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# Rhodium-Catalyzed Arylzincation of Alkynes: Ligand Control of 1,4-Migration Selectivity

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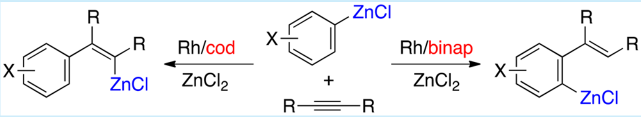
Supporting Information

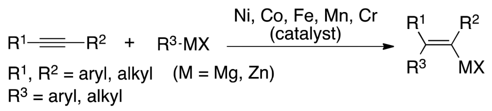
**ABSTRACT:** The addition of arylzinc reagents ArZnCl **1** to alkynes **2** was found to be catalyzed by rhodium complexes in the presence of a catalytic amount of zinc chloride. The selectivity in giving 2-arylalkenylzinc species **3** or *ortho*-alkenylarylzinc species **4**, the latter of which is generated through 1,4-Rh migration from alkenyl to aryl in the catalytic cycle, is controlled by the ligands on rhodium. Ligands cod and binap gave **3** and **4**, respectively, with high selectivity.



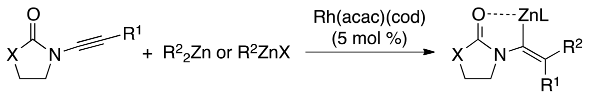
Carbometalation of alkynes is one of the most efficient methods of generating substituted alkenylmetals which are useful synthetic intermediates for the multisubstituted alkenes, and addition of arylmetals to simple unfunctionalized alkynes has been a challenging reaction because of their low reactivity.[1] The first-row transition metals including Ni, Co, Fe, Mn, and Cr have been reported to catalyze the addition of arylmagnesium[2] and -zinc[3] reagents to the unfunctionalized alkynes (Scheme 1a). A Rh complex has been reported to catalyze the carbozincation of ynamides[4] (Scheme 1b), but no reports have appeared on the carbozincation of unfunctionalized alkynes using Rh catalysis. In 2012, Yoshikai reported[5] a new type of Co-catalyzed arylzincation of alkynes where *ortho*-alkenylarylzinc species are formed through 1,4-migration of cobalt from an alkenyl carbon to aryl carbon (Scheme 1c). Here, we report our findings that arylzincation of unfunctionalized alkynes is catalyzed by Rh complexes in the presence of a catalytic amount of ZnCl$_2$ and the arylzincation with or without 1,4-migration is controlled with high selectivity by the ligands on rhodium (Scheme 1d). The 1,4-shift of rhodium from alkenyl to aryl carbons has been reported to be involved in the catalytic cycle of Rh-catalyzed multiple carbon−carbon bond forming reactions including asymmetric reactions.[6−8] As a related arylmetalation reaction, we recently reported that the addition of arylstannanes to alkynes giving *ortho*-alkenylarylstannanes is catalyzed cooperatively by a rhodium complex and zinc chloride.[9]

**Scheme 1. Addition of ArZnX to Alkynes and 1,4-Migration**

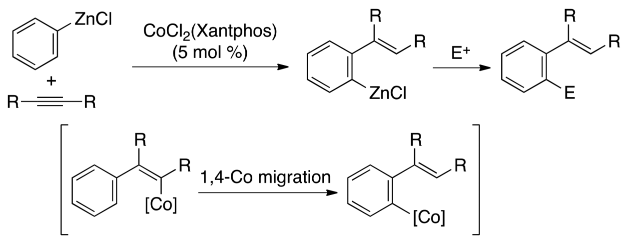
(a) Catalytic carbometalation of alkynes



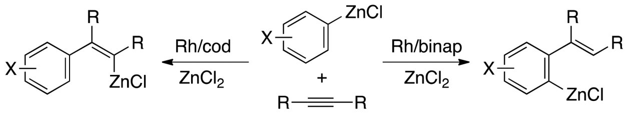
(b) Rhodium-catalyzed arylzincation of ynamides



(c) Cobalt-catalyzed addition of ArZnX to alkynes forming ortho-alkenylarylzincs



(d) Rh-catalyzed arylzincation. Selective in 1,4-migration or not (This Work)



