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Copper-Catalyzed Chemoselective Silylative Cyclization of 2,2′-Diethynylbiaryl Derivatives

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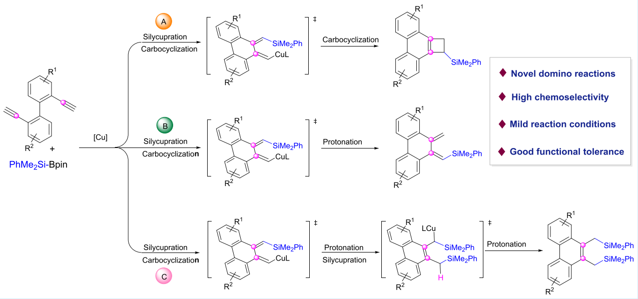
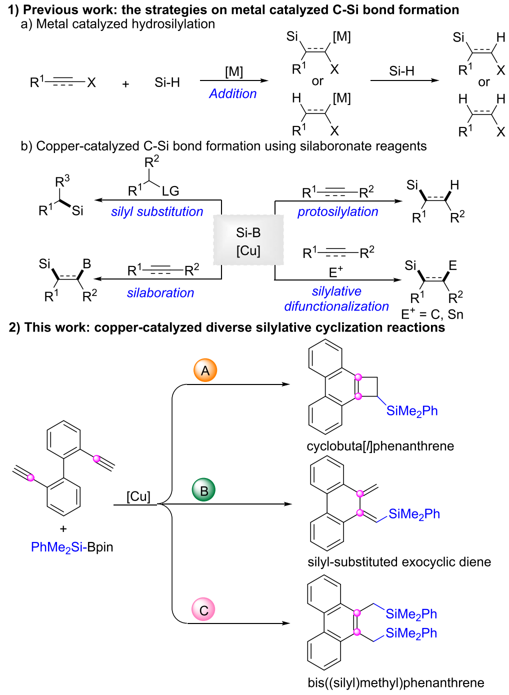
ABSTRACT: In this protocol, copper-catalyzed diverse silylative carbocyclization reactions of 2,2′-diethynylbiaryl derivatives with silaboronate were reported. Three new and novel types of domino reactions for the copper-catalyzed transformation of silaboronate were discovered. The corresponding cyclobuta[*l*]phenanthrene, bis((silyl)methyl)phenanthrene, and silyl-substituted exocyclic diene products were chemoselectively formed with high efficiency.



Organosilicon reagents play a crucial role in organic synthesis.[1] During the past several decades, organosilicon chemistry has substantially matured, and many new methodologies have been discovered for the construction of different C−Si bonds.[2] Among them, classic hydrosilylation is one of the most direct and powerful methods for introducing the silyl group into unsaturated molecules (Scheme 1, 1a).[3] It should be noticed that the hydrosilylation strategy is limited to the addition reaction pathway for the synthesis of organosilicon compounds, which hampers the magnification of the product scope to a considerable extent. To solve this problem, other silyl sources were explored to enhance the conversion ability.[4] In new approaches, the copper-catalyzed C−Si bond formation using silaboronate reagents via the activation of the Si−B interelement bond has achieved rapid development due to its flexible reaction styles,[5] including the currently developed protosilyaltion,[6] nucleophilic substitution,[7] silaboration,[8] and radical addition (Scheme 1, 1b).[9] However, it is worth pointing out that the construction of complex molecules via this strategy still has much room for development. Recently, copper-catalyzed silylation-induced domino reactions have gradually appeared as powerful tools to prepare functionalized organic compounds with linear structures (Scheme 1, 1b).[10] Compared with other transition-metal-catalyzed carbocyclization reactions of diynes for constructing cyclic molecular skeletons,[11] so far, examples of copper-catalyzed silylative cyclization have very rarely been realized. In 2015, Tian and coworkers elegantly demonstrated a copper-catalyzed asymmetric silylative cyclization of cyclohexadienone-tethered allenes to access bicyclo[4.3.0]nonanes.[12] Following this work, the enantioselective case of 1,6-enynes was reported by the same group.[13]

