# **ORGANOMETALLICS**

examples).

# Synthesis and Application of Silylene-Stabilized Low-Coordinate Ag(I)–Arene Cationic Complexes

Nasrina Parvin, Nilanjana Sen, Srinu Tothadi, Shahila Muhammed, Pattiyil Parameswaran,\* and Shabana Khan\*



= [LAg]<sup>+</sup>

he coinage metals (Cu, Ag, Au) in +1 oxidation states are important in catalysis, especially for various crosscoupling reactions.<sup>1</sup> In most of the cases,  $[L-M]^+$  [L =monocoordinate ligands, M = Cu(I), Ag(I), and Au(I)] is considered as the active catalytic species; although, such a type of naked cations have not yet been isolated. A closely related class of the complex [L-M-arene]<sup>+</sup>, where arene is weakly bound to the metal center, has some limited examples.<sup>2</sup> To date, there are only two reports of monocoordinate Ag(I)arene cationic complexes: one where phosphine ligands were used to stabilize Ag(I)-toluene/m-xylene cationic complexes,<sup>3a</sup> and the other one is N-heterocyclic carbene (NHC)stabilized Ag(I)-fluorobenzene/mesitylene cations.<sup>3b</sup> Being a heavier congener of NHCs, silvlenes have been widely used as ligands in transition-metal-based catalysis due to their strong  $\sigma$ donation property.<sup>4</sup> The current interest of our group is to prepare well-defined coinage metal complexes stabilized by a benz-amidinatosilylene ligand.<sup>5</sup> Toward this end, we have isolated a series of Si(II)-Cu(I)-arene (arene = toluene and *m*-xylene) and Si(II)-Au(I)-arene (arene = benzene, *m*xylene) cationic complexes and further utilized them as catalysts in click chemistry and glycosidation reactions, respectively (Chart 1).<sup>6</sup> To complete the series, we have turned our attention toward silver; however, due to its large size, multiple coordination is feasible, which makes the synthesis formidable.<sup>7</sup> In this communication, we report the synthesis of silylene-stabilized monocordinate Ag-arene cationic complexes and their targeted use as catalysts.

afforded a series of propargylamines in good to excellent yields

with low catalyst loading under a solvent-free condition (19

The treatment of  $[\{PhC(N^{t}Bu)_{2}\}Si\{N-(SiMe_{3})_{2}\}]_{2}Ag_{2}(OTf)_{2} (1)^{Sb}$  with NaBAr<sup>F</sup><sub>4</sub> in a CH<sub>2</sub>Cl<sub>2</sub>arene (C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>Me<sub>6</sub> and MeC<sub>6</sub>H<sub>5</sub>) mixture at room temperature afforded monocoordinate Si(II)  $\rightarrow$  Ag(I) cationic complexes,  $[\{PhC(N^{t}Bu)_{2}SiN(SiMe_{3})_{2}\}Ag(\eta^{2}-C_{6}H_{6})]^{+}[BAr^{F}_{4}]^{-}$  (2),  $[\{PhC(N^{t}Bu)_{2}-SiN(SiMe_{3})_{2}\}Ag(\eta^{3}-C_{6}Me_{6})]^{+}[BAr^{F}_{4}]^{-}$  (3), and  $[\{PhC(N^{t}Bu)_{2}SiN(SiMe_{3})_{2}\}Ag(\eta^{3}-C_{6}Me_{6})]^{+}[BAr^{F}_{4}]^{-}$  (3), and  $[\{PhC(N^{t}Bu)_{2}SiN(SiMe_{3})_{2}]^{+}[BAr^{F}_{4}]^{-}$ 

Chart 1. Silylene-Stabilized Monocoordinated M(I)–Arene (M = Cu, Ag, Au) Cationic Complexes

Very efficient A3 coupling reaction

Use of silylene ligand to isolate  $Si(II) \rightarrow Ag^+$  complexes Well established structure of the catalysts by X-ray analysis



 $(MeC_6H_5)]^+[BAr^F_4]^-$  (4), respectively (Scheme 1). These are the first reports of silylene-stabilized monocoordinated Ag(I) cationic complexes weakly bound to benzene, hexamethylbenzene , and toluene. All the complexes are well-characterized by using routine NMR techniques and X-ray diffraction studies.



Received: February 10, 2021 Published: June 3, 2021





**Figure 1.** Molecular structures of **2** (ellipsoids are shown at the probability level of 30%). Hydrogen atoms and the  $[BAr^{F}_{4}]^{-}$  anion are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Si1–Ag1 2.37(2), Ag1–C25 2.43(8), Ag1–C24 2.54(1); Si1–Ag1–C25 170.8(2), Si1–Ag1–C24 147.0(2).

The coordination of the arene rings to the Ag(I) atom is accompanied by a slight shift in the <sup>1</sup>H NMR values: **3** shows a sharp singlet at 2.34 ppm for 18 protons of the hexamethyl group (free C<sub>6</sub>Me<sub>6</sub>:  $\delta$  2.22 ppm), **4** shows a peak at 2.45 ppm for methyl group of toluene shifted downfield compared to the free toluene ( $\delta$  2.36 ppm). The central Si(II) atom resonates at  $\delta$  -3.03 (**2**), -3.03 (**3**), and -3.97 (**4**) ppm in the respective <sup>29</sup>Si NMR spectrum, which are upfield-shifted relative to **1** ( $\delta$ 8.57 ppm). The presence of the [BAr<sup>F</sup><sub>4</sub>]<sup>-</sup> anion was supported by <sup>19</sup>F NMR ( $\delta$ ) (-62.37 (**2**), -62.42 (**3**), and -62.40 (**4**) ppm) and <sup>11</sup>B NMR ( $\delta$ ) (-6.60 (**2**), -6.61 (**3**), and -6.60 (**4**) ppm) studies. **2** crystallizes in the monoclinic *Cc* space group.