In our present studies, arylzinc reagents ArZnCl were prepared by lithiation of ArBr with BuLi in THF at −80 °C followed by addition of an excess amount (1.3 equiv) of ZnCl$_2$ to the THF solution of ArLi.[10,11] The results obtained for the reaction of 3,5-(MeO)$_2$C$_6$H$_3$ZnCl (**1a**) with 4-octyne (**2a**) in the presence of several rhodium catalysts are summarized in Table 1. The reaction mixture containing 2-arylalkenylzinc **3aa** and/or *ortho*-alkenylarylzinc **4aa** was hydrolyzed with D$_2$O, and the location of D (**5aa**/**6aa**) was analyzed by $^1$H and $^2$H NMR spectra. The yield of the arylzincation and the selectivity with or without 1,4-migration are heavily dependent on the ligand on rhodium. Thus, the THF solution of ArZnCl (**1a**, 0.60 mmol, 3.0 equiv to **2a**) containing ZnCl$_2$ (0.18 mmol, 0.9 equiv to **2a**) was added to the alkyne (**2a**, 0.20 mmol) in the presence of a rhodium catalyst generated from [RhCl(coe)$_2$]$_2$ (3 mol % of Rh) and binap[12] (3.3 mol %) in THF, and the mixture was heated at 50 °C for 5 h. The arylzincation

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Table 1. Rhodium-Catalyzed Arylzincation of 4-Octyne (**2a**) with 3,5-$(MeO)_2C_6H_3ZnCl$ (**1a**)[a]

| entry | ligand on Rh[b] | additive (mmol)[c] | yield (%)[d] **5aa** + **6aa** | ratio[e] of **5aa**/**6aa** |
|---|---|---|---|---|
| 1 | binap | $ZnCl_2$ (0.18) | 91 | <1:99 |
| 2 | cod | $ZnCl_2$ (0.18) | 82 | 92:8 |
| 3[f] | binap | $ZnCl_2$ (0.09) | 90 | <1:99 |
| 4 | binap | – | 22 | 4:96 |
| 5[g] | binap | – | <3 | – |
| 6[h] | binap | $ZnBr_2$ (0.18) | 81 | 5:95 |
| 7[h] | binap | $ZnI_2$ (0.18) | 87 | 3:97 |
| 8 | dppe | $ZnCl_2$ (0.18) | 23 | 37:63 |
| 9 | dppp | $ZnCl_2$ (0.18) | 52 | 48:52 |
| 10 | dppf | $ZnCl_2$ (0.18) | 27 | 19:81 |
| 11 | biphep | $ZnCl_2$ (0.18) | 83 | 12:88 |
| 12 | $PPh_3$ | $ZnCl_2$ (0.18) | 78 | 6:94 |
| 13 | xantphos | $ZnCl_2$ (0.18) | <3 | — |
| 14 | nbd | $ZnCl_2$ (0.18) | 83 | 5:95 |

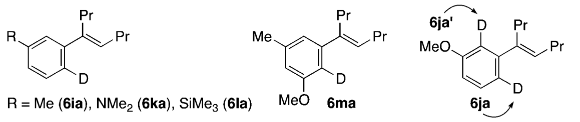
[a] Reaction conditions: 4-Octyne (**2a**) (0.20 mmol), ArZnCl (**1a**) (0.60 mmol), $ZnCl_2$ (0.18 mmol), and Rh catalyst (3 mol % of Rh) in THF (2.0 mL) at 50 °C for 5 h. The reaction was quenched with $D_2O$ (0.2 mL). [b] $[RhCl(coe)_2]_2$ (6.0 μmol of Rh) + bisphosphine (6.6 μmol), $RhCl(PPh_3)_3$ (6.0 μmol), or ($[RhCl(diene)]_2$ (diene = cod or nbd, 6 μmol of Rh). [c] The excess amount of $ZnX_2$ used at the generation of ArZnX. [d] Isolated yield. [e] Determined by $^1H$ and $^2H$ NMR spectra. [f] ArZnCl (**1a**) (0.30 mmol), $ZnCl_2$ (0.09 mmol), THF (1.0 mL) for 1 h. [g] Reaction of $Ar_2Zn$ generated from ArLi (0.60 mmol) and $ZnCl_2$ (0.30 mmol). [h] ArZnX was generated from ArLi (0.60 mmol) and $ZnX_2$ (0.78 mmol, X = Br or I).