Recently, during our investigation of the copper-catalyzed silaboration of alkynes, the unexpected silaborative carbocyc-

Scheme 1. Metal-Catalyzed C−Si Bond Formation



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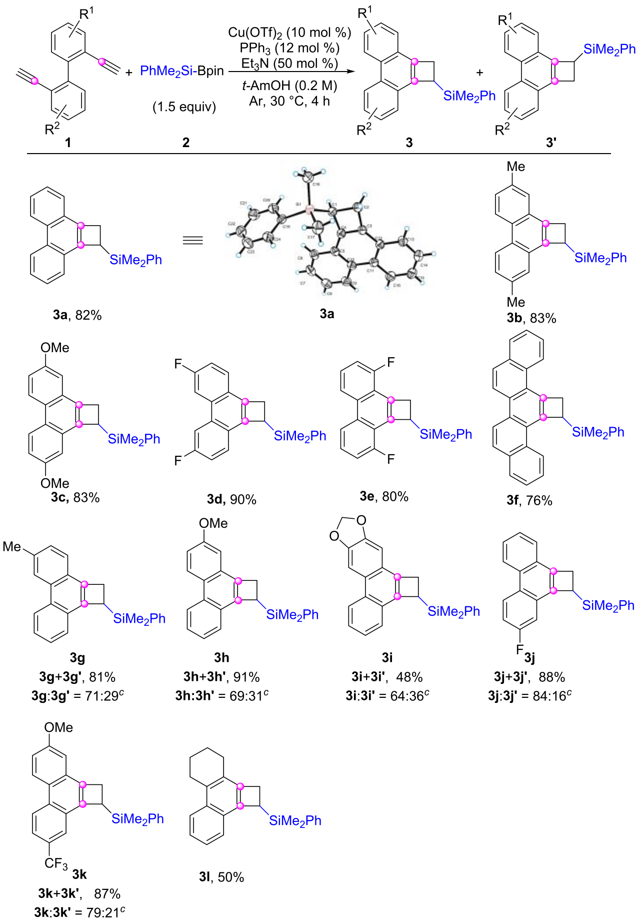
lization of hepta-1,6-diyne and octa-1,7-diyne was observed. To expand the utility of this copper-catalyzed silaborative carbocyclization of diynes for the synthesis of useful phenanthrene derivatives, 2,2′-diethynylbiphenyl was tried as a substrate. Surprisingly, the designed reaction did not work, whereas three previously undeveloped and novel copper-catalyzed domino reactions including the silycupration/dual carbocyclization/protonation to form cyclobuta[*l*]-phenanthrene (Schemes 1 and 2A), the silycupration/carbocyclization/protonation to give silyl-substituted exocyclic diene (Schemes 1 and 2B), and the dual silycupration/carbocyclization/dual protonation to generate bis((silyl)-methyl)phenanthrene (Schemes 1 and 2C) products were achieved, respectively, with high chemoselectivity and efficiency.

Scheme 2. Substrate Scope for the Synthesis of Products 3[a,b]

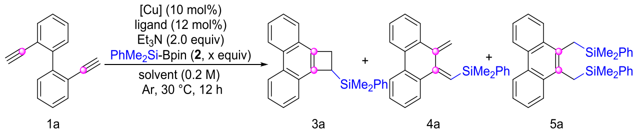


[a]Condition A: The mixture of **1** (0.1 mmol), **2** (0.15 mmol), $Cu(OTf)_2$ (10 mol %), PPh_3 (12 mol %), and Et_3N (50 mol %) in extra dry EtOH (0.2 M) was stirred at 30 °C in an oil bath for 4 h under an argon atmosphere. [b]Isolated yield. [c]Regioselectivities (**3**/**3′**) were determined by ^1H NMR of the crude mixture.