The molecular structures of 2, 3, and 4 disclose an  $\eta^2$  binding mode between the Ag(I) cation and arene ring. F atoms are prone to manifest disorder in many crystal structures, and we have also observed disorder of F in complexes 3 and 4. Since the assignment of low hapticity is a tough job, we followed the method of Alvarez and co-workers to assign the hapticity of the complexes 2, 3, and 4 (Table 1).<sup>8</sup>

Table 1. Hapticity Calculation of 2 and 3 by Comparing the Three Shortest Ag(I)– $C_{\text{arene}}$  Distances,  $d_1 < d_2 < d_3$ , via the Distance Ratios  $\rho_1$  and  $\rho_2^{\ \alpha}$ 

	M-C <sup>a</sup>	distance ratio $\rho_1$	distance ratio $\rho_2$	η
	$d_1, d_2, d_3$			
2	2.43, 2.54, 2.88	1.04	1.18	2
3	2.50, 2.52, 2.74	1.00	1.09	2
4	2.43, 2.55, 2.76	1.04	1.13	2
<sup><i>a</i></sup> M =	$cu, d_1 < d_2 < d_3, \rho_1$	$= d_2/d_1, \rho_2 = d_3/d_1$	. If $\rho_1 \approx \rho_2 \gg 1$ , th	en $\eta^1$

if  $\rho_2 > \rho_1 \approx 1$ , then  $\eta^2$ , and if  $\rho_1 \approx \rho_2 \approx 1$ , then  $\eta^3$ .

This method supports  $\eta^2$  coordination in 2, 3, and 4 with Ag– C<sub>benzene</sub> bond distances of 2.43(8) and 2.54(1) Å, Ag–C<sub>C6Me6</sub> bond distances of 2.50(2) and 2.52(3) Å, and Ag–C<sub>toluene</sub> bond distances of 2.43(3) and 2.55(3) Å. The central Si(II) atom adopts distorted tetrahedral geometry in all the three complexes. The lone pair of silylene is donated to the Ag(I) center in 2, 3, and 4 with the bond distances of 2.37(2), 2.35(3), and 2.37(8) Å, respectively. These bonds are in good agreement with 1 (2.337(2) Å) and other literature values.<sup>7d,9</sup>

To explore the potential of 2, 3, and 4 as catalysts, we utilized them for the  $A^3$ -coupling reaction.  $A^3$ -coupling is wellknown for the synthesis of propargylamines, which involves a multicomponent reaction of an aldehyde, an amine, and an alkyne in the presence of a transition-metal-based catalyst.<sup>10</sup> Exploration of Ag(I) complexes as catalysts for the formation of propargylamine was initiated by Li and co-workers<sup>11</sup> in



**Figure 2.** Molecular structures of 3 (left) and 4 (right) (ellipsoids are shown at the probability level of 30%). Hydrogen atoms and the  $[BAr_4^F]^-$  anion are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for 3: Si1–Ag1 2.35(7), Ag1–C1 2.50(2), Ag1–C2 2.52(3); Si1–Ag1–C1 162.86(6), Si1–Ag1–C2 161.60(6); for 4: Si1–Ag1 2.37(8), Ag1–C63 2.43(3), Ag1–C61 2.55(3); Si1–Ag1–C63 174.99(7), Si1–Ag1–C61 151.94(7).

2003, and after that, several research groups used either silver salts or combined them with nanoparticles, nanocomposites, metal–organic frameworks, and polymers for the A<sup>3</sup>-coupling.<sup>12–16</sup> A variety of ligands have also been exploited with silver metal to see the effect of the ligand in such transformations.<sup>17</sup> Unlike copper and gold, silver is not much explored, though it has advantages like (a) low cost, (b) low catalyst loading, and (c) less reaction time.

The literature suggests that the A<sup>3</sup>-coupling reaction involves the generation of the Ag(I) cations at first, which is weakly coordinated with the arene ring of the solvent or amine to generate an active catalyst.<sup>10</sup> In this context, our  $[Ag(I)-\eta^2$ arene]<sup>+</sup> complexes (2–4) would be the ideal catalysts for the A<sup>3</sup>-coupling reaction.

#### Scheme 2. Chemoselectivity of Catalyst 2



We first performed a model reaction involving paraformaldehyde, phenylacetylene, and piperidine under microwave irradiation (MW) with various catalysts under a solvent-free condition (Tables 2 and S1). The neutral complexes LSi(II)-AgOTf (1) and LSi(II)-AgBr (5) afforded moderate yields of the products (48 and 53%, respectively, Table 2, entries 1 and 2), whereas the  $\eta^2$ -coordinated Ag(I)-arene cationic complexes 2, 3, and 4 give ~90% product conversion (Table 2, entries 3, 4 and 5). The higher efficiency of the Ag(I) $-\eta^2$ arene cationic complexes could be explained by the strong electrophilic cationic silver atom (presumably arising due to the presence of the noncoordinating anion), which favors the coordination of the Ag(I) center to alkyne and subsequently the formation of the silver alkynide intermediate.<sup>11b</sup> We noticed that changing the arene ring coordinated to the Ag(I)center did not have a considerable effect in the formation of the product (Table 2). We compared the efficiency of our catalysts with the reported NHC–Ag(I) complexes (71–96%, Table 2, entries 10 and 11):<sup>17c,d</sup> while the reported catalysts give a low TOF (2.9–48  $h^{-1}$ ), our catalysts show a TOF of 3320-3640 h<sup>-1</sup> (for 0.1 mol % catalyst loading) and 14 160

 Table 2. Catalyst Screening for the A<sup>3</sup>-Coupling Reaction

 and Comparison with the Previously Reported Catalysts<sup>a</sup>

	+ [CH <sub>2</sub> O] <sub>n</sub> + Ph <del></del>	Cataly Solvent MW, 15 r	vst free min, 100°C	∕_N	<del>──</del> Ph
entry	catalyst	mol %	solvent	yield (%) <sup>d</sup>	$\begin{array}{c} TOF \\ (h^{-1}) \end{array}$
1	1	0.1	neat	53	2120
2	Si(II)→AgBr (5)	0.1	neat	48	1920
3	2	0.1	neat	90	3600
4	3	0.1	neat	88	3520
5	4	0.1	neat	90	3600
6	2 <sup>b</sup>	0.05	$CH_2Cl_2$	64	15 360
7	2 <sup>c</sup>	0.1	neat	95	950
8	-	-	neat	~20	-
9	-	-	neat <sup>c</sup>	~12	-
10	NHC $-Ag(I)^{17c}$ ,	0.5-3	neat	81— 96	48
11	PS-NHC-Ag(I) <sup>17d</sup>	1	neat	71	2.9
12	$\underset{(MOF)^{15}}{\text{MIL-101(Cr)}-SO_3Ag}$	0.06	neat	33	6600
13	PS-PEG-BPy-CuBr <sub>2</sub> (PS-PEG- supported) <sup>16b</sup>	0.05	neat	88	7320

<sup>*a*</sup>Reaction conditions: alkyne (1.0 mmol), aldehyde (1.1 mmol), amine (1.1 mmol), catalyst (0.1 mol %), neat reaction, 15 min, 100 °C, microwave irradiation (MW). <sup>*b*</sup>Catalyst (0.05 mol %), stock solution in dichloromethane (DCM), 5 min, 150 °C. <sup>*c*</sup>Conventional heating, 60 min, 100 °C. <sup>*d*</sup>Isolated yield (average of two runs).

