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Cross-Coupling

Stereospecific Pd-Catalyzed Intermolecular C(sp^3)–C(sp) Cross-Coupling of Diarylmethyl Carbonates and Terminal Alkynes Under Base-Free Conditions

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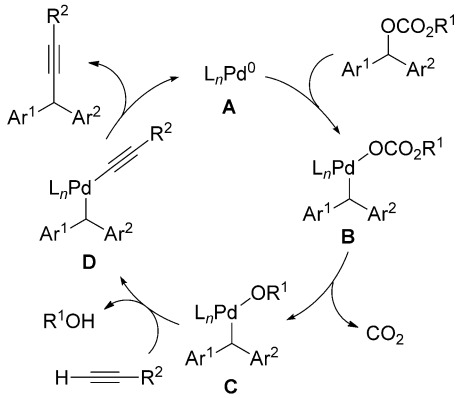
Abstract: A palladium-catalyzed intermolecular decarboxylative C(sp^3)–C(sp) coupling of diarylmethyl carbonates and terminal alkynes has been developed. The reaction proceeds smoothly under external base-free conditions to deliver the corresponding alkynylated diarylmethanes with the liberation of CO_2 and MeOH as the sole byproducts. Moreover, enantioenriched diarylmethyl carbonates are stereospecifically converted to optically active cross-coupling products with inversion of configuration. Thus, the stereospecific palladium catalysis can provide new and unique access to the alkynylated chiral tertiary stereocenters, which are relatively difficult to construct by conventional methods.

Palladium-catalyzed C–C forming cross-coupling reactions are well-recognized as highly powerful and reliable synthetic tools for the construction of various carbon frameworks in modern organic chemistry.[1] Organic (pseudo)halides and organometallic reagents are usually employed as electrophiles and nucleophiles, respectively. However, inevitable formation of halogenated and/or metallic wastes associated with the above starting substrates is often problematic. To address such problems, many synthetic chemists have recently developed alternative cross-coupling methodologies via C–H activation,[2] C–O activation,[3] or decarboxylation.[4] Particularly, the decarboxylative cross-coupling often proceeds even under base-free conditions and efficiently constructs C–C bonds with liberation of CO_2 only.[4a,5] However, they are mostly limited to the intramolecular reactions; the addition of a stoichiometric amount of external bases is generally required to promote the intermolecular variants.[5c,6] Thus, expansion of base-free, decarboxylative-type cross-coupling into the intermolecular version is still challenging and highly desirable. Herein, we report a palladium-catalyzed intermolecular C(sp^3)–C(sp) coupling of diarylmethyl carbonates and terminal alkynes with liberation of CO_2 and MeOH only. The reaction occurs smoothly even under external base-free conditions to form the corresponding alkynylated diarylmethanes in good yields. Moreover, otherwise difficult construction of the alkynylated chiral tertiary stereocenters is possible by the stereospecific coupling with relatively easily accessible enantioenriched secondary alcohol derivatives.

Our scenario is illustrated in Scheme 1, which is prompted by our recent success of palladium-catalyzed direct couplings of heteroarene C–H bonds with primary and even more challenging secondary benzylic C–O electrophiles.[7] The initial oxidative addition of the diarylmethyl carbonate to Pd^0 (**A** to **B**) is followed by the decarboxylation to form the (alkyl)(RO)Pd intermediate **C**. Subsequent alkoxide-ligand-assisted C–H palladation of the terminal alkyne forms the (alkyl)(alkynyl)Pd species **D** with concomitant elimination of the alcohol R^1OH. Final reductive elimination affords the desired cross-coupling product and regenerates the starting Pd^0 complex **A** to complete the catalytic cycle. The challenges of the proposed pathway are 1) competition between the oxidative addition of sterically demanding secondary benzylic carbonates and coordination to the terminal alkyne,[8] 2) external-base-free direct palladation of the terminal alkyne, and 3) conceivable homocoupling side reaction of diarylmethyl electrophiles.[9]



Scheme 1. Working hypothesis. L = ligand.

