Alkenes

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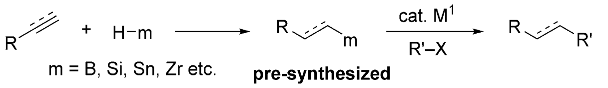
Reductive Cross-Coupling of Conjugated Arylalkenes and Aryl Bromides with Hydrosilanes by Cooperative Palladium/Copper Catalysis

Kazuhiko Semba, Kenta Ariyama, Hong Zheng, Ryohei Kameyama, Shigeyoshi Sakaki,* and Yoshiaki Nakao**

Abstract: *A method for the reductive cross-coupling of conjugated arylalkenes and aryl bromides with hydrosilanes by cooperative palladium/copper catalysis was developed, thus resulting in the highly regioselective formation of various 1,1-diarylalkanes, including a biologically active molecule. Under the applied reaction conditions, high levels of functional-group tolerance were observed, and the reductive cross-coupling of internal alkynes with aryl bromides afforded trisubstituted alkenes.*

Transition metal catalyzed cross-coupling reactions of alkyl and alkenyl organometallic reagents represent a powerful method for the alkylation and alkenylation, respectively, of organic electrophiles.[1] The hydrometallation of alkenes and alkynes is an atom-efficient and practical way to prepare alkyl and alkenyl metal reagents, respectively, because a variety of main-group metal hydrides, alkenes, and alkynes are readily available.[2] However, these organometallic nucleophiles are usually presynthesized and often purified prior to subsequent cross-coupling reactions [Eq. (1)], and such processes generally involve multistep operations. In contrast, cross-coupling reactions based on organometallic nucleophiles generated by hydrometallation of alkenes and alkynes with a catalytic amount of transition-metal hydrides in situ can be more step-economical, because this process requires just a single operation, and isolation of the organometallic reagents is not necessary [Eq. (2)].[3]



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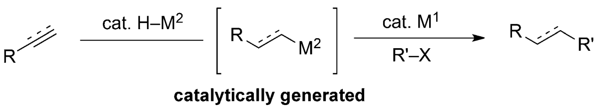

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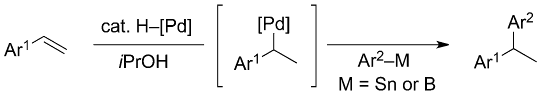
Cross-coupling reactions of aryl halides with 1-arylalkyl metal species represent a convenient method to prepare 1,1-diarylalkanes,[4] which are often found in biologically active compounds.[5] 1-Arylalkylmetal reagents such as organoboron and organosilicon compounds are conventionally prepared by the transition metal catalyzed hydrometallation of styrenes.[6] The resulting 1-arylalkylmetal reagents are subsequently purified and used for the cross-coupling with aryl halides. Sigman and co-workers then developed reductive cross-coupling reactions of styrenes with arylstannanes[7a] or arylboronic esters[7b] in the presence of *i*PrOH as a hydrogen source to afford 1,1-diarylethanes via an alkylpalladium species [Eq. (3)]. However, in these reactions, the scope with respect to the alkenes is limited to vinylarenes, and in many cases the main-group aryl nucleophiles have to be prepared from the corresponding aryl halides. Herein, we report the reductive cross-coupling of conjugated arylalkenes and aryl bromides with hydrosilanes by cooperative palladium/copper catalysis [Eq. (4)].[8,9] This reaction furnishes a variety of 1,1-diarylalkanes in a highly regioselective manner from the palladium-catalyzed coupling of the 1-arylalk-1-ylcopper species generated in situ by catalytic hydrocupration[10] of arylalkenes with aryl halides.[11]



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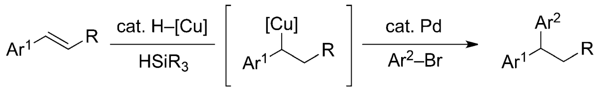

(4)

To evaluate the validity of Equation (4), we carried out cross-coupling reaction of the alkylcopper **1a**, which is prepared from hydrocupration of styrene (**2a**), with *p*-bromoanisole (**3a**) in the presence of $Pd(OAc)_2$/tricyclopentylphosphane ($PCyp_3$) [Equation (5); see Equation (S1) in the Supporting Information].[12] As a result, **4a** was obtained in 98% yield. This result encouraged us to develop a catalytic reaction.