19 200  $h^{-1}$  upon reducing the catalyst loading to 0.05 mol % (Table 2 and Table 3).

Table 3. A<sup>3</sup>-Coupling Reaction with 0.05 mol % of Catalyst  $2^{a}$ 

product	catalyst	mol %	solvent	yield (%)	TOF $(h^{-1})$		
Ι	2	0.05	$CH_2Cl_2$	64	15 360		
XIV	2	0.05	$CH_2Cl_2$	59	14 160		
XVIII	2	0.05	$CH_2Cl_2$	80	19 200		
$^a$ Catalyst (0.05 mol %) stock solution in DCM, 5 min, 150 °C.							

Since the best yield is obtained with 0.1 mol % catalyst loading, we performed the substrate scope with 0.1 mol % catalyst. Nevertheless, we tried three reactions with 0.05 mol % catalyst loading (stock solution), which demonstrated satisfactory yields (Table 3). The efficiency of our catalyst is even better than the Ag(I)-functionalized MOF (MIL-101-SO<sub>3</sub>Ag)<sup>15</sup> and polymer-supported Cu(II)-bipyridine (PS-PEG-BPy-CuBr<sub>2</sub>)<sup>16b</sup> (Table 2, entries 12 and 13), which are regarded as highly efficient catalysts for the A<sup>3</sup>-coupling reactions. We have also examined the effect of various other reaction parameters such as mol % of catalyst, temperature, solvent, and reaction time (Table S1). It was observed that the catalyst 2 is highly efficient in the solvent-free condition compared to when used with toluene or acetonitrile (70 and 79%, Table S1, entries 5 and 6). The blank test experiment gives a very small amount ( $\sim 20\%$ ) of product conversion even after 1 h (Table 2, entry 8). The catalytic reaction in the conventional method (without MW) at 100 °C yielded 95% product conversion in 60 min (Table 2, entry 7). To probe the substrate scope of catalyst 2, different types of alkynes and amines were investigated (Chart 2). We have examined various



"Used 1 mol % of catalyst 2 (neat). <sup>b</sup>Used 0.1 mol % of catalyst (neat) 2. <sup>c</sup>Used 0.05 mol % catalyst 2 (stock solution in DCM), 5 min, 150 °C. <sup>d</sup>Reaction conditions: alkyne (1.0 mmol), aldehyde (1.1 mmol), amine (1.1 mmol), neat reaction, 15 min, 100 °C, in inert atmosphere, Isolated yields (average of two runs).

alkynes featuring aromatic, deactivated aromatic, aliphatic, and heterocyclic rings with cyclic and acyclic secondary amines in the presence of paraformaldehyde. Gratifyingly, high yield (~81–99%) is observed for propargylamines containing phenylacetylene (I, II, III, and IV) and heterocyclic alkynes such as 3-ethynylthiophene (V, VI, VII, and VIII) and 2ethynylpyridine (XIII, XIV, XV, and XVI) with piperidine, diisopropylamine, diethylamine, and dimethylamine. Similarly, catalyst 2 efficiently activated aliphatic alkyne to give XVII in 82% yield. Of note, propargylamines IX, X, XI, and XII could also be isolated in a good yield (~74–89%) upon starting from highly unactivated alkynes containing an electron-withdrawing  $-CF_3$  moiety. The TOFs of all the complexes were calculated and reached up to 19 200 h<sup>-1</sup>, reflecting the higher efficiency of our catalyst, comparable with highly efficient catalysts, PS– PEG–BPy–CuBr<sub>2</sub><sup>16b</sup> and MIL-101–SO<sub>3</sub>Ag.<sup>15</sup> Interestingly, catalyst **2** also shows selectivity for 2-ethynylbenzaldehyde containing an alkyne group as well as aldehyde group to afford **XVIII** (>99%) and **XIX** (86%), where the –CHO group remains intact after the reaction. Based on NMR studies (of a 1:1 reaction of the catalyst and substrates), a tentative mechanism was proposed (Scheme 3): the first step involves

Scheme 3. Mechanism for A<sup>3</sup>-Coupling Reaction Calculated at the M06/def2-TZVPP//BP86-D3BJ/def2-TZVPP Level of Theory Using Catalyst 2 and Phenylacetylene, Formaldehyde, and Diisopropylamine as Reactants<sup>*a*</sup>



<sup>*a*</sup>Energies are in kcal/mol.

the displacement of the weakly coordinating arene upon the addition of an alkyne, which leads to the formation of a  $\pi$ -complex I.<sup>11b</sup> This increases the acidity of acetylenic hydrogen, which is further attacked by an amine to give silver acetylide II. The proton-assisted condensation between the amine and the aldehyde generates a molecule of water and the iminium halide III, which reacts with II to afford the final product. We have also carried out the A<sup>3</sup>-coupling reaction in the presence of H<sub>2</sub>O to check the stability of our catalyst, which gives 96% product conversion (Table S1, entry 7, see SI).

We performed quantum mechanical calculations at the M06/def2-TZVPP//BP86-D3BJ/def2-TZVPP level of theory to explore the reaction mechanism for the A<sup>3</sup>-coupling reaction using catalyst **2** and phenylacetylene, formaldehyde, and diisopropylamine as reactants.<sup>19</sup> The overall reaction is highly exothermic ( $\Delta E = -20.2 \text{ kcal/mol}$ ) and slightly exergonic ( $\Delta G = -6.7 \text{ kcal/mol}$ ). Among the several possible reaction pathways, the most feasible pathway is shown in Scheme 3.