Initially, the 2,2′-diethynylbiphenyl **1a** and Suginome silaboronate **2** were selected for the model reaction to optimize the conditions, and the results are shown in Table 1. First, the reaction was tried in the presence of CuTC (copper(I) thiophene-2-carboxylate) as a catalyst in ethanol solution via changing different phosphine ligands (Table 1, entries 1−3). It was found that cyclobuta[*l*]phenanthrene **3a**, exocyclic diene **4a**, and bis((silyl)methyl)phenanthrene **5a**, three interesting products, were formed. Our aim was to improve the reaction chemoselectivities and the yields of the desired products. Significantly, when 10 mol % CuTC as a catalyst, 12 mol % PPh_3 as a ligand, and 2.0 equiv of Et_3N as an additive were applied in this reaction, the ratio of product **3a** of the three products was significantly increased (Table 1, entry 3). Therefore, other copper salts were screened to catalyze this reaction. When $CuCl_2$ was used, bis((silyl)methyl)-phenanthrene **5** as a major product was obtained in 38% yield (Table 1, entry 4). In contrast, product **3a** was observed when $Cu(OTf)_2$ (copper(II) trifluoromethanesulfonate) was employed (60% yield, Table 1, entry 5). To further improve the yield of the cyclobuta[*l*]phenanthrene product **3a**, different alcohols as the solvent were investigated (Table 1, entries 6 and 7). With an increase in the steric hindrance of alcohol, the yield of product **3a** was improved. Finally, **3a** could be obtained in 82% isolated yield by using 1.5 equiv of $PhMe_2Si$-Bpin (**2**) in *tert*-amylalcohol solution (Table 1, entry 8). We further optimized the reaction conditions for the highly selective synthesis of product **4a**. We noticed that the $CuCl_2$ catalyst could favor the formation of exocyclic diene product **4a** (Table 1, entry 4). Additionally, to achieve a higher yield of product **4a**, the loading of $PhMe_2Si$-Bpin **2** was reduced (38% yield, Table 1, entry 9). Therefore, after carefully screening different phosphine ligands, the exocyclic diene product **4a** could be detected in 67% yield by using (*o*-tolyl)Cy_2P (Table 1, entries 10−12). Furthermore, by increasing the concentration of the reaction and decreasing the amount of silylboronate reagent **2** used in the reaction, a 73% isolated yield of **4a** was obtained (Table 1, entry 14). When bipyridine instead of the phosphine ligand was applied in reaction, bis((silyl)methyl)phenanthrene **5a** as a single product was obtained (Table 1, entries 15−17). To improve the yield of product **5a**, ethanol was used as a proton source to screen other solvents (Table 1, entries 18 and 19). Finally, it was found that the desired product **5a** was obtained in 85% isolated yield with diethyl ether as the solvent (Table 1, entry 19).

Under the optimized reaction conditions (Table 1, entry 8), the substrate scope of compound **1** to synthesize the cyclobuta[*l*]phenanthrene derivatives was examined. The results are summarized in Scheme 2. A series of substituted cyclobuta[*l*]phenanthrene derivatives **3a**−**3l** were synthesized in good to excellent yields. The reaction was mainly affected by the substituents on the aromatic rings. Both electron-donating (**3b**, **3c**, **3g**, **3h**, **3i**) and electron-withdrawing (**3d**, **3e**, **3j**) groups on the rings were well tolerated in this reaction. Notably, the cyclobuta[*s*]picene derivative **3f** could be obtained in high yield. On the contrary, unsymmetrical diethynylbiphenyl derivatives were also subjected to this reaction. It was found that compound **1g** with a methyl group at the five-position of the biphenyl underwent the protosilylation and cyclization processes to give the corresponding substituted cyclobuta[*l*]phenanthrene product in 81% yield (**3g**/**3g′** 71:29).[14] Similarly, biphenyls with different substituents (**1h**−**1k**) could be well tolerated to furnish the corresponding products in good yields with moderate regioselectivity under the standard reaction conditions. Interestingly, when the 2′,6-diethynyl-2,3,4,5-tetrahydro-1,1′-biphenyl (**1l**) reacted with silylboronate **2** under the optimized reaction conditions, the ring-fused naphthalene derivative **3l** was isolated in 50% yield. The structure of cyclobuta[*l*]-