accompanied by the 1,4-migration proceeded selectively to give, after the $D_2O$ quenching, a 91% yield of **6aa**, where the deuterium is incorporated at the *ortho*-position of the phenyl ring (entry 1). On the other hand, the reaction in the presence of a rhodium catalyst coordinated with cod[12] under otherwise the same conditions gave an 82% yield of the arylation product where the deuterium is found mainly at the alkenyl carbon (**5aa**/**6aa** = 92:8) (entry 2). In the Rh/binap-catalyzed reaction, the amounts of ArZnCl **1a** and $ZnCl_2$ were reduced to 1.5 and 0.45 equiv, respectively, without loss of the arylzincation yield or 1,4-migration selectivity (entry 3). The presence of $ZnCl_2$ as a catalyst, which was added in an excess amount (1.3 equiv to ArLi) at the generation of ArZnCl from ArLi, is essential for the present arylzincation. The yield of arylzincation was much lower (22%) in the reaction with ArZnCl generated with 1.0 equiv of $ZnCl_2$ (entry 4). Diarylzinc $Ar_2Zn$ generated from ArLi and 0.50 equiv of $ZnCl_2$ did not give the arylzincation products (entry 5). Other zinc salts, $ZnX_2$ (X = Br and I), which were used in an excess amount at the generation of ArZnX[13] from ArLi, also catalyzed the reaction, but the yields and the migration selectivity were somewhat lower (entries 6 and 7). The lower yield and selectivity were observed with other phosphine ligands, dppe, dppp, dppf, biphep, and $PPh_3$ (entries 8−12). The arylzincation did not proceed with the xantphos ligand (entry 13), which has been reported to be the best ligand in the cobalt-catalyzed migratory arylzincation.[5] Interestingly, the high selectivity in giving **3aa** without the 1,4-migration was observed only with 1,5-cyclooctadiene (cod). Other diene ligands including norbornadiene (nbd) promoted the migratory arylzincation, giving **4aa** preferentially (entry 14).

Table 2. Rhodium-Catalyzed Arylzincation of 4-Octyne (**2a**) with Arylzinc Reagents **1**[a]