The benzene ring is  $\eta^2$ -coordinated to the silylene-stabilized Ag(I) center in catalyst **2**, and the corresponding bonding interaction is rather weak.<sup>6</sup> The calculated energy for the dissociation of benzene from catalyst **2** is  $\Delta E = 21.2$  kcal/mol and  $\Delta G = 10.1$  kcal/mol. The first step of the reaction mechanism is the formation of intermediate II, wherein both phenylacetylene and arene (benzene here) are coordinated to the silylene-stabilized Ag(I) center. The Ag-C<sub>arene</sub> bond (2.699 and 2.762 Å) and C=C bond (1.229 Å) are significantly elongated as compared to those in catalyst **2** (2.386 and 2.683 Å) and phenylacetylene (1.215 Å). The reaction energy and Gibbs free energy for the formation of II are -8.3 and 5.6 kcal/mol, respectively. The subsequent dissociation of the benzene molecule from II results in  $\pi$ -

complex I2. This step is slightly endothermic (5.0 kcal/mol) and exergonic (-7.2 kcal/mol). The NBO charge analysis indicates that the complexation increases the acidity of acetylenic hydrogen in I2 (NBO charge = 0.27 e) as compared to that in phenylacetylene (NBO charge = 0.22 e).

Concurrently, the amine and aldehyde react together to form I3. The  $\Delta E$  and  $\Delta G$  for this reaction are -9.3 and 2.8 kcal/mol, respectively.<sup>20</sup> The C–O bond length in I3 (1.47 Å) is longer than the C-O bond length in alcohol (in the range of 1.41–1.43 Å), facilitating proton abstraction by coupling with I2, resulting in the formation of I4. The intermediate I4 is a  $\pi$ complex formed between the Ag(I) center and the C $\equiv$ C bond of the product molecule. Note that the OH group in I3 has a significantly high negative charge (-0.30 e), enabling the easy abstraction of a proton from I2. The formation of I4 is exothermic and exergonic ( $\Delta E = -16.3$  kcal/mol and  $\Delta G =$ -12.0 kcal/mol). The subsequent removal of the product by coordinating with phenylacetylene regenerates the active species I2, which can further react with I3 and continue the catalytic cycle. This step has  $\Delta E$  and  $\Delta G$  vales of 5.4 and 2.3 kcal/mol, respectively.

We have also calculated the abstraction of proton from I2 by amine (Scheme S1). The reaction energetics was found to be highly endothermic and endergonic ( $\Delta E = 33.6 \text{ kcal/mol}$  and  $\Delta G = 32.7 \text{ kcal/mol}$ ). A hydroxyl ion alone abstracting the proton from I2 was also considered as another possibility (Scheme S2), but the generation of a hydroxyl ion from an aldehyde and amine was found to be highly endothermic and endergonic ( $\Delta E = 171.1 \text{ kcal/mol}$  and  $\Delta G = 179.3 \text{ kcal/mol}$ ).

In summary, we have reported the rare examples of monocoordinate Ag(I)-arene cationic complexes (2-4) stabilized by an N-heterocyclic silylene. The electrophilic Ag(I) centers of 2-4 are involved in weak coordination with free benzene, hexamethylbenzene, and toluene. Consequently, we have investigated them as catalysts in the  $A^3$ -coupling reactions for a range of substrates and found them as a highly efficient catalyst in the solvent-free condition with a significantly higher TOF than the previously reported catalysts for this reaction. Our results will spur further interest in developing silylene-stabilized well-defined coinage metal complexes as catalysts for other organic transformations.

# EXPERIMENTAL SECTION

All experiments were carried out under an atmosphere of dry argon or in vaccuo using a standard Schlenk technique and in a dinitrogenfilled MBRAUN MB 150-G1 glovebox. The solvents used were purified by the MBRAUN solvent purification system MB SPS-800. The starting materials 1 were prepared as reported in the literature.<sup>5b</sup> All other chemicals purchased from Aldrich were used without further purification. <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si, <sup>11</sup>B, and <sup>19</sup>F NMR spectra were recorded with a Bruker 400 MHz spectrometer, using CDCl<sub>3</sub> as the solvent with an external standard (SiMe<sub>4</sub> for <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si; BF<sub>3</sub>·OEt<sub>2</sub> for <sup>11</sup>B; and CHF<sub>3</sub> for <sup>19</sup>F).

Synthesis of 2. First, 1 (0.270 g, 0.200 mmol) in 10 mL of benzene was added into another flask containing NaBArF<sub>4</sub> (0.354g, 0.400 mmol) in 25 mL of DCM. After overnight stirring at room temperature, NaOTf was precipitated out from the reaction mixture and was filtered off. The volume was reduced to 15 mL and kept at 0 °C. The colorless, block-shaped crystals suitable for X-ray analysis were observed after 1 day. Yield: 0.385 g (65%). Mp: 133–136 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  0.31 (s, 9H, SiMe<sub>3</sub>), 0.34 (s, 9H, SiMe<sub>3</sub>), 1.13 (s, 18H, CMe<sub>3</sub>), 7.01 (d, *J* = 7.5 Hz, 1H, Ph), 7.37 (d, *J* = 7.6 Hz, 1H, Ph), 7.48–7.53 (m, 2H, Ph), 7.57–7.64 (m, 9H, Ph), 7.74–7.82 (m, 10H, Ph) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100.613 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  3.44 (SiMe<sub>3</sub>), 4.82 (SiMe<sub>3</sub>), 30.60 (CH<sub>3</sub>, toluene),

31.70 (CMe<sub>3</sub>), 54.10 (CMe<sub>3</sub>), 116.70, 122.10, 124.81, 126.47, 126.88, 127.35, 127.72, 127.92, 128.25, 128.65, 130.53, 131.49, 133.69 (Ph–C), 168.49 (NCN) ppm. <sup>29</sup>Si{<sup>1</sup>H} NMR (79.495 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  6.36 (SiMe<sub>3</sub>), 4.84 (SiMe<sub>3</sub>), -3.03 (SiN(SiMe<sub>3</sub>)<sub>2</sub>) ppm. <sup>19</sup>F{<sup>1</sup>H} NMR (376.49 MHz, CDCl<sub>3</sub>, 298):  $\delta$  -62.37 ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (128.387 MHz, CDCl<sub>3</sub>, 298):  $\delta$  -6.60 ppm.