After optimization of various reaction parameters,[12] we found that in the presence of $Pd(OAc)_2$ (1.0 mol%), $PCyp_3$ (2.0 mol%), (SIPr)CuCl (10 mol%), and LiO*t*Bu (1.2 mmol), the reductive cross-coupling of **2a** with **3a** and $HSi(OEt)_3$ afforded 1,1-diarylalkane **4a** in 94% yield with concomitant

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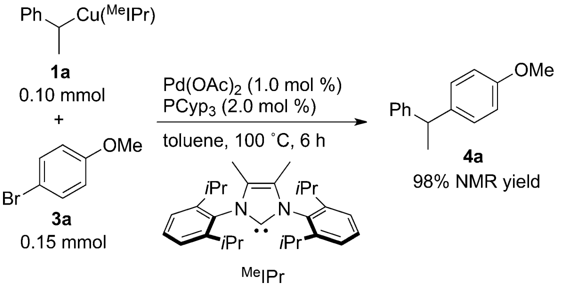
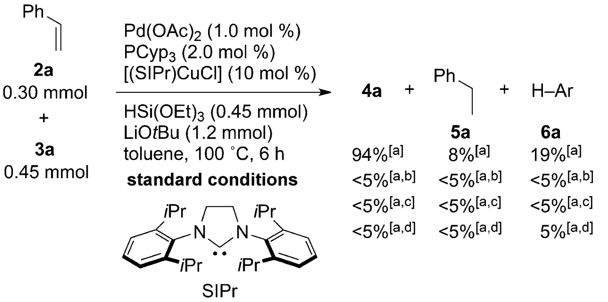


(5)

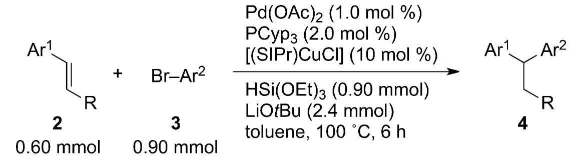
formation of small amounts of ethylbenzene (**5a**) and anisole (**6a**) [Eq. (6)]. In the absence of Pd(OAc)$_2$, Pd(OAc)$_2$/PCyp$_3$, or (SIPr)CuCl under otherwise identical reaction conditions, **4a** was not formed. These results clearly demonstrate that the cooperative palladium/copper catalysis is indispensable for the present reaction.

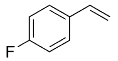
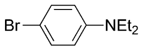
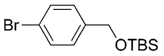
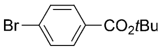
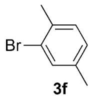
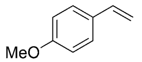
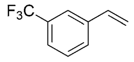
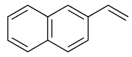
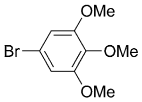
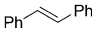
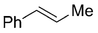
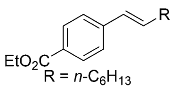


(6)

[a] GC yield. [b] Without Pd(OAc)$_2$. [c] Without Pd(OAc)$_2$/PCyp$_3$. [d] Without [(SIPr)CuCl].

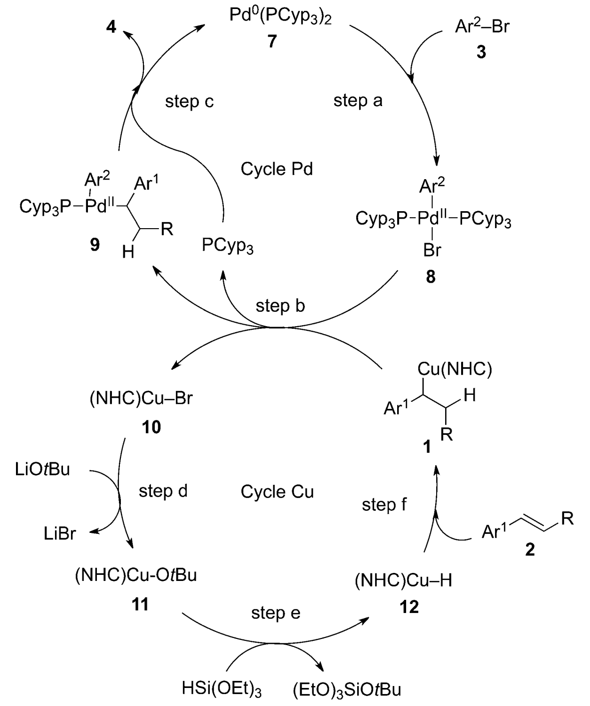
Table 1: Reductive cross-coupling of arylalkenes with aryl bromides and HSi(OEt)$_3$.