On the basis of the above working hypothesis, we chose the Boc (Boc = *tert*-butoxycarbonyl) carbonate **1a'** and triisopropylsilylacetylene (**2a**) as model substrates and began optimization studies by the evaluation of ligand structures, in conjunction

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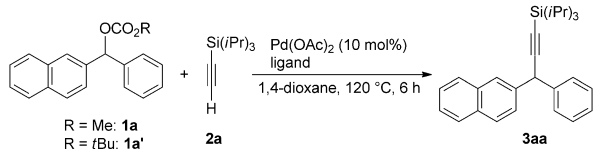
Table 1. Optimization studies for palladium-catalyzed cross-coupling of diarylmethyl carbonates **1** with triisopropylsilylacetylene (**2a**) under base-free conditions.[a]



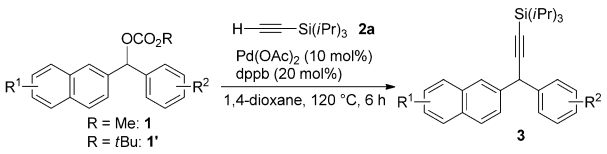
Entry	1	Ligand [mol%]	3aa, Yield [%][b]
1	1a′	PPh_3 (20)	2
2	1a′	SPhos (20)	8
3	1a′	RuPhos (20)	21
4	1a′	XPhos (20)	13
5	1a′	dppe (10)	4
6	1a′	dppp (10)	Trace
7	1a′	dppb (10)	54
8	1a′	dpppen (10)	21
9	1a′	dppf (10)	3
10	1a′	binap (10)	1
11	1a′	DPEphos (10)	2
12	1a′	dppb (20)	63
13[c]	1a	dppb (20)	(78)

[a] Conditions: **1a′** (0.25 mmol), **2a** (0.50 mmol), $Pd(OAc)_2$ (0.025 mmol), ligand, 1,4-dioxane (3.0 mL), 120 °C, 6 h, N_2. [b] Yields are estimated by GC. Yield of the isolated product is given in parentheses. [c] With **1a** (0.50 mmol) and **2a** (0.25 mmol).

with $Pd(OAc)_2$ catalyst (Table 1).[10] Monodentate phosphines including simple PPh_3 and representative Buchwald's biarylphosphines showed poor to moderate activity (Table 1, entries 1–4). Most bisphosphine ligands also gave less efficiency (entries 5–6 and 8–11). However, dppb was found to uniquely promote the reaction, and the desired cross-coupling **3aa** was formed in 54% GC yield (entry 7). A 1:2 ratio of Pd/dppb further increased the yield to 63% (entry 12).[11] Subsequent investigation of the leaving group identified the methyl carbonate **1a** to be optimal, and **3aa** was obtained in 78% isolated yield (entry 13). Although solvents and palladium salts were also extensively screened, 1,4-dioxane and $Pd(OAc)_2$ proved to be best as far as we tested (see the Supporting Information for more detailed optimization studies).

We subsequently tested a variety of diarylmethyl carbonates **1** for the cross-coupling reaction with **2a**. Conditions with methyl carbonates **1** (Table 1, entry 13) generally gave better results, while some specific cases required conditions with Boc carbonates **1′** (Table 1, entry 12). Representative products are shown in Table 2. The palladium catalysis was compatible with electronically diverse methoxy, trifluoromethyl, and chloro groups at the para position on the phenyl ring (Table 2, entries 1–3). In addition, the *meta*- and sterically more demanding *ortho*-substituted substrates underwent the coupling reaction without any difficulties (entries 4 and 5). The primary benzyl carbonates **1g′** and **1h** also worked well under the standard conditions (entries 6 and 7). Moreover, the reaction tolerated methoxy-substituted 2-naphthalene, 1-naphthalene, and higher condensed phenanthrene rings equally to form **3ia**–**3ka** in good yields (entries 8–10). Unfortunately, simple di-

