

## Bimetal Cooperatively Catalyzed Arylalkynylation of Alkynylsilanes

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E nyne-condensed arenes are pervasive in numerous natural products and organic materials.<sup>1</sup> These unsaturated carbon skeletons represent versatile transformation platforms for assembling complex molecules through classical coupling cyclizations.<sup>2</sup> Thus, the method development for a concurrent installation of aryl and alkynyl moieties into arenes, alkenes, and alkynes remains important in synthetic chemistry. However, the exploration of the direct arylalkynylation of unsaturated hydrocarbons was very scarce; the challenges of this methodology are mainly derived from its chemo- and regioselectivity of unsaturated alkenes and alkynes. Until now, although much progress in the arylalkynylation of alkenes has been made,<sup>3</sup> the arylalkynylation of alkynes has not been well-documented.<sup>4</sup> Therefore, it remains valuable to develop efficient methods of arylalkynylation of alkynes to assemble aryl-enyne skeletons.

A C/Si switch generally endows the corresponding silahydrocarbons with distinct physical-chemical properties.<sup>5</sup> Accordingly, intermolecular arylsilylation strategies of alkynes with arylsilanes have been pioneeringly explored by Xi,<sup>6</sup> Nakamura,<sup>7</sup> and Chatani<sup>8</sup> to furnish 1-silaindans (Scheme 1a). However, the development of an arylalkynylation strategy of alkynylsilanes to merge enyne and the Si element into silacycles is often difficult to achieve, because alkynylsilanes possess diversified reaction sites;<sup>9</sup> moreover, alkynylsilanes still suffer from a C–Si bond cleavage transmetalation or oxidative addition with metal catalysts (Scheme 1b).<sup>10</sup>

In answer to this challenge, we posited that  $\alpha$ -alkynylalcohols (**B**) possibly possess a higher reactivity than alkynylsilanes (**A**) to interact with Rh catalysts, producing alkynylrhodiums (**D**) through a  $\beta$ -C elimination. Meanwhile, Pd catalysts could preferentially attack a phenyl Csp<sup>2</sup>-Br bond instead of an alkynyl Csp-Si bond of **A** via an oxidative addition, affording arylpalladiums (**C**), which could further be trapped by **D** to enable this arylalkynaylation (Scheme 1c). To verify this hypothesis, we described herein a bimetal Pd/Rh-catalyzed arylalkynylation of *ortho*-bromoaryl-tethered alkynylsilanes with  $\alpha$ -alkynylalcohols. A broad range of substrates efficiently participate in this reaction, leading to valuable silacyclic

# Scheme 1. Coupling Strategies of Alkynes with Arylsilanes and Alkynylsilanes

a) Arylsilation of alkynes with arylsilanes via C-Si bond cleavage



molecules. These enyne-tethered benzosilacycles possibly possess promising application potential in optoelectronic materials.<sup>11</sup>

Our studies began by probing the reaction of *ortho*bromobenzyl alkynylsilane **1a** with 1,1,3-triphenylprop-2-yn-1ol **2a** to screen different catalytic systems in the presence of  $Ag_2CO_3$ , *t*-BuOK, and 1,2-bis(diphenylphosphino)ethane (dppe) in 1.0 mL of 1,4-dioxane under Ar at 100 °C for 12 h (Table 1, entries 1–7). It was found that the dual catalytical systems Rh(III)/Pd(OAc)<sub>2</sub>, Ir(III)/Pd(OAc)<sub>2</sub>, and Rh(I)/ Pd(OAc)<sub>2</sub> could provide the desired arylalkynylation product

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#### Table 1. Optimization of the Reaction Parameters<sup>a</sup>



"Unless otherwise noted, all the reactions were performed using alkynylsilane **1a** (0.10 mmol), alkynyl alcohols **2** (0.10 mmol), Ag<sub>2</sub>CO<sub>3</sub> (1.0 equiv), ligand (40 mol %), and *t*-BuOK (1.0 equiv) with Rh catalysts (5 mol %) and Pd(OAc)<sub>2</sub> (PdL<sub>2</sub>, 10 mol %) in 1,4-dioxane (1.0 mL) at 100 °C for 12 h under Ar in a sealed tube, followed by flash chromatography on SiO<sub>2</sub>. <sup>b</sup>Isolated yields were based on the alkynylating reagent **2**. <sup>c</sup>dppe refers to 1,2-bis(diphenylphosphino)ethane. <sup>d</sup>dppm refers to 1,2-bis(diphenylphosphino)methane. <sup>e</sup>dppp refers to 1,2-bis(diphenylphosphino)methane. <sup>g</sup>2.0 equiv of **1a** was used. <sup>h</sup>Reaction time was extended to 24 h. <sup>i</sup>Only 20 mol % of Pd(OAc)<sub>2</sub> was employed.