Entry	2	3	Yield [%][a]
1	**2a**	**3a**	60 (**4a**)
2	 **2b**	PhBr (**3b**)	52 (**4b**)
3[b]	**2b**	 **3c**	52 (**4c**)
4	**2b**	 **3d**	61 (**4d**)
5[c]	**2b**	 **3e**	76 (**4e**)
6	**2a**	 **3f**	81 (**4f**)
7[c,d]	 **2c**	**3b**	71 (**4a**)
8[e]	 **2d**	**3b**	85 (**4g**)
9[e]	 **2e**	**3b**	71 (**4h**)
10[e]	**2e**	 **3g**	85 (**4i**)
11[c,d,e]	 **2f**	**3b**	48 (**4j**)
12[d,e]	 **2g**	**3b**	46 (**4k**)
13[e]	 R = n-C$_6$H$_{13}$ **2h**	**3b**	81 (**4l**)

[a] Yield of isolated product. [b] Used 0.60 mmol **3c**. [c] Used 1.2 mmol alkene and 0.60 mmol aryl bromide. [d] Used 0.50 mol % Pd(OAc)$_2$ and 1.0 mol % PCyp$_3$. [e] Used 10 mol % [(^{Me}IPr)CuCl] instead of [(SIPr)CuCl]. TBS = *tert*-butyldimethylsilyl.

The reaction of **2a** and **3a** could be scaled up to 0.60 mmol with respect to **2a**, and **4a** was isolated in 60 % yield (Table 1, entry 1). The substrate scope was examined by using various styrene derivatives (**2a**–**h**) and aryl bromides (**3a**–**g**) as shown in Table 1. In all cases, the reactions proceeded in a highly regioselective manner (> 20:1) to afford a range of 1,1-diarylalkanes. In some cases, the reactivity of [(^{Me}IPr)CuCl] was observed to be superior to that of [(SIPr)CuCl] (entries 8–13). When electron-rich or electron-deficient aryl bromides were employed, the corresponding 1,1-diarylalkanes were obtained in moderate to good yields (entries 1–5). The presence of an *ortho* substituent on the aryl bromide did not affect the yield and regioselectivity (entry 6). Moreover, 4-methoxystyrene (**2c**), 3-trifluoromethylstyrene (**2d**), and 2-vinylnaphthalene (**2e**) reacted in good yield (entries 7–9). Notably, the biologically active 1,1-diarylethane **4i**[5c] was obtained in 85 % yield (entry 10). However, not only vinylarenes, but also internally conjugated arylalkenes are viable substrates for reaction conditions similar to the standard ones (entries 11–13). A modest yield was observed for *trans*-stilbene (**2f**) and *trans*-1-phenyl-1-propene (**2g**), whereas the 1,1-diaryloctane **4l** was obtained in 81 % yield from (*E*)-1-aryl-1-octene (**2h**). Various functional groups such as F, CF$_3$, NEt$_2$, OTBS, and CO$_2$R remained unaffected under the applied reaction conditions. Other alkenes such as *cis*-stilbene, indene, α-methylstyrene, or 1-octene did not afford

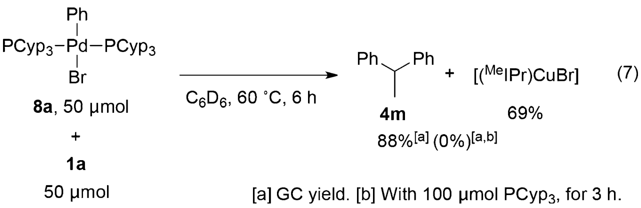


Scheme 1. Proposed reaction mechanism.

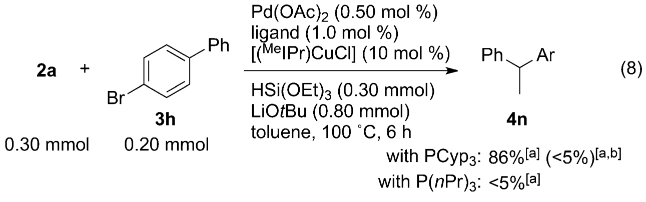
the corresponding cross-coupling products under the standard reaction conditions.