Table 2. Palladium-catalyzed cross-coupling of various benzyl carbonates **1** with triisopropylsilylacetylene (**2a**).[a]



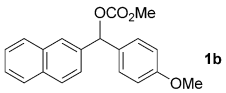
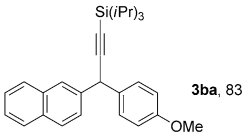
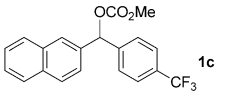
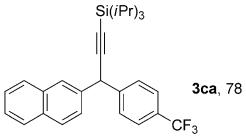
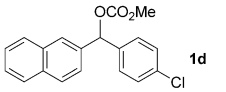
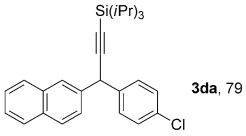
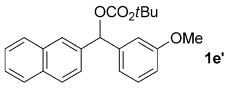
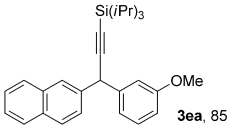
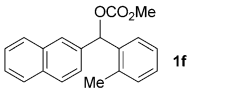
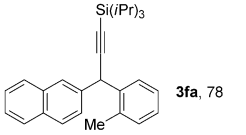
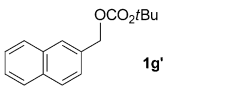
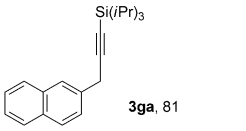
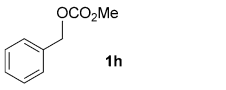
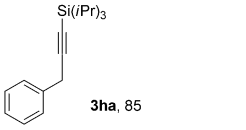
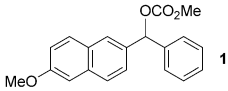
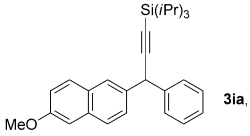
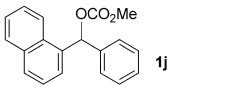
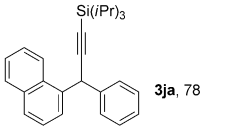
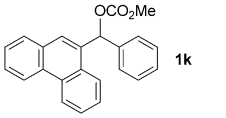
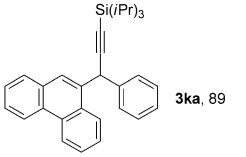
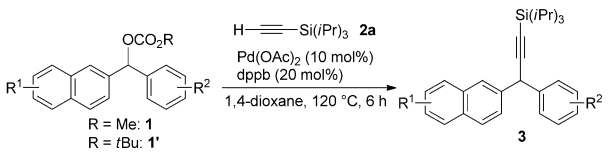
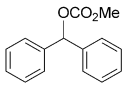
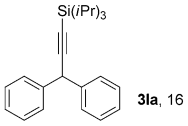
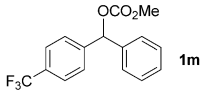
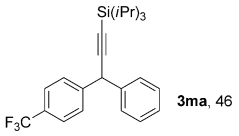
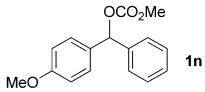
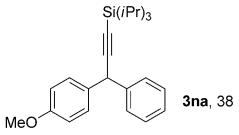
Entry	1	3, Yield [%][b]
1		
2		
3		
4[c]		
5		
6[c]		
7		
8		
9		
10		

Table 2. (Continued)