Synthesis of 3. First, 1 (0.270 g, 0.200 mmol), hexamethylbenzene (0.065 g, 0.400 mmol), and NaBArF<sub>4</sub> (0.354 g, 0.400 mmol) were added into a flask containing 25 mL of DCM. After overnight stirring at room temperature, NaOTf was precipitated out from the reaction mixture and was filtered off. Then, 3 was crystallized in a DCM-pentane mixture and kept at 0 °C. The colorless, block-shaped crystals suitable for X-ray analysis were observed after 1 day. Yield: 0.439 g (70%). Mp: 126–130 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ 0.20 (s, 9H, SiMe<sub>3</sub>), 0.25 (s, 9H, SiMe<sub>3</sub>), 1.04 (s, 18H, CMe<sub>3</sub>), 2.27 (s, 18H, CH<sub>3,C6Me6</sub>), 7.26–7.28 (m, 1H, Ph), 7.41–7.49 (m, 7H, Ph), 7.63 (bs, 9H, Ph) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100.613 MHz, CDCl<sub>3</sub>, 298 K): δ 3.36 (SiMe<sub>3</sub>), 4.41 (SiMe<sub>3</sub>), 16.28 (CH<sub>3</sub>, C<sub>6</sub>Me<sub>6</sub>), 30.62 (CMe<sub>3</sub>), 54.04 (CMe<sub>3</sub>), 116.53, 122.13, 124.84, 127.02, 127.42, 130.64, 131.42, 133.75 (Ph-C), 160.24 (NCN) ppm. <sup>29</sup>Si{<sup>1</sup>H} NMR (79.495 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  4.62 (SiMe<sub>3</sub>), 4.60 (SiMe<sub>3</sub>), -3.03 (SiN(SiMe<sub>3</sub>)<sub>2</sub>) ppm. <sup>19</sup>F{<sup>1</sup>H} NMR (376.49 MHz, CDCl<sub>3</sub>, 298):  $\delta$ -62.42 ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (128.387 MHz, CDCl<sub>3</sub>, 298):  $\delta$  -6.61 ppm.

Synthesis of 4. First, 1 (0.270 g, 0.200 mmol) in 10 mL of toluene was added into another flask containing NaBArF<sub>4</sub> (0.354 g, 0.400 mmol) in 25 mL of DCM. After overnight stirring at room temperature, NaOTf was precipitated out from the reaction mixture and was filtered off. The volume was reduced to 12 mL and kept at 0 °C. The colorless, block-shaped crystals suitable for X-ray analysis were observed after 1 day. Yield: 0.420 g (70%). Mp: 140-143 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  0.31 (s, 9H, SiMe<sub>3</sub>), 0.35 (s, 9H, SiMe<sub>3</sub>), 1.15 (s, 18H, CMe<sub>3</sub>), 2.45 (s, 3H, CH<sub>3</sub>, toluene), 7.01-7.03 (d, 1H, Hz, Ph), 7.34.7.38 (m, 2H, Ph), 7.42-7.53 (m, 5H, Ph), 7.57 (s, 5H, Ph), 7.75 (s, 9H, Ph) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100.613 MHz, CDCl<sub>3</sub>, 298 K): δ 4.58 (SiMe<sub>3</sub>), 5.79 (SiMe<sub>3</sub>), 21.49 (CH<sub>3</sub>, toluene), 31.64 (CMe<sub>3</sub>), 55.09 (CMe<sub>3</sub>), 117.88, 123.07, 125.78, 127.15, 127.94, 128.41, 128.74, 129.20, 131.57, 134.70 (Ph-C), 169.47 (NCN) ppm. <sup>29</sup>Si{<sup>1</sup>H} NMR (79.495 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$ 6.50 (SiMe<sub>3</sub>), 4.81 (SiMe<sub>3</sub>), -3.97 (d,  $J_{Si-Ag} = 567.3$  Hz, SiN(SiMe<sub>3</sub>)<sub>2</sub>) ppm. <sup>19</sup>F{<sup>1</sup>H} NMR (376.49 MHz, CDCl<sub>3</sub>, 298):  $\delta$  -62.40 ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (128.387 MHz, CDCl<sub>3</sub>, 298):  $\delta$  -6.60 ppm.

General Reaction Procedure for Propargylamine Synthesis. Alkyne (1.00 mmol), amine (1.10 mmol), and aldehyde (1.10 mmol) were taken into a sealed tube. The catalyst (neat or stock solution in  $CH_2Cl_2$ ) was added into the mixture. The suspension was heated under microwave irradiation at 100 °C for 15 min. After cooling to room temperature, the mixture was purified by flash column chromatography over a silica gel to afford desired propargylamines. The amount of product shown is the average of two runs. A concentrated solution of the samples in  $CDCl_3$  was sealed off in an NMR tube for measurement. Mass spectra were recorded using AB Sciex, 4800 plus MALDI TOF/TOF.

**Crystallographic Details.** Crystal data for 2–4 were collected on a Bruker Smart Apex Duo diffractometer at 100 K using Mo K $\alpha$ radiation ( $\lambda = 0.71073$  Å). The absorption correction was done using a multiscan method (SADABS). The structures were solved by direct methods and refined by full-matrix least-squares methods against F2 (SHELXL-2014/6).<sup>18</sup> The crystallographic data file (including structure factors) for 2, 3, and 4 has been deposited with the Cambridge Crystallographic Data Centre: 2056511 (2), 2056512 (3), and 2056513 (4).

**Computational Methodology.** DFT calculations were performed in the G09 program package.<sup>21</sup> The geometry optimizations were carried out using the GGA functional BP86 that is composed of a Becke 1988 exchange functional and Perdue 98 correlation functional.<sup>22</sup> D3BJ empirical dispersion was included while optimizing, which adds the D3 version of Grimme dispersion along with Becke–Johnson damping.<sup>23</sup> The def2-TZVPP basis set, which is of the triple- $\zeta$  valence type and augmented with two sets of polarization functions, was used for geometry optimization.<sup>24</sup> The single-point and natural bond orbital (NBO)<sup>25</sup> calculations were done using the meta-GGA functional M06 and def2-TZVPP basis set.<sup>26</sup>

# ASSOCIATED CONTENT

### **③** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.1c00083.

Experimental details, X-ray data, DFT data, and NMR spectra (PDF)

# **Accession Codes**

CCDC 2056511–2056513 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.