Table 1. Optimization of Reaction Conditions[a]



					yield (%)[b]		
entry	[Cu] (mol %)	ligand (mol %)	solvent (extra dry)	2 (x equiv)	**3a**	**4a**	**5a**
1	CuTC	JohnPhos	EtOH	2.0	6	7	1
2	CuTC	BINAP	EtOH	2.0	24	10	1
3	CuTC	PPh_3	EtOH	2.0	37	8	6
4	$CuCl_2$	PPh_3	EtOH	2.0	2	5	38
5	$Cu(OTf)_2$	PPh_3	EtOH	2.0	60		19
6	$Cu(OTf)_2$	PPh_3	^{i}PrOH	2.0	72		17
7	$Cu(OTf)_2$	PPh_3	^{t}AmOH	2.0	83		10
8[c]	**$Cu(OTf)_2$**	**PPh_3**	**^{t}AmOH**	**1.5**	**88 (82)**[d]		**6**
9	$CuCl_2$	PPh_3	EtOH	1.5	4	38	15
10	$CuCl_2$	P^tBu_3	EtOH	1.5	28	50	2
11	$CuCl_2$	PCy_3	EtOH	1.5	6	59	1
12	$CuCl_2$	(o-tolyl)Cy_2P	EtOH	1.5	4	67	13
13	$CuCl_2$	(o-tolyl)Cy_2P	EtOH (0.4 M)	1.5	3	73	9
14[e]	**$CuCl_2$**	**(o-tolyl)Cy_2P**	**EtOH (0.4 M)**	**1.4**	**3**	**75 (73)**[d]	**8**
15	$CuCl_2$	6,6′-Me-bpy	EtOH	2.5			5
16	$CuCl_2$	dtbbpy	EtOH	2.5			58
17	$CuCl_2$	bpy	EtOH	2.5			69
18	$CuCl_2$	bpy	EtOH (3.0 equiv) in DMSO	2.5			53
19	**$CuCl_2$**	**bpy**	**EtOH (3.0 equiv) in Et_2O**	**2.5**			**85 (85)**[d]

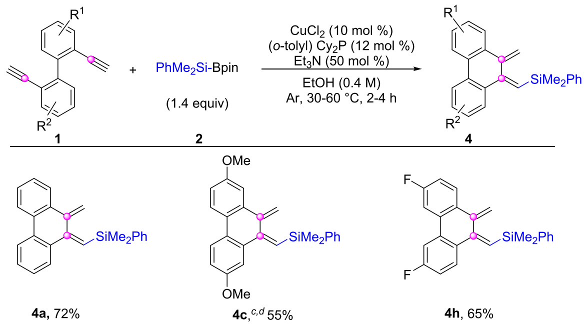
[a]Mixture of 0.1 mmol **1** (1.0 equiv), **2** (x equiv), copper catalyst (10 mol %), ligand (12 mol %), and Et_3N (2.0 equiv) in extra dry solvent (0.2 M) was stirred at 30 °C in an oil bath for 12 h under an argon atmosphere. (See the SI.) [b]Determined by ^1H NMR with the use of $(CHCl_2)_2$ as an internal standard. [c]0.05 mmol Et_3N (0.5 equiv), stirred for 4 h. [d]Isolated yield. [e]0.05 mmol Et_3N (0.5 equiv), stirred for 2 h. 6,6′-Me-bpy, 6,6′-dimethyl-2,2′-bipyridine; dtbbpy, 4,4′-di-*tert*-butyl-2,2′-bipyridine.

phenanthrene derivatives **3a** was confirmed by X-ray single-crystal diffraction analysis (CCDC no. 2063184).