Entry	1	3, Yield [%][b]
11[d]		
12		
13		

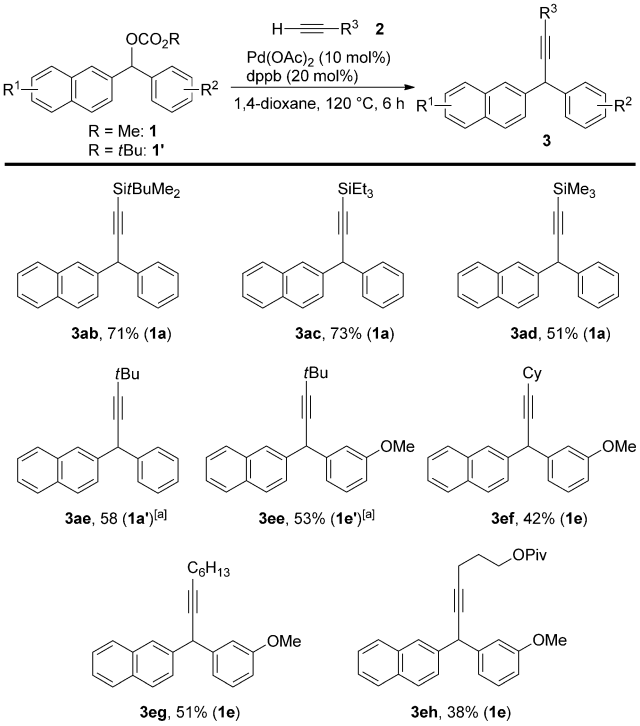
[a] Conditions: **1** (0.50 mmol), **2a** (0.25 mmol), $Pd(OAc)_2$ (0.025 mmol), dppb (0.050 mmol), 1,4-dioxane (3.0 mL), 120 °C, 6 h, N_2. [b] Yields of the isolated product are given. [c] With **1'** (0.25 mmol) and **2a** (0.50 mmol). [d] Yield is estimated by ^1H NMR.

phenylmethyl carbonate **1l** showed sluggish reactivity (entry 11),[12] but the introduction of electron-withdrawing trifluoromethyl and electron-donating methoxy groups improved the yields (entries 12 and 13).

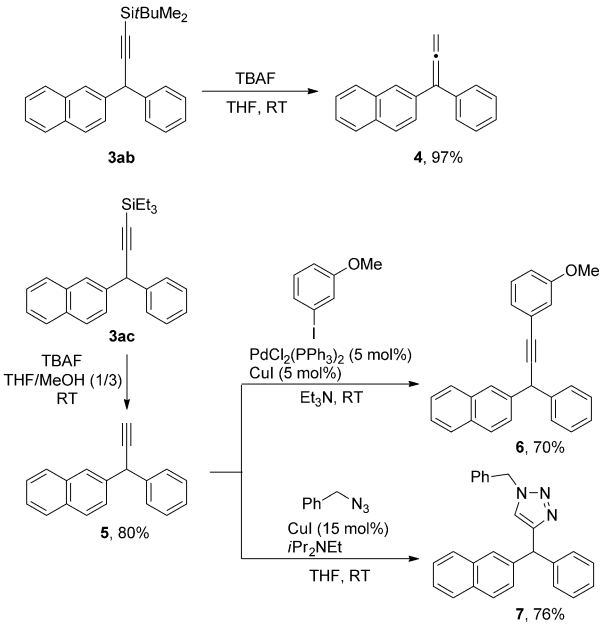
Some terminal alkynes participated in the reaction (Scheme 2). Silylacetylenes that bear *t*BuMe$_2$Si (**3ab**), Et$_3$Si (**3ac**), and Me$_3$Si (**3ad**) groups could be employed under the standard reaction conditions. The alkyl substituents at the alkyne terminus were also accommodated: *tert*-butylacetylene (**3ae** and **3ee**), cyclohexylacetylene (**3ef**), and 1-octyne (**3eg**) gave the corresponding coupling products in synthetically useful yields. The alkyne containing the pivalate function was also converted to the product in an acceptable yield (**3eh**). A current limitation of this transformation is that arylacetylenes could not be used as substrates.[13]