#### AUTHOR INFORMATION

#### **Corresponding Authors**

- Shabana Khan Department of Chemistry, Indian Institute of Science Education and Research Pune, Pune 411008, India;
  orcid.org/0000-0002-6844-3954; Email: shabana@ iiserpune.ac.in
- Pattiyil Parameswaran National Institute of Technology Calicut, Kozhikode 673601, Kerala, India; Orcid.org/ 0000-0003-2065-2463; Email: param@nitc.ac.in

# Authors

- Nasrina Parvin Department of Chemistry, Indian Institute of Science Education and Research Pune, Pune 411008, India Nilanjana Sen – Department of Chemistry, Indian Institute of
- Science Education and Research Pune, Pune 411008, India
- Srinu Tothadi Organic Chemistry Division, CSIR-National Chemical Laboratory, Pune 411008, India; <sup>©</sup> orcid.org/ 0000-0001-6840-6937
- Shahila Muhammed National Institute of Technology Calicut, Kozhikode 673601, Kerala, India

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.1c00083

#### **Author Contributions**

The manuscript was written through contributions of all authors.

#### Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

S.K. thanks BRNS and SERB (India) for the financial support. S.K. also thanks DST-FIST for single-crystal X-ray diffractometer. N.P. thanks to UGC for providing the fellowships. P.P. thanks DST, India, for the financial support, and S.M. thanks NIT Calicut for the fellowship.

#### REFERENCES

 (1) (a) Dorel, R.; Echavarren, A. M. Gold(I)-Catalyzed Activation of Alkynes for the Construction of Molecular Complexity. *Chem. Rev.* 2015, 115, 9028. (b) Díez-González, S.; Marion, N.; Nolan, S. P. N-Heterocyclic Carbenes in Late Transition Metal Catalysis. *Chem. Rev.* 2009, 109, 3612. (c) Fang, G.; Bi, X. Silver-Catalysed Reactions of Alkynes: Recent Advances. *Chem. Soc. Rev.* 2015, 44, 8124.
 (d) Nechaev, M. S.; Rayón, V. M.; Frenking, G. Energy Partitioning Analysis of the Bonding in Ethylene and Acetylene Complexes of Group 6, 8, and 11 Metals:  $(CO)_5TM-C_2H_x$  and  $Cl_4TM-C_2H_x$  (TM = Cr, Mo, W),  $(CO)_4TM-C_2H_x$  (TM = Fe, Ru, Os), and TM<sup>+</sup>-C<sub>2</sub>H<sub>x</sub> (TM = Cu, Ag, Au). *J. Phys. Chem. A* **2004**, *108*, 3134.

(2) (a) Wright, A. M.; İrving, B. J.; Wu, G.; Meijer, A. J. H. M; Hayton, T. W. A Copper(I)–Arene Complex with an Unsupported  $\eta^6$ Interaction. Angew. Chem., Int. Ed. **2015**, 54, 3088. (b) Herrero-Gómez, E.; Nieto-Oberhuber, C.; López, S.; Benet-Buchholz, J.; Echavarren, A. M. Cationic  $\eta^1/\eta^2$ -Gold(I) Complexes of Simple Arenes. Angew. Chem., Int. Ed. **2006**, 45, 5455. (c) Lavallo, V.; Frey, G. D.; Kousar, S.; Donnadieu, B.; Bertrand, G. Allene Formation by Gold Catalyzed Cross-Coupling of Masked Carbenes and Vinylidenes. Proc. Natl. Acad. Sci. U. S. A. **2007**, 104, 13569. (d) Weber, S. G.; Rominger, F.; Straub, F. B. Isolated Silver Intermediate of Gold Precatalyst Activation. Eur. J. Inorg. Chem. **2012**, 2012, 2863.

(3) (a) Pérez-Galán, P.; Delpont, N.; Herrero-Gómez, E.; Maseras, F.; Echavarren, A. M. Metal–Arene Interactions in Dialkylbiarylphosphane Complexes of Copper, Silver, and Gold. *Chem. - Eur. J.* **2010**, *16*, 5324. (b) Roy, M. M. D.; Ferguson, M. J.; McDonald, R.; Rivard, E. Approaching Monocoordination at a Silver(I) Cation. *Chem. Commun.* **2018**, *54*, 483.

(4) (a) Zhou, Y. P.; Driess, M. Isolable Silylene Ligands Can Boost Efficiencies and Selectivities in Metal-Mediated Catalysis. Angew. Chem., Int. Ed. 2019, 58, 3715. (b) Troadec, T.; Prades, A.; Rodriguez, R.; Mirgalet, R.; Baceiredo, A.; Saffon-Merceron, N.; Branchadell, V.; Kato, T. Silacyclopropylideneplatinum(0) Complex as a Robust and Efficient Hydrosilylation Catalyst. Inorg. Chem. 2016, 55, 8234. (c) Iimura, T.; Akasaka, N.; Iwamoto, T. A Dialkylsilylene-Pt(0) Complex with a DVTMS Ligand for the Catalytic Hydrosilvlation of Functional Olefins. Organometallics 2016, 35, 4071. (d) Frisch, P.; Inoue, S. Coinage Metal Complexes of NHC-stabilized Silvliumylidene Ions. Chem. Commun. 2018, 54, 13658. (e) Paesch, A. N.; Kreyenschmidt, A.-K.; Herbst-Irmer, R.; Stalke, D. Side-Arm Functionalized Silylene Copper(I) Complexes in Catalysis. Inorg. Chem. 2019, 58, 7000. (f) Inagawa, Y.; Ishida, S.; Iwamoto, T. Twocoordinate Dialkylsilylene-Coinage Metal Complexes. Chem. Lett. 2014, 43, 1665. (g) Meltzer, A.; Präsang, C.; Milsmann, C.; Driess, M. The Striking Stabilization of Ni<sup>0</sup>( $\eta^6$ -Arene) Complexes by an Ylide-Like Silylene Ligand. Angew. Chem., Int. Ed. 2009, 48, 3170. (h) Meltzer, A.; Präsang, C.; Driess, M. Diketiminate Silicon(II) and Related NHSi Ligands Generated in the Coordination Sphere of Nickel(0). J. Am. Chem. Soc. 2009, 131, 7232. (i) Meltzer, A.; Inoue, S.; Präsang, C.; Driess, M. J. Am. Chem. Soc. 2010, 132, 3038. (j) Asay, M.; Jones, C.; Driess, M. N-Heterocyclic Carbene Analogues with Low-Valent Group 13 and Group 14 Elements: Syntheses, Structures, and Reactivities of a New Generation of Multitalented Ligands. Chem. Rev. 2011, 111, 354. (k) Wang, W.; Inoue, S.; Enthaler, S.; Driess, M. Bis(silylenyl)- and Bis(germylenyl)-Substituted Ferrocenes: Synthesis, Structure, and Catalytic Applications of Bidentate Silicon(II)-Cobalt Complexes. Angew. Chem., Int. Ed. 2012, 51, 6167. (1) Blom, B.; Stoelzel, M.; Driess, M. New Vistas in N-Heterocyclic Silylene (NHSi) Transition-Metal Coordination Chemistry: Syntheses, Structures and Reactivity towards Activation of Small Molecules. Chem. - Eur. J. 2013, 19, 40. (m) Blom, B.; Gallego, D.; Driess, M. Nheterocyclic Silylene Complexes in Catalysis: New Frontiers in an Emerging Field. Inorg. Chem. Front. 2014, 1, 134. (n) Raoufmoghaddam, S.; Zhou, Y.-P.; Wang, Y.; Driess, M. N-heterocyclic Silylenes as Powerful Steering Ligands in Catalysis. J. Organomet. Chem. 2017, 829, 2. (o) Luecke, M.-P.; Porwal, D.; Kostenko, A.; Zhou, Y.-P.; Yao, S.; Keck, M.; Limberg, C.; Oestreich, M.; Driess, M. Bis(silylenyl)-Substituted Ferrocene-stabilized  $\eta^6$ -Arene Iron(p) Complexes: Synthesis, Structure and Catalytic Application. Dalton. Trans. 2017, 46, 16412. (q) Shan, C.; Yao, S.; Driess, M. Where Silylene-Silicon Centres Matter in the Activation of Small Molecules. Chem. Soc. Rev. 2020, 49, 6733.

