium. Acetonitrile (CH_3CN) and toluene were distilled from calcium hydride. 1,2-Dichloroethane (DCE) was dried over 4 Å molecular sieve. Hexanes refer to the petroleum fraction bp 40–60 °C. Commercial reagents were used without purification unless otherwise noted. Kobayashi's aryne precursors were prepared according to the literature [5]. Flash chromatography was performed using the indicated solvent system on silica gel standard grade 60 (230–400 mesh). ^1H NMR spectra were recorded on a 400 MHz spectrometer. ^{13}C NMR spectra were recorded on a 100 MHz spectrometer. ^{19}F NMR spectra were recorded on a 376 MHz spectrometer. Chemical shifts are reported relative to $CDCl_3$ (δ 7.26 ppm) for ^1H NMR and $CDCl_3$ (δ 77.00 ppm) for ^{13}C NMR.

2.2. General procedure for gold-catalyzed cyclotrimerization of arynes

To a solution of Kobayashi's silylaryl triflate **1** (0.60 mmol) in anhydrous acetonitrile (3.0 mL), catalytic PPh_3AuCl (32 mg, 0.060 mmol) and CsF (182 mg, 1.2 mmol) were added. The mixture was stirred at 60 °C or room temperature for 6 h or 12 h. After removal of the solvent, the

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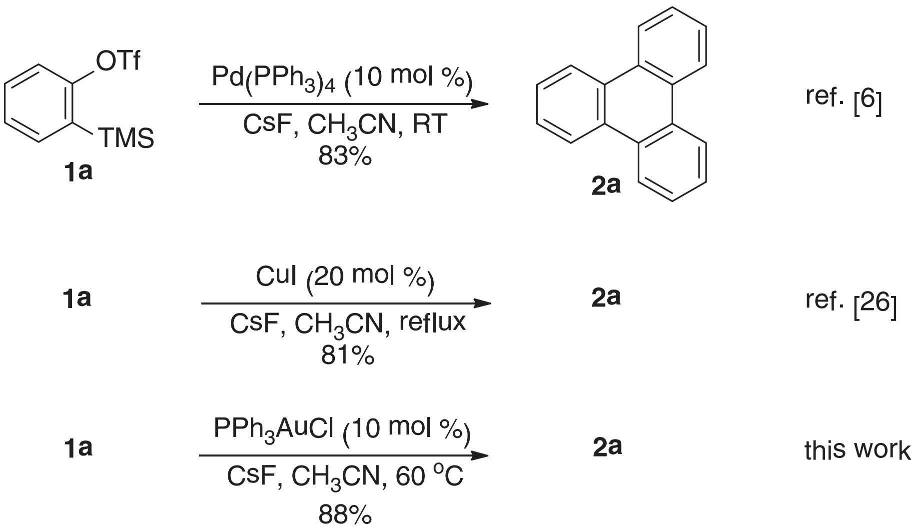


Scheme 1. Overview of cyclotrimerization of benzyne using Kobayashi's precursor.

residue was then purified by flash column chromatography on silica gel (eluent = hexanes/ethyl acetate 40:1 v/v) to give the desired triphenylene **2**.

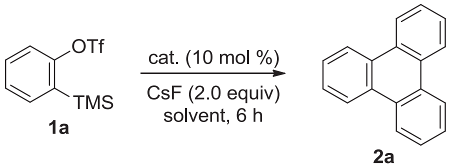
3. Results and discussion

The catalytic activity of $AuCl_3$ (10 mol%) was first tested for the reaction of benzyne precursor **1a** in the presence of CsF in DCE at room temperature (Table 1, entry 1) [31], and the desired triphenylene **2a** was not detected even when the reaction temperature was set to 60 °C (entry 2). To our delight, switching the solvent from DCE to CH_3CN led to the formation of cyclotrimerization product **2a** in 76% yield (entry 3) [32]. We then turned to screen other Au/Ag/Pt catalysts, and PPh_3AuCl was proved to be the optimum catalyst (92% yield, entry 8). When the catalytic amount of PPh_3AuCl was decreased to 5 mol%, the yield of **2a** was significantly decreased to 66% (entry 11). When the reaction was carried out at RT or 40 °C, the yield of **2a** was also decreased (entries 12, 13). Switching solvent from CH_3CN to THF did not increase the yield of triphenylene (entry 14). Thus, we concluded that the optimized combination for the cyclotrimerization of benzyne was to use 10 mol% of PPh_3AuCl as the catalyst, 2 equiv. of CsF as the fluoride ion, CH_3CN as the solvent, and the reaction was set at 60 °C (entry 8).