**3a** in 16-23% yields (entries 4-7). By contrast, the monometal catalysts [Rh(cod)Cl]<sub>2</sub>, [Cp\*RhCl<sub>2</sub>]<sub>2</sub>, and [Cp\*IrCl<sub>2</sub>]<sub>2</sub> did not enable this transformation at all (entries 1-3). Then, we employed  $[Rh(cod)Cl]_2$  (5 mol %)/Pd(OAc)<sub>2</sub> (10 mol %) as a bimetal cocatalyst to evaluate the effect of alkynyl alcohols (2b, 2c, 2d) and even alkynyl bromide (2e) on this transformation and found that tertiary alcohols 2a and 2b were the most effective alkynylating reagents (entries 9-11 vs 7 and 8). Various types of phosphine ligands were then evaluated for further improving the reaction conversions of 1a with 2b; PPh<sub>3</sub> was the best ligand, which could give 49% yield of 3a (entries 8, 12, and 13 vs 14). Increasing the catalyst loading (Rh salts: 10 mol %; Pd salts: 20 mol %) dramatically increased the reaction yield to 60% (entry 14 vs 15). Meanwhile, switching the ratio of 1a/2a from 1/1 to 2/1 could further enhance this transformation for yielding 75% of 3a, possibly due to 1a being easily suffered from an intramolecular coupling cyclization and decomposition<sup>12</sup> (entry 15 vs 16). Extending the reaction time to 24 h was also beneficial for achieving a higher yield (entry 17, 88%). By the way, a very poor yield of 3a (18%) was obtained in the absence of  $[Rh(cod)Cl]_2$  (entry 18), and the monometal Rh(I)-, Pd(II)-, and Ag(I)-catalyzed arylalkynaylation of 1a with

**2b** could not give **3a** at all [see the Supporting Information for details].

Next, we evaluated the coupling cyclization of different 3arylprop-2-yn-1-ols **2** with alkynylsilane **1a**, as shown in Scheme 2. A comparison with electroneutral 3-phenylprop-2-yn-1-ol **2b**,

## Scheme 2. Arylalkyne Scope $^{a,b}$



<sup>*a*</sup>The mixture of **1a** (0.20 mmol), alcohols **2** (0.10 mmol), Ag<sub>2</sub>CO<sub>3</sub> (1.0 equiv), PPh<sub>3</sub> (40 mol %), and *t*-BuOK (1.0 equiv) with  $[Rh(cod)Cl]_2$  (10 mol %) and Pd(OAc)<sub>2</sub> (20 mol %) in dioxane (1.0 mL) was stirred at 100 °C for 24 h under Ar in a sealed tube, followed by flash chromatography on SiO<sub>2</sub>. <sup>*b*</sup>Isolated yields were based on the alkynylating reagent **2**. <sup>*c*</sup>The catalytical reaction was performed on a 1.0 mmol scale.

arylalkynyl alcohols that contain alkyl-, methoxyl-, and fluorosubstituted phenyl groups, showed that **2b** could efficiently react with alkynylsilane **1a** to furnish the desired products (**3b**-**3f**, **3g**, **3i**, and **3j**) in 53–82% yields. Among them, *meta*- or *ortho*substituted congeners resulted in slightly sluggish conversions (53–61%), possibly due to the steric hindrance (**3c**, **3d**, and **3j**). Meanwhile, 4-acetamido-, 4-chloro-,<sup>13</sup> and 4-CF<sub>3</sub>-phenylsubstituted alkynylalcohols, naphthylalkynyl alcohol, 3-pyridylalkynyl alcohol, and even 2-thiothylalkynyl alcohol also furnished the corresponding 2-silaindan-fused enynes (**3h**, **3k**-**3o**) in acceptable yields (32–54%). Unfortunately, when *n*-heptynyl alcohol **2t** was subjected to the standard reaction system, no desired product **3p** was obtained.