(5) (a) Sen, S. S.; Hey, J.; Herbst-Irmer, R.; Roesky, H. W.; Stalke, D. Striking Stability of a Substituted Silicon(II) Bis(trimethylsilyl)amide and the Facile Si–Me Bond Cleavage without a Transition Metal Catalyst. J. Am. Chem. Soc. **2011**, 133, 12311. (b) Khan, S.; Ahirwar, S. K.; Pal, S.; Parvin, N.; Kathewad, N. Silicon(II) Bis(trimethylsilyl)amide ( $LSiN(SiMe_3)_2$ , L = PhC(NtBu)\_2) Supported Copper, Silver, and Gold Complexes. *Organometallics* **2015**, 34, 5401. (c) Parvin, N.; Dasgupta, R.; Pal, S.; Sen, S. S.; Khan, S. Strikingly Diverse Reactivity of Structurally Identical Silylene and Stannylene. *Dalton Trans.* **2017**, *46*, 6528.

(6) (a) Parvin, N.; Pal, S.; Echeverría, J.; Alvarez, S.; Khan, S. Taming a monomeric  $[Cu(\eta^6-C_6H_6)]^+$  complex with silylene. *Chem. Sci.* **2018**, *9*, 4333. (b) Parvin, N.; Hossain, J.; George, A.; Parameswaran, P.; Khan, S. N-Heterocyclic Silylene Stabilized Monocordinated Copper(I)–Arene Cationic Complexes and Their Application in Click Chemistry. *Chem. Commun.* **2020**, *56*, 273. (c) Parvin, N.; Mishra, B.; George, A.; Neralkar, M.; Hossain, J.; Parameswaran, P.; Hotha, S.; Khan, S. N-Heterocyclic Silylene/Germylene Ligands in Au(I) Catalysis. *Chem. Commun.* **2020**, *56*, 7625.

(7) (a) Munakata, M.; Wu, L. P.; Ning, G. L. A New Type of Multilayer System-Silver(I) Somplexes of Polycyclic Aromatic Compounds. *Coord. Chem. Rev.* **2000**, *198*, 171. (b) Ogawa, K.; Kitagawa, T.; Ishida, S.; Komatsu, K. Synthesis and Structure of a New Tetrakis(pentafluorophenyl)borate Salt of the Silver(I) Cation with Novel Trigonal Planar Tris(benzene) Coordination. *Organometallics* **2005**, *24*, 4842. (c) Wong, V. H. L.; White, A. J. P.; Hor, T. S. A.; Hii, K. K. *Chem. Commun.* **2015**, *51*, 17752. (d) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Ning, G. L.; Kojima, T. Supramolecular Silver(I) Complexes with Highly Strained Polycyclic Aromatic Compounds. *J. Am. Chem. Soc.* **1998**, *120*, 8610. (8) Falceto, A.; Carmona, E.; Alvarez, S. Electronic and Structural Effects of Low-Hapticity Coordination of Arene Rings to Transition

Metals. Organometallics 2014, 33, 6660. (9) (a) Bayler, A.; Schier, A.; Bowmaker, G. A.; Schmidbaur, H. Gold Is Smaller than Silver. Crystal Structures of [Bis-(trimesitylphosphine)gold(I)] and [Bis(trimesitylphosphine)silver-(I)] Tetrafluoroborate. J. Am. Chem. Soc. 1996, 118, 7006. (b) Fianchini, M.; Dai, H.; Dias, H. V. R. Organometallic Wheels Based on Coinage Metal Ions and Norbornene: Syntheses and Structural Characterization of  $[M(norbornene)_3][SbF_6]$  (M = Au, Ag, Cu). Chem. Commun. 2009, 6373.

(10) (a) Peshkov, V. A.; Pereshivko, O. P.; Van der Eycken, E. V. A
Walk Around the A<sup>3</sup>-coupling. *Chem. Soc. Rev.* 2012, 41, 3790.
(b) Jesin, I.; Nandi, G. C. Recent Advances in the A<sup>3</sup> Coupling Reactions and their Applications. *Eur. J. Org. Chem.* 2019, 2019, 2704.
(c) Hashmi, A. S. K. In *Silver in Organic Chemistry*; Harmata, M., Ed.; Wiley: Hoboken, NJ, 2010; p 357.

(11) (a) Wei, C.; Li, Z.; Li, C.-J. The First Silver-Catalyzed Three-Component Coupling of Aldehyde, Alkyne, and Amine. Org. Lett. **2003**, *5*, 4473. (b) Abbiati, G.; Rossi, E. Silver and Gold-Catalyzed Multicomponent Reactions. Beilstein J. Org. Chem. **2014**, *10*, 481.