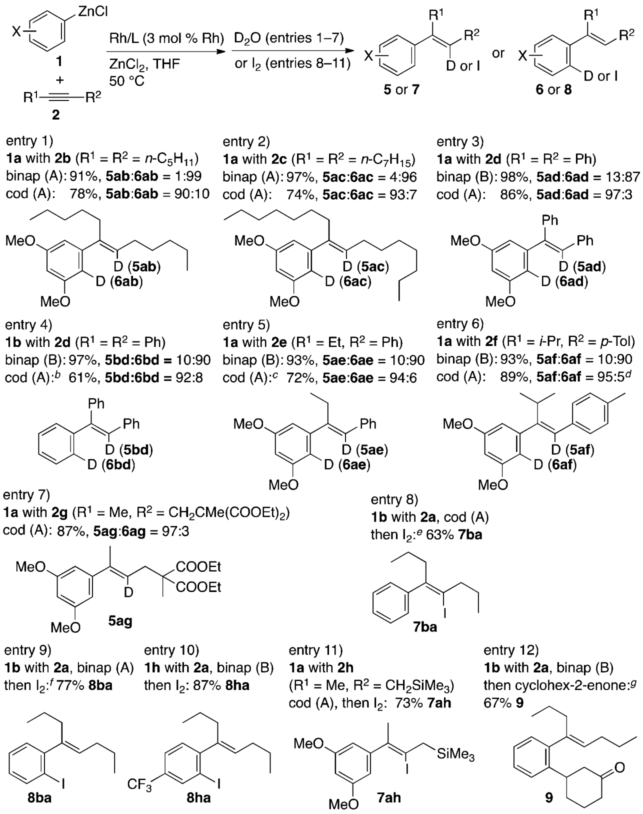
| entry | **1**: Ar in ArZnCl | L on Rh[b] (A) or (B)[a] | yield (%)[c] of **5** + **6** | ratio[d] of **5**:**6** |
|---|---|---|---|---|
| 1 | **1a**: 3,5-$(MeO)_2C_6H_3$ | binap (B) | 90 | <1:99 |
| | | cod (A) | 82 | 92:8 |
| 2 | **1b**: Ph | binap (A) | 87 | 2:98 |
| | | cod (A) | 80 | 80:20 |
| 3 | **1c**: 4-$MeC_6H_4$ | binap (B) | 91 | 1:99 |
| | | cod (A) | 68 | 77:23 |
| 4 | **1d**: 4-$MeOC_6H_4$ | binap (A) | 94 | 1:99 |
| | | cod (A) | 84 | 74:26 |
| 5 | **1e**: 4-$Me_2NC_6H_4$ | binap (B) | 87 | 1:99 |
| | | cod (A) | 71 | 94:6 |
| 6 | **1f**: 4-$Me_3SiC_6H_4$ | binap (B) | 85 | 6:94 |
| | | cod (A) | 86 | 81:19 |
| 7 | **1g**: 4-$FC_6H_4$ | binap (B) | 83 | <1:99 |
| | | cod (A) | 52 | 49:51 |
| 8 | **1h**: 4-$CF_3C_6H_4$ | binap (B) | 93 | <1:99 |
| | | cod (A) | 87 | <1:99 |
| 9 | **1i**: 3-$MeC_6H_4$ | binap (B) | 87 | 1:99[e] |
| | | cod (A) | 72 | 86:14[e] |
| 10 | **1j**: 3-$MeOC_6H_4$ | binap (A) | 93 | 1:99[f] |
| | | cod (A) | 82 | 80:20[f] |
| 11 | **1k**: 3-$Me_2NC_6H_4$ | binap (B) | 95 | 1:99[e] |
| | | cod (A) | 72 | 95:5[e] |
| 12 | **1l**: 3-$Me_3SiC_6H_4$ | binap (B) | 87 | 1:99[e] |
| | | cod (A) | 79 | 83:17[e] |
| 13 | **1m**: 3-Me-5-$MeOC_6H_3$ | binap (B) | 97 | 1:99[e] |
| | | cod (A) | 79 | >99:1 |
| 14 | **1n**: 2-$MeOC_6H_4$ | binap (A) | 88 | 13:87 |
| | | cod (A) | 64 | 94:6 |

[a] Reaction condition (A): ArZnCl **1** (0.60 mmol), $ZnCl_2$ (0.18 mmol), 4-octyne (**2a**) (0.20 mmol), and Rh catalyst (3 mol % of Rh), THF (total 2.0 mL) at 50 °C for 5 h. The reaction was quenched with $D_2O$ (0.2 mL). (B): ArZnCl **1** (0.30 mmol), $ZnCl_2$ (0.09 mmol), 4-octyne (**2a**) (0.20 mmol), and Rh catalyst (3 mol % of Rh), THF (total 1.0 mL) at 50 °C for 1 h. [b] $[RhCl(coe)_2]_2$ (6 μmol of Rh) + binap (6.6 μmol) or $[RhCl(cod)]_2$ (6 μmol of Rh). [c] Isolated yield. [d] Determined by $^1H$ and $^2H$ NMR. [e] Regioselective 1,4-shift giving the products **6** shown below. [f] A mixture of **6ja** and **6ja′** in a ratio of 2:1 and 4:1 with binap and cod, respectively.