Subsequently, the scope of the present procedure with regard to different *ortho*-bromophenyl-tethered alkynylsilanes was also tested systematically (Scheme 3). Generally, this transformation is sensitive to the electronic effect of substituents in silylalkynyl and silylalkyl phenyl rings. Electron-donating (Me-, MeO-) and electron-withdrawing (F-) groups on the silylalkylnyl and silylalkyl benzene ring of silanes 1 could efficiently react with  $\alpha$ -phenylethynyl isopropyl alcohol 2b to furnish good yields (61–77%) of the products (4a–4c, 4g, and 4h). On the contrary, electron-withdrawing CF<sub>3</sub>- or Cl-substituted phenyl ring-containing silanes 1 gave the corresponding silacycles 4d (46%),<sup>13</sup> 4e (51%), and 4i (50%)<sup>13</sup> in moderate yields. We stress that this transformation was also compatible with alkylalkynyl-substituted phenylmethylsilane, producing the desired 2-silaindan 4f in a 42% yield.

More importantly, the scope of *ortho*-bromophenylmethyl alkynylsilanes could be extended to *ortho*-bromophenylethyl alkynylsilanes, in which 2-bromophenethyl/phenylethynyl silanes smoothyl reacted with various arylethynyl isopropyl alcohols **2** via a coupling cyclization to assemble six-membered 2-silatetralins **4j**-**4t** in 46–73% yields. Among them, the branched  $\beta$ -methylphenethyl/phenylethynyl silane still showed a high reactivity toward arylethynyl isopropyl alcohols regardless

## Scheme 3. Alkynylsilane Scope<sup>*a,b*</sup>



<sup>a</sup>The mixture of silanes **1** (0.20 mmol), alcohols **2** (0.10 mmol),  $Ag_2CO_3$  (1.0 equiv), PPh<sub>3</sub> (40 mol %), and *t*-BuOK (1.0 equiv) with  $[Rh(cod)Cl]_2$  (10 mol %) and Pd(OAc)<sub>2</sub> (20 mol %) in dioxane (1.0 mL) was stirred at 100 °C for 24 h under Ar in a sealed tube. <sup>b</sup>Isolated yields were based on the alkynylating reagent **2**. <sup>c</sup>Recovered yield.

of the steric hindrance from methyl-substitutent effect, producing **4s** and **4t** in good yields of 64-67%. However, when a phenylpropylsilane was subjected to the standard reaction system, only the coupling product **4u**' (see the Supporting Information for details) was obtained in 4% yield; no desired benzo-fused seven-membered silacyclic compound **4u** was observed.

To evaluate the luminescent properties of these enyne-fused benzosilacycles, the photophysical properties of different sizes of silacycles 3a, 3m, 4j, and 4r were investigated by UV-vis absorption and photoluminescence (PL) spectra in a diluted tetrahydrofuran (THF) solution. As illustrated in the absorption spectra (Figure S1a in the Supporting Information), the naphthalene-containing benzosilacycles 3m and 4r show bathochromic absorption bands relative to that of the phenylsubstituted silacycles 3a and 4j. Also, the hypsochromic shifted absorption bands were noticed more for 2-silatetralins 4j and 4r than those of 2-silaindans 3a and 3m, respectively. Similar redshifted emission profiles were further observed in their PL spectra from phenyl-substituted structures to naphthalenesubstituted structures, also from 2-silatetralin derivatives to 2silaindan derivatives (Figure S1b), indicating that these envnefused benzosilacyclical skeletons could be a promising building block for deep blue/violet luminescent materials. More interesting, a striking fluorescence enhancement phenomenon was observed for all the compounds 3a, 3m, 4j, and 4r in a mixed THF/water solvent, indicating that all these silacyclic skeletons exhibit an aggregation-induced emission (AIE) characteristic<sup>14</sup> (Figure S1c), possibly due to the incorporation of multiple rotational phenyl or naphthyl groups. A flexible enyne group and a twisted multimembered silacycle endow the isolated molecule adequately with active intramolecular motions to dissipate an exciton energy in the isolated state.<sup>15</sup>

The postsynthetic transformations (Scheme 4) demonstrated that the silacycle of **3a** could undergo a ring-opened reaction to produce  $\alpha$ -silylalcohol **3–1a** (49%) by employing a PtCl<sub>2</sub>/CO catalytical system. On the one hand, of course, the tandem ring-

#### Scheme 4. Synthetic Applications



opening/coupling cyclization of **3a** with Na<sub>2</sub>S could also afford 2,3,5-triarylthiophene **3–2a** (49%) via a C–Si bond cleavage/C–S bond formation. On the other hand, the 1,3-enyne moiety of the benzosilacycle **3a** would regioselectively react with Et<sub>3</sub>SiH employing H<sub>2</sub>PtCl<sub>6</sub> (1 mol %) as catalysts to produce 1,3-bis-silyl-1,3-diene-containing silacycle **3–3a** in 75% yield. Meanwhile, the 1,3-enyne group of **3a** still underwent Pd-catalyzed hydrostannation with (*n*-Bu)<sub>3</sub>SnH, delivering vinyltin **3–4a** in 88% yield.