Because of the rich chemistry of the alkyne group, it was possible to manipulate the reaction to afford specific products (Scheme 3). Upon treatment with tetrabutylammonium fluoride (TBAF) in THF, the *t*BuMe$_2$Si-substituted product **3ab** underwent the desilylation/isomerization sequence to form the *gem*-1,1-disubstituted terminal allene **4** in 97% yield. On the other hand, a THF/MeOH mixed solvent system afforded the terminal alkyne **5** exclusively. The terminal alkyne moiety could be further converted to the internal alkyne **6** and triazole-containing triarylmethane **7** through the Pd-catalyzed Sonogashira coupling and Cu-catalyzed azide–alkyne cycloaddition, respectively. In particular, the former transformation can complement the inaccessibility to the arylacetylene mentioned in Scheme 2.

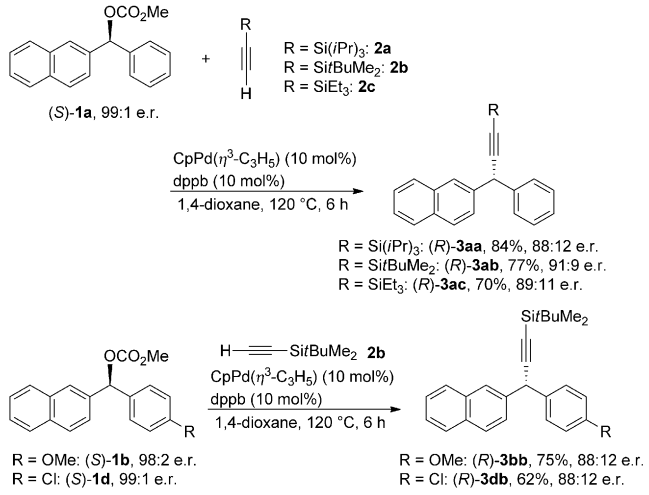
We finally attempted the asymmetric synthesis by using the relatively easily accessible enantioenriched diarylmethyl carbonate (*S*)-**1a** (99:1 enantiomeric ratio (e.r.), prepared by Braga's method)[14] as the starting substrate (Scheme 4). Gratifyingly, in the presence of a modified CpPd(η^3-C$_3$H$_5$)/dppb cata-



Scheme 2. Palladium-catalyzed cross-coupling of diarylmethyl carbonates **1** with various terminal alkynes **2**. Conditions: **1** (0.50 mmol), **2** (0.25 mmol), $Pd(OAc)_2$ (0.025 mmol), dppb (0.050 mmol), 1,4-dioxane (3.0 mL), 120 °C, 6 h, N_2. Yields of the isolated product are given. The coupling carbonates are shown in parentheses. [a] With **1'** (0.25 mmol) and **2** (0.50 mmol). Piv = *tert*-butylcarbonyl.

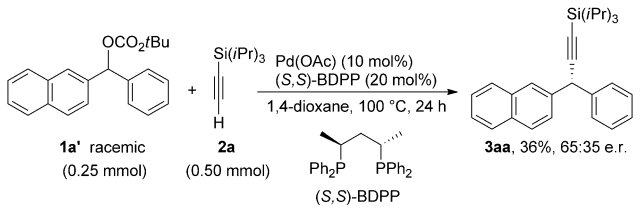


Scheme 3. Transformations of silyl-substituted cross-coupling products **3**.