To investigate the scope of the cyclotrimerization protocol, we applied the optimum reaction conditions to a variety of Kobayashi's aryne precursors **1** and the results are illustrated in Table 2. Benzyne precursor **1a**, 4-methoxy-, 4-methyl-, 4-*tert*-butyl-, 4-trifluoromethoxy-, and 3,6-dimethyl-substituted aryne precursors **1b**–**1f** and napthalyne precursor **1g** were all well tolerated for the cyclotrimerization to give the corresponding triphenylenes in 45–88% yields. For unsymmetrical aryne precursors **1b**–**1e** and **1g**, the consistent 1:3 ratio of triphenylene regioisomers, which was in good agreement with the experimental results of Pd(0)-catalyzed cyclotrimerization of arynes [33], strongly demonstrated that these reactions involved an aryne pathway. It is noteworthy that the cyclotrimerization of **2c**, **2e** and **3g** also was achieved smoothly at room temperature, and the yields were even higher than those at 60 °C. We also tried the cyclotrimerization of **1** under optimum conditions with addition of a small amount of water (~5 equiv., 0.05 mL), and the reaction gave the desired product in 80% yield. We then tried $Pd(PPh_3)_4$-catalyzed cyclotrimerization [6] of **1** with addition of the same amount of water, however, no desired product was detected. In comparison with Pd(0)-catalyzed reaction conditions, the Au(I)-catalyzed cyclotrimerization of arynes was neither air nor moisture sensitive, which only decreased the yields slightly.

Based on the experimental results, a plausible mechanism [34] for the formation of triphenylenes, which is similar to that of Pd(0)-catalyzed cyclotrimerization [35], is proposed as shown in Scheme 2. Benzyne **3**, which is generated by fluoride-induced elimination of benzyne precursor **1a**, interacts with a cationic gold(I) complex ($[PPh_3Au^+]$ was probably formed in the presence of an excess of CsF) to form complex **4**. Subsequent cyclometallation of two molecules of **4** gives the organogold intermediate **5**, followed by one more benzyne insertion to produce complex **6**, which liberates the cyclotrimerization product triphenylene **2a** and the cationic gold(I) complex by demetallation.

Table 1
Gold-, silver- and platinum-catalyzed cyclotrimerization of benzyne.[a]



Entry	Catalyst	Solvent	Temperature	Yield (%)[b]
1	$AuCl_3$	DCE	RT	–
2	$AuCl_3$	DCE	60 °C	–
3	$AuCl_3$	CH_3CN	60 °C	76
4	AuCl	CH_3CN	60 °C	14
5	PPh_3AuSbF_6	CH_3CN	60 °C	50
6	$AgSbF_6$	CH_3CN	60 °C	–
7[c]	$AgSbF_6$	CH_3CN	60 °C	Trace
8	**PPh_3AuCl**	**CH_3CN**	**60 °C**	**92 (88)**[d]
9	$PtCl_2$	CH_3CN	60 °C	–
10	$PtCl_4$	CH_3CN	60 °C	12
11[e]	PPh_3AuCl	CH_3CN	60 °C	66
12	PPh_3AuCl	CH_3CN	40 °C	78
13	PPh_3AuCl	CH_3CN	RT	46
14	PPh_3AuCl	THF	60 °C	40

The significance of bold entries in table 1 shows the optimum conditions.

[a] The reaction of **1a** (0.20 mmol) was carried out in the presence of 10 mol% of catalysts and CsF (0.40 mmol) in the corresponding solvent (1.0 mL) for 6 h.

[b] Yield was determined by ^1H NMR analysis of crude products using an internal standard.

[c] PPh_3 (10 mol%) was added.

[d] Isolated yield on 0.6 mmol scale in parentheses.

[e] 5 mol% of PPh_3AuCl was used.