To get a better insight into the mechanism, we ran control experiments to evaluate the behavior of  $\alpha$ -alkynylalcohols, alkynylsilanes, arylbromides, and bimetal catalysts (Scheme 5).

#### Scheme 5. Preliminary Mechanism Studies



It is well-known that terminal alkynes would produce alkynylmetal species under base conditions. However, the arylalkynylation of 1a with 4-methoxyphenyl ethyne 2u under the standard conditions only provided phenylethynyl-containing 2-silaindan 3a (9%) instead of 4-methoxylphenylethynylsubstituted congener 3g (Equation (Eq) a), implying that 2alkynylpropan-2-ols 2 more easily underwent metalation than terminal alkynes and alkynylsilanes; accordingly, alkynylsilanes possessed a higher reactivity than terminal alkynes to form Although the reaction condition screening in Table 1 (entry 18) suggested that the arylalkynylation between alkynylsilane 1a and  $\alpha$ -phenylethynyl isopropyl alcohol 2b still occurred with a poor yield in the absence of Rh(I) catalysts, the alkynyl source was not clear. We therefore performed the coupling cyclization of alkynylsilane 1a with 4-methoxyphenylethynyl alcohol 2k in the absence of Rh catalysts and obtained 3a (11%) and 3g (24%), in which both alkynylsilane 1a and alkynylalcohol 2k acted as an alkynyl source to enable the arylalkynaylation (Eq d). More importantly, in comparison with the 60% yield of 3g in Scheme 2, this result clearly demonstrated that Rh catalysts significantly increased the reactivity and chemical selectivity of alkynyl alcohols.

To establish the role of Rh(I) catalysts and Pd(II) catalysts during this transformation, we conducted the cross-coupling of alkynyl alcohol 2a with phenyl bromide 7 in the absence of  $Pd(OAc)_2$  (Eq e). It was found that Rh(I) catalysts could efficiently interact with 2a to produce alkynyl rhodium species and ketone 9 (95%) via a  $\beta$ -alkynyl elimination,<sup>17</sup> and Pd(II) catalysts mainly participated in trapping aryl bromides through an oxidative addition and subsequent reductive elimination. Given that Rh(I) salts could be oxidized to Rh(III) species by  $Ag_2CO_{3}$ <sup>18</sup> a Rh(III) (10 mol %)/Pd(II) (20 mol %) catalyzed coupling cyclization of alkynylsilane 1a with 2k was performed in the absence of  $Ag_2CO_3$ , and both silacycles 3a and 3g were not detected (Eq f), implying that stoichiometric Ag salts<sup>19</sup> possibly played an important role of transmetalation instead of acting as an oxidant. Finally, the intramolecular cyclization of 1a in the presence of CH<sub>3</sub>OD gave 8% yield of 1-benzylidene-2-silaindan d1-10, in which the incorporation of deuterium into the vinyl Csp<sup>2</sup>-H bond (13% D) was observed. On the contrary, this transformation did not happen at all in the absence of Pd catalysts (Eq g), indicating a vinyl Pd(II) species was possibly involved in this reaction.

On the basis of the above experimental observations, a plausible mechanism is proposed in Scheme 6. On the one hand, *ortho*-bromobenzyl alkynylsilanes 1 preferentially undergo an oxidative addition with Pd(0) catalysts in the presence of phosphine ligands to produce arylpalladiums A, followed by an

#### Scheme 6. Proposed Mechanism



In summary, we have presented an unprecedented bimetal Pd/Rh cooperatively catalyzed arylalkynylation cyclization of alkynylsilanes with alkynyl alcohols through a sequential arylmetalation, alkynylmetalation, and transmetalation process. Intriguing mechanistic details triggering these perfect processes were elucidated. This newly developed methodology enables a direct access to distinctive alkynylidene-fused benzosilacycles that possess an unusual AIE feature.

#### ASSOCIATED CONTENT

#### **3** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c02283.

Detailed experimental procedures, characterization data, crystallographic data for **3a**, **4d**, and **4o** (CIF), copies of <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra for all isolated compounds (PDF)

#### **Accession Codes**

CCDC 2074954, 2074953, and 2074955 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/ cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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