(12) (a) Reddy, K. M.; Babu, N. S.; Suryanarayana, I.; Prasada, P. S. S.; Lingaiah, N. The Silver Salt of 12-Tungstophosphoric Acid: An Efficient Catalyst for the Three-Component Coupling of an Aldehyde, an Amine and an Alkyne. *Tetrahedron Lett.* **2006**, *47*, 7563. (b) Huang, B.; Yao, X.; Li, C.-J. Diastereoselective Synthesis of  $\alpha$ -Oxyamines via Gold-, Silver- and Copper-Catalyzed, Three-Component Couplings of  $\alpha$ -Oxyaldehydes, Alkynes, and Amines in Water. *Adv. Synth. Catal.* **2006**, *348*, 1528.

(13) (a) Elhampour, A.; Malmir, M.; Kowsari, E.; Boorboorajdari, F.; Nemati, F. Ag-Doped Nano Magnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@DA Core-Shell Hollow Spheres: An Efficient and Recoverable Heterogeneous Catalyst for A<sup>3</sup> and KA<sup>2</sup> Coupling Reactions and [3 + 2] Cycloaddition. RSC Adv. **2016**, 6, 96623. (b) GhavamiNejad, A.; Kalantarifard, A.; Yang, G. S.; Kim, C. S. In-situ Immobilization of Silver Nanoparticles on ZSM-5 type Zeolite by Catechol Redox Chemistry, a Green Catalyst for A3-Coupling Reaction. *Microporous Mesoporous Mater.* **2016**, 225, 296.

(14) Salam, N.; Sinha, A.; Roy, A. S.; Mondal, P.; Jana, N. R.; Islam, S. M. Synthesis of Silver–Graphene Nanocomposite and its Catalytic Application for the One-Pot Three-Component Coupling Reaction

and One-PotS of 1,4-Disubstituted 1,2,3-Triazoles in Water. *RSC Adv.* **2014**, *4*, 10001.

(15) Sun, W.-J.; Xi, F.-G.; Pan, W.-L.; Gao, E.-Q. MIL-101(Cr)-SO<sub>3</sub>Ag: An Efficient Catalyst for Solvent-Free A<sup>3</sup> Coupling Reactions. *J. Mol. Catal. A: Chem.* **2017**, *430*, *36*.

(16) (a) Cao, J.; Xu, G.; Li, P.; Tao, M.; Zhang, W. Polyacrylonitrile Fiber Supported N-Heterocyclic Carbene Ag(I) As Efficient Catalysts for Three-Component Coupling and Intramolecular 1,3-Dipolar Cycloaddition Reactions under Flow Conditions. ACS Sustainable Chem. Eng. 2017, 5, 3438. (b) Yan, S.; Pan, S.; Osako, T.; Uozumi, Y. Solvent-Free A<sup>3</sup> and KA<sup>2</sup> Coupling Reactions with mol ppm Level Loadings of a Polymer-Supported Copper(II)–Bipyridine Complex for Green Synthesis of Propargylamines. ACS Sustainable Chem. Eng. 2019, 7, 9097. (c) Zeng, T.; Chen, W.-W.; Cirtiu, C. M.; Moores, A.; Song, G.; Li, C.-J. Fe<sub>3</sub>O<sub>4</sub> Nanoparticles: a Robust and Magnetically Recoverable Catalyst for Three-Component Coupling of Aldehyde, Alkyne and Amine. Green Chem. 2010, 12, 570.

(17) (a) Prakash, O.; Joshi, H.; Kumar, U.; Sharma, A. K.; Singh, A. K. Acridine Based (S,N,S) Pincer Ligand: Designing Silver(I) Complexes for the Efficient Activation of A<sup>3</sup> (Aldehyde, Alkyne and Amine) Coupling. *Dalton Trans.* **2015**, *44*, 1962. (b) Grirrane, A.; Álvarez, E.; García, H.; Corma, A. Catalytic Activity of Cationic and Neutral Silver(I)–XPhos Complexes with Nitrogen Ligands or Tolylsulfonate for Mannich and Aza-Diels–Alder Coupling Reactions. *Chem. - Eur. J.* **2016**, *22*, 340. (c) Demir Atlı, D.; Gülle, S. Dinuclear N-Heterocyclic Carbene Silver Complexes: Synthesis, Luminescence and Catalytic Studies. *J. Mol. Struct.* **2019**, *1179*, 576. (d) Li, P.; Wang, L.; Zhang, Y.; Wang, M. Highly Efficient Three-Component (Aldehyde–Alkyne–Amine) Coupling Reactions Catalyzed by a Reusable PS-supported NHC–Ag(I) Under Solvent-Free Reaction Conditions. *Tetrahedron Lett.* **2008**, *49*, 6650.

(18) (a) Kottke, T.; Stalke, D. Crystal Handling at Low Temperatures. J. Appl. Crystallogr. 1993, 26, 615. (b) Stalke, D. Cryo Crystal Structure Determination and Application to Intermediates. Chem. Soc. Rev. 1998, 27, 171. (c) Sheldrick, G. M. Crystal Structure Refinement with SHELXL. Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 3. (d) Schulz, T.; Meindl, K.; Leusser, D.; Stern, D.; Graf, J.; Michaelsen, C.; Ruf, M.; Sheldrick, G. M.; Stalke, D. A Comparison of a Microfocus X-ray Source and a Conventional Sealed Tube for Crystal Structure Determination. J. Appl. Crystallogr. 2009, 42, 885. (e) Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. Comparison of Silver and Molybdenum Microfocus X-ray Sources for Single-Crystal Structure Determination. J. Appl. Crystallogr. 2015, 48, 3.

(19) See the Supporting Information for the detailed computational data.

(20) Neshat, A.; Afrasi, M.; Gilanchi, S.; Gholinejad, M. An Efficient A<sup>3</sup> Coupling Catalyst Based on a Silver Complex Bearing N-Heterocyclic Carbene and Homoscorpionate Bis(3-methyl-mercaptoimidazolyl)borate Ligands. *ChemistrySelect.* **2019**, *4*, 9268.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision B.01; Gaussian, Inc.: Wallingford, CT, 2009.

(22) (a) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, *38*, 3098. (b) Perdew, J. P. Density-Functional Approximation for the Correlation Energy of the Inhomogeneous Electron Gas. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, 33, 8822.

(23) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping Function in Dispersion Corrected Density Functional Theory. J. Comput. Chem. 2011, 32, 1456.

(24) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

(25) (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. Intermolecular Interactions from a Natural Bond Orbital, Donor-Acceptor View-Point. *Chem. Rev.* **1988**, *88*, 899. (b) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO*, Version 5.9.

(26) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 other Functionals. *Theor. Chem. Acc.* **2008**, *120*, 215.