Previously, copper-catalyzed protosilylation and carbocyclization domino reactions of diynes were still undiscovered. Herein the silyl-substituted exocyclic diene product **4a** was successfully obtained in 73% isolated yield (Table 1, entry 14), but it was found that this kind of exocyclic diene compound could not be exposed to the air for a long time due to its partial decomposition at ambient temperature. The reason might be O_2-induced oligomerization. This high reactivity indicated that the silyl-substituted exocyclic dienes **4** could be a candidate for Diels−Alder cyclization. Therefore, the substrates with both electron-donating and electron-withdrawing groups were representatively chosen to react with silaboronate **2** under the optimized reaction conditions. The corresponding products **4c** and **4h** were obtained in 55 and 65% isolated yields, respectively (Scheme 3).

As shown in Scheme 4, a series of bis((silyl)methyl)-phenanthrene compounds **5** were prepared in good yields under the standard reaction conditions. Various functional groups including electron-donating and electron-withdrawing groups were also well tolerated (Scheme 4). It was believed that the silyl-substituted exocyclic dienes were the intermediates during these carbocyclization/dual protosilylation domino reactions. To confirm the relationships of the previously described domino reactions, the products **3a**, **4a**, and **5a** were isolated and subjected to the mutual transformations under the corresponding standard reaction conditions, respectively.[15] It was observed that no reaction happened between the products **3a** and **4a** at all. On the contrary, when compound **4a** was used as the substrate, product **5a** was obtained in 88% yield.

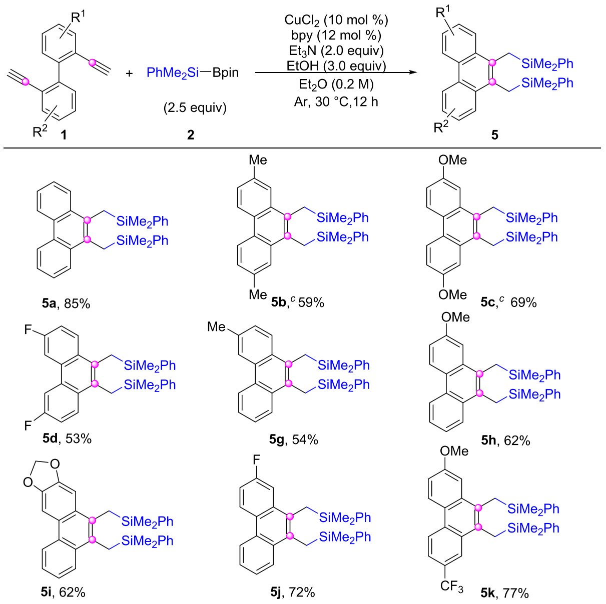
Scheme 3. Substrate Scope for the Synthesis of Product 4[a,b]



[a]Condition B: The mixture of **1** (0.1 mmol), **2** (0.14 mmol), $CuCl_2$ (10 mol %), (o-tolyl)Cy_2Ph (12 mol %), and Et_3N (50 mol %) in extra dry EtOH (0.4 M) was stirred at 30 °C in an oil bath for 2 h under an argon atmosphere. [b]Isolated yield. [c]60 °C in an oil bath, stirred for 4 h. [d]Yield was determined according to the mixed weight and the ^1H NMR ratio between **4c** and **5c**.

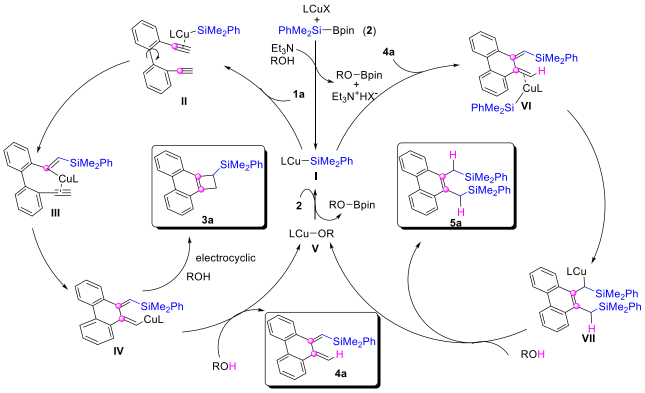
On the basis of the previously described results and previous work, a plausible mechanism for the synthesis of products **3a**, **4a**, and **5a** from 2,2′-diethynylbiphenyl is depicted in Scheme 5. First, the LCu-$SiMe_2Ph$ species **I** could be generated from silylboronate **2**, CuX, and Et_3N in alcohol. After the silylcupration of one triple bond of 2,2′-diethylbiphenyl, a vinyl cuprate species **III** would be formed. Subsequently, the dienylcuprate intermediate **IV** generated in situ via carbocyc-