The rhodium-catalyzed arylzincation was also successful with several other arylzinc reagents ArZnCl, and similar selectivity control in giving arylzincation products with or without 1,4-migration was observed in the arylzincation of 4-octyne (**2a**), whose results are summarized in Table 2. The selectivity of the addition/1,4-migration sequence giving *ortho*-alkenylphenylzinc **4** with binap as a ligand is very high for all the arylzinc reagents shown in Table 2, including unsubstituted phenylzinc (entry 2) and *para*-substituted ones with both electron-donating and -withdrawing groups (entries 3−8). The ratio of **5**:**6** ranges between <1:99 and 6:94. The 1,4-shift was regioselective in the reaction of *meta*-substituted phenylzinc reagents with Me, $NMe_2$, and $SiMe_3$, deuterium being incorporated at the less hindered position exclusively (entries 9, 11, 12). The regioselectivity was low with 3-$MeOC_6H_4ZnCl$ (entry 10). Interestingly, the 1,4-migration took place selectively to the position next to the MeO group in the reaction of 3-Me-5-MeO$C_6H_3$ZnCl (entry 13). The selective formation of 2-arylethenylzincs **3** without 1,4-migration was also realized using cod as a ligand of the rhodium catalyst for most of the arylzinc reagents examined, although the selectivity is generally not as high as that for the reaction with migration. The ratio of **5**:**6** after $D_2O$ quenching is higher than 7:3, except for the arylzinc reagents substituted with electron-withdrawing groups. Zinc reagents 4-F$C_6H_4$ZnCl and 4-$CF_3C_6H_4$ZnCl gave the corresponding arylation products with **5**:**6** = 49:51 and <1:99, respectively[14] (entries 7 and 8).

### Scheme 2. Rhodium-Catalyzed Arylzincation of Alkynes 2 with Arylzinc Reagents 1[a]

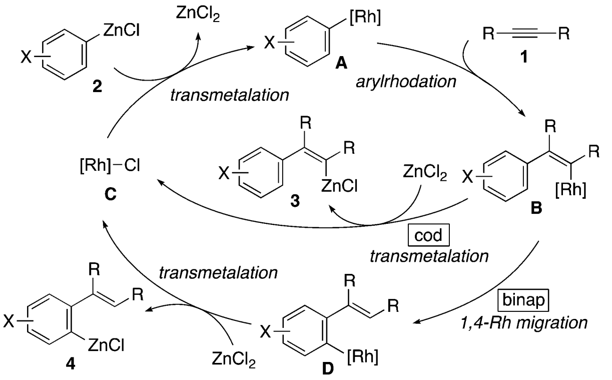


[a]For reaction conditions (A) and (B), see footnote *a* in Table 2. For iodination, $I_2$ (0.60 mmol) was added after the Rh-catalyzed arylzincation. [b]THF solutions of $[RhCl(cod)]_2$ and alkyne **2d** were added dropwise to PhZnCl (**1b**) and $ZnCl_2$ in THF over 40 min. [c]1.5 mol % of Rh catalyst. [d]Containing 5% of its regioisomer. [e]5 mmol scale. [f]20 mmol scale, 1 mol % of Rh catalyst. [g]Cyclohex-2-enone (0.36 mmol) and $[RhCl(cod)]_2$ (15 mol % Rh) were added, and the mixture was heated at THF reflux for 12 h.

The reaction conditions used for the arylzincation of 4-octyne are applicable to other unfunctionalized alkynes. The results are summarized in Scheme 2, which also contains examples where the generated zinc reagents were used for a few transformations other than the deuteration.[15] The arylzincation with **1a** took place for symmetrically substituted dialkylalkynes **2b**−**2c** and diphenylacetylene (**2d**) to give the corresponding *ortho*-alkenylarylzinc or 2-arylalkenylzinc products with high selectivity using binap or cod (entries 1−4). In the reactions of alkyl(aryl)alkynes **2e**−**2f**, high regioselectivity was observed for the bond formation between the aryl group of the arylzinc and the alkyl-substituted alkyne carbon (entries 5 and 6). This selectivity is as expected from the reported regiochemistry at carbometalation of alkyl(aryl)alkynes.[1] The high regioselectivity was also observed in the arylzincation of methyl(alkyl)alkyne **2g**, where the alkyl group is much bigger than methyl (entry 7). The iodination of arylzinc reagents, 2-arylalkenylzinc **3** and *ortho*-alkenylarylzinc **4**, with $I_2$ proceeded smoothly to give the corresponding alkenyl and aryl iodides in high yields (entries 8−11). As another example of transformation of the resulting zinc reagents, Rh-catalyzed conjugate addition of the arylzinc species[16] generated from 4-octyne (**2a**) and PhZnCl (**1b**) is shown in entry 12.[17]