A plausible mechanism for this reaction, consisting of individual palladium- and copper-catalyzed cycles, is outlined in Scheme 1. Initially, the copper hydride **12** is generated from the copper alkoxide **11** and HSi(OEt)$_3$ (step e). The regioselective hydrocupration of the 1-arylalkene with **12** then affords the alkylcopper **1** [step f; Eq. (S1)]. Transmetallation of **1** with [(PCyp$_3$)$_2$Pd(Ar)Br] (**8**), which is generated from the oxidative addition of **3** across [Pd(PCyp$_3$)$_2$] (**7**), is followed by a reductive elimination from the three-coordinated palladium species **9** to afford **4** and **10** (steps b and c).[13] The copper alkoxide **11** is then regenerated from [(NHC)CuBr] (**10**) and LiO*t*Bu (step d).

To gain some insight into the reaction mechanism, the reaction of **2a** with **3b** was monitored by ^{31}P NMR spectroscopy. During the course of the reaction, [(PCyp$_3$)$_2$Pd(Br)Ph] (**8a**) was the only species observed by ^{31}P NMR spectroscopy [Eq. (S2)].[12] Thus, **8a** is likely a resting state in the palladium cycle. The stoichiometric reaction of **8a** and **1a** afforded **4m** in 88% yield, and [(^{Me}IPr)CuBr] was isolated in 69% yield [Eq. (7)]. In contrast, addition of PCyp$_3$ retarded the reaction. Excess PCyp$_3$ also hampered the catalytic reaction [Eq. (8)].

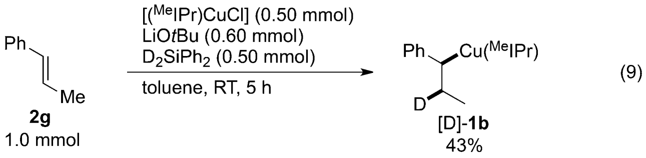


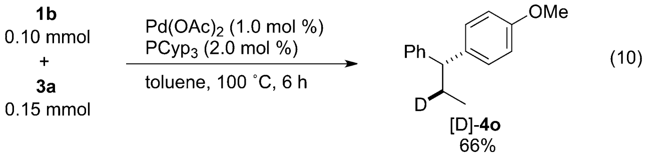
[a] GC yield. [b] With 100 µmol PCyp$_3$, for 3 h.



[a] NMR yield. [b] With 2.0 mol % PCyp$_3$.

These results imply that a three-coordinated palladium complex, which would be generated through dissociation of PCyp$_3$ from **8a**, is reactive for the transmetallation. In the catalytic reaction, a less sterically hindered phosphane such as P(*n*Pr)$_3$ did not afford **4n** [Eq. (8)], probably because P(*n*Pr)$_3$ stabilizes the corresponding four-coordinated palladium complex, thus making it unreactive for the transmetallation. In fact, transmetallation between {[P(*n*Pr)$_3$]$_2$Pd(*p*-biphenyl)(Br)} and **1a** was sluggish at 60 °C for 15 hours [Eq. (S3)].[12] To determine the stereochemistry of the transmetallation, [D]-**1b** was prepared by *syn* addition of copper deuteride, which was generated from [(^{Me}IPr)CuCl], LiO*t*Bu, and D$_2$SiPh$_2$, to **2g** [Eq. (9)].[14] The cross-coupling reaction of [D]-**1b** with **3a** in the presence of Pd(OAc)$_2$/PCyp$_3$ gave [D]-**4o** in a stereospecific manner [Eq. (10)].





This result indicates that the transmetallation proceeds with inversion of the configuration.[15] To better understand the transmetallation process, we carried out theoretical calculations by using DFT method.[12] As shown in Figure 1, the transmetallation occurs through weak Pd–Cu adducts (**13** and **14**) and via a transition-state **TS$_{14-15}$**. The initial adduct **13** is moderately more stable than the sum of the starting complexes and reluctant to undergo the transmetallation before the phosphane dissociation to give **14**. The transmetallation of the 1-phenylethyl group (abbreviated as R below) takes place from **14** via **TS$_{14-15}$**, in which the Pd–C (of R) distance somewhat decreases, the Cu–C (of R) distance moderately increases, and the geometry change occurs in the alkyl group [Pd–C (of R) = 2.529 Å, Cu–C (of R) = 2.008 Å, Pd–Cu = 4.202 Å, and the dihedral angle around the alkyl C = 197°; see Figure S14].[12] The evaluated Gibbs activation energy is 28.0 kcal mol^{-1} relative to **13**, and is not very large for a thermal reaction.[16] This value matches well with the idea that the transmetallation would be rate-determining and