Scheme 4. Substrate Scope for the Synthesis of Products 4[a,b]



[a]Condition C: The mixture of **1** (0.1 mmol), **2** (0.25 mmol), $CuCl_2$ (10 mol %), bpy (12 mol %), Et_3N (2.0 equiv), and EtOH (3.0 equiv) in dry Et_2O (0.2 M) was stirred at 30 °C in an oil bath for 12 h under an argon atmosphere. [b]Isolated yield. [c]16 h.

Scheme 5. Possible Mechanistic Pathways



lization would undergo two different pathways: (1) Direct cyclization/protonation reactions to give the cyclobuta[*l*]-phenanthrene **3a** would happen.[16] (2) The exocyclic diene product **4a** would be furnished via a protonation process. The LCu-OR species released as catalyst **V** would be involved in another catalytic cycle to activate silylboronate **2** again. Then, the regenerated LCu-$SiMe_2Ph$ species I would further react with the exocyclic diene product **4a**. Finally, the bis((silyl)-methyl)phenanthrene product **5a** would also be generated.

In conclusion, we have developed general and straightforward catalytic approaches to access three silyl-substituted polycyclic phenanthrene derivatives, respectively. Starting from the readily available 2,2′-diethynylbiaryl derivatives, these copper-catalyzed silylative cyclization domino reactions can be applied to construct complex molecules with high efficiency under mild conditions. The transformations of the cyclobuta-[*l*]phenanthrene and the exocyclic diene products indicate their potential applications in organic synthesis.[17] Further experiments on exploring the diverse utilities of these compounds are in progress in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00968.

Experimental procedures, characterization data, and ^1H, ^{19}F, and ^{13}C NMR spectra (PDF)

Accession Codes

CCDC 2063184 contains 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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(14) The structures of products were confirmed by ^{1}H-^{1}H NOESY measurement. See the Supporting Information for details.

(15) It was observed that no reaction occurred between products **3a** and **4a** at all, but when compound **4a** was used as a substrate, product **5a** was obtained in 88% yield (details in the Supporting Information).

(16) (a) Xue, W.; Oestreich, M. Beyond carbon: enantioselective and enantiospecific reactions with catalytically generated boryl- and silulcopper intermediates. *ACS Cent. Sci.* **2020**, *6*, 1070−1081. (b) Kiel, G. R.; Ziegler, M. S.; Tilley, T. D. Zirconacyclopentadiene-annulated polycyclic aromatic hydrocarbons. *Angew. Chem. Angew. Chem.* **2017**, *129*, 4917−4922. (c) Kirmse, W.; Konrad, W. Intramolekulare Einschiebung von Arylcarbenen in C-Si-Bindungen. *Angew. Chem.* **1990**, *102*, 682−683. (d) Segura, J. L.; Martin, N. *o*-Quinodimethanes: efficient inermediates in organic synthesis. *Chem. Rev.* **1999**, *99*, 3199−3246.

(17) The utilities of **3a** and **4a** were demonstrated by their derivatizations. With regard to the compound **3a**, unusual ring-opening and rearrangement reactions occurred under the Tamao−Fleming conditions. Afterwards, a polycyclic compound was obtained from the Diels−Alder reaction of *N*-methyl maleimide with exocyclic diene **4a**. See the Supporting Information for details.