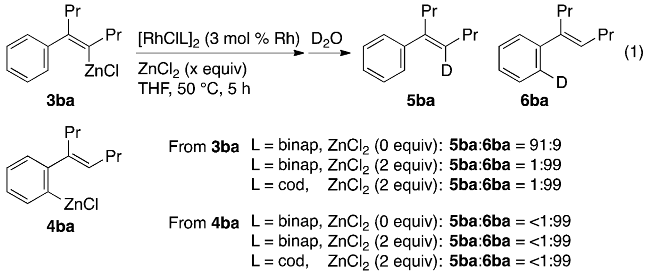
The catalytic cycle of the present arylzincation of alkynes with/without 1,4-migratory is proposed as shown in Scheme 3.

### Scheme 3. A Catalytic Cycle Proposed for Arylzincation of Alkynes Catalyzed by Rh Complexes and $ZnCl_2$



Thus, the syn-addition of aryl−Rh intermediate **A** to the alkyne generates 2-arylalkenyl−Rh species **B**. Transmetalation of the alkenyl group from Rh to $ZnCl_2$ takes place to produce alkenylzinc product **3** and Cl−Rh **C**. Arylation of **C** with ArZnCl regenerates aryl−Rh **A**.[18,19] Direct transmetalation between alkenyl−Rh **B** and ArZnCl **2** giving aryl−Rh **A** and alkenylzinc **3** is less likely because a catalytic amount of $ZnCl_2$ is necessary for the present arylzincation to take place (see entries 4 and 5 in Table 1). When the transmetalation of alkenyl−Rh intermediate **B** with $ZnCl_2$ is relatively slow, it undergoes 1,4-migration of Rh giving *ortho*-alkenylpheny-Rh intermediate **D**, which is thermodynamically more stable than **B**.[7e] Transmetalation with $ZnCl_2$ finally leads to the *ortho*-alkenylarylzinc **4**.[20] The selectivity in producing **3** or **4** is dependent on the reactivity of alkenyl−Rh intermediate **B** toward transmetalation with $ZnCl_2$. It is our understanding that the transmetalation, which is an intermolecular reaction, is faster with a smaller cod ligand and the Rh 1,4-migration which is an intramolecular event is not strongly affected by the ligands on rhodium.

The reactions starting with alkenylzinc **3ba** and *ortho*-alkenylarylzinc **4ba** (eq 1) gave us further insight into the reaction mechanism. The isomerization of **3ba** into **4ba** was observed in the presence of $ZnCl_2$ with both Rh/binap and Rh/cod catalysts, while the isomerization is very slow without $ZnCl_2$. The isomerization from **4ba** to **3ba** was not observed under the same conditions with the binap or cod ligand. These results demonstrate that $ZnCl_2$ plays a key role at the transmetalation steps in the catalytic cycle and that *ortho*-alkenylarylzinc **4ba** is thermodynamically more stable than alkenylzinc **3ba**. It is remarkable that the ratio of 2-arylalkenylzinc **3** to *ortho*-alkenylarylzinc **4** in the reaction of alkyne **2** with arylzinc **1** is not dependent on the reaction time or conversion. Thus, $D_2O$ quench of the reaction of **1a** with **2a** at 15 min reaction time gave a 47% yield of **5aa**/**6aa** (1/99) and a 29% yield of **5aa**/**6aa** (93/7) with binap and cod ligands, respectively. The **5aa**/**6aa** ratios are essentially the same as those observed in entries 1 and 2 in Table 1. The organozincs **3** and **4** generated by the reaction of alkyne **2** with an excess amount of ArZnCl **1** do not go back to the catalytic cycle shown in Scheme 2 in the presence of excess **1**, although both Rh/binap and Rh/cod catalyze the isomerization of **3** to **4** in the absence of ArZnCl **1** (eq 1).



From **3ba** L = binap, $ZnCl_2$ (0 equiv): **5ba**:**6ba** = 91:9
L = binap, $ZnCl_2$ (2 equiv): **5ba**:**6ba** = 1:