Scheme 4. Enantiospecific cross-coupling of enantioenriched diarylmethyl carbonates.

lyst (Cp = cyclopentadienyl),[15] the enantiospecific cross-coupling of (*S*)-**1a** and **2a** occurred with inversion of configuration to form the optically active alkynylated product (*R*)-**3aa** in 84% yield with 88:12 e.r.[16] Other silylacetylenes **2b** and **2c** also took part in the reaction, and the enantioenriched cross-coupling products (*R*)-**3ab** and (*R*)-**3ac** were obtained with 91:9 and 89:11 e.r., respectively. The methoxy- and chloro-substituted diaryl methyl carbonates (*S*)-**1b** and (*S*)-**1d** underwent the same chirality transfer to afford (*R*)-**3bb** and (*R*)-**3db** with similar levels of stereochemical fidelity. Although similar stereospecificity is observed in the nickel-catalyzed cross-coupling of optically active diarylmethanol derivatives with Mg, Zn, and B-based sp^3 and sp^2 carbon nucleophiles,[17] application to sp carbon nucleophiles still remains underdeveloped. Thus, the present stereospecific palladium catalysis can provide a unique approach to the alkynylated chiral tertiary stereocenters, which are relatively difficult to construct by conventional methods.[18] On the other hand, from the mechanistic point of view, the observed stereochemical outcome suggests the stereoinvertive S_N2-like oxidative addition and stereoretentive reductive elimination pathways (Scheme 1).[19] Additionally, while preliminary, the catalytic stereoinduction in the reaction of racemic **1a'** with **2a** was also achieved with a $Pd(OAc)_2$/(*S,S*)-BDPP catalyst system (Scheme 5).[20] Further mechanistic studies on the stereochemical course and evaluations of chiral ligands for the asymmetric catalysis are ongoing in our laboratory.



Scheme 5. Catalytic enantioselective cross-coupling of racemic diarylmethyl carbonate under $Pd(OAc)_2$/(*S,S*)-BDPP catalysis.

In conclusion, we have developed a palladium-catalyzed intermolecular $C(sp^3)$–C(sp) cross-coupling of diarylmethyl carbonates and terminal alkynes. The reaction proceeds smoothly under external base-free conditions, and CO_2 and MeOH are thus the sole byproducts. Moreover, the stereoinvertive, enantiospecific reaction with optically active carbonates can provide unique access to the chiral alkynyl-substituted diarylmethanes, which are difficult to prepare by other means. Further studies on related decarboxylative couplings are currently underway and will be reported in due course.

Experimental Section

Typical procedure for Pd-catalyzed coupling of methyl carbonates and terminal alkynes

The synthesis of **3aa** is representative (Table 1, entry 13): $Pd(OAc)_2$ (5.6 mg, 0.025 mmol) and dppb (21.3 mg, 0.050 mmol) were placed in a 20 mL two neck flask, which was filled with nitrogen. 1,4-Dioxane (2.0 mL) was added to the flask, and suspension was stirred for 10 min. A solution of methyl (2-naphthyl)(phenyl)methyl carbonate (**1a**; 146.2 mg, 0.50 mmol) and triisopropylsilylacetylene (**2a**; 45.6 mg, 0.25 mmol) in 1,4-dioxane (1.0 mL) was then added to the flask, and the suspension was stirred for 6 h at 120 °C. The resulting mixture was quenched with water (20 mL) and then extracted three times with ethyl acetate (20 mL x 3). The combined organic layer was dried over sodium sulfate. Concentration in vacuo and subsequent purification by column chromatography on silica gel with hexane as an eluent gave triisopropyl[3-(naphthalen-2-yl)-3-phenylprop-1-yn-1-yl]silane (**3aa**; 77.7 mg, 0.19 mmol) in 78% yield.

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[10] Abbreviations: dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane, dppb = 1,4-bis(diphenylphosphino)butane, dpppen = 1,5-bis(diphenylphosphino)pentane, dppf = 1,1′-bis(diphenylphosphino)ferrocene, binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, DPEphos = bis[2-(diphenylphosphino)phenyl] ether, SPhos = 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl, RuPhos = 2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl, XPhos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl.

[11] The exact reason is not clear, but we believe that excess dppb can reduce $Pd(OAc)_2$ to a catalytically active Pd^0 species.

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