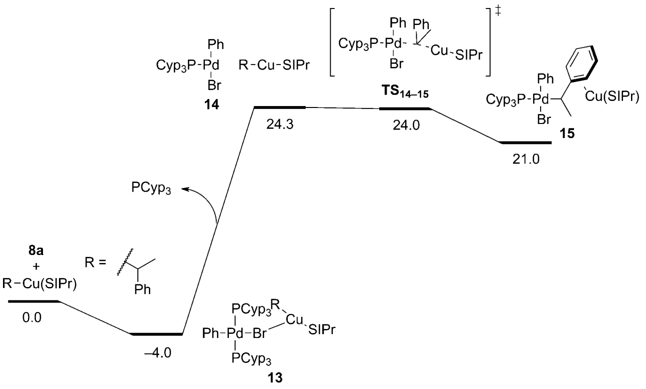
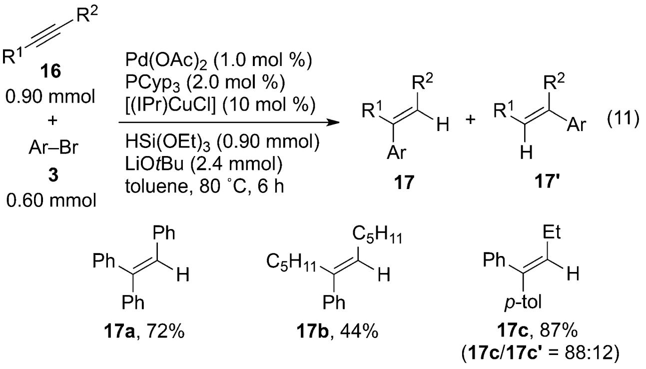


Figure 1. Geometry and Gibbs free energy changes in the transmetallation between **8a** and (SIPr)CuR (R = 1-phenylethyl).

the experimental result that the high temperature (100 °C) is needed [Eq. (8)]. Though the product **15** is less stable than **13**, it is likely that the subsequent reductive elimination easily occurs in the case of a palladium complex. It is noted that this activation energy is smaller than that of the stereoretentive transmetallation, which agrees well with the experimental result (see Figure S16). Finally, it is worth mentioning that the crossover of the ligands PCyp$_3$ and $^{\mathrm{Me}}$IPr coordinated to palladium and copper, respectively, is unlikely under the catalytic and stoichiometric reaction conditions [Equation (7); see Equation (S2)].

To extend the present strategy to alkenylation reactions, we examined the reductive cross-coupling of the alkynes **16** with the aryl bromides **3** using a similar catalytic system [Eq. (11)]. Whereas Maleczka and co-workers have already reported similar transformations using catalytically generated alkenylstannanes to access disubstituted alkenes,[17] the present reaction allows concise synthesis of trisubstituted alkenes.[18] A good yield was observed in the case of diphenylacetylene (**16a**), whereas a modest yield was observed in the case of 6-dodecyne (**16b**). When 1-phenyl-1-butyne (**16c**) was employed, the reaction afforded a regioisomer mixture of trisubstituted alkenes **17c** and **17c″** in 87 % total yield (**17c**/**17c′** = 88:12). Terminal alkynes such as 1-octyne and phenylacetylene were not viable substrates for these reaction conditions.[19]



In conclusion, the reductive cross-coupling of conjugated arylalkenes or internal alkynes with aryl bromides and hydrosilanes by cooperative palladium/copper catalysis has been developed, thus giving 1,1-diarylalkanes and trisubstituted alkenes in a highly regio- and stereoselective manner. Mechanistic studies revealed that stereoinvertive transmetallation including dissociation of one phosphane is likely rate-determining and that PCyp$_3$ and $^{\mathrm{Me}}$IPr selectively coordinate to palladium and copper, respectively, in both catalytic and stoichiometric reactions. This information is quite beneficial for the new palladium/copper-catalyzed reactions. Further studies on details of the reaction mechanism and the development of an asymmetric variation are currently in progress.

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Keywords: alkenes · alkynes · copper · cross-coupling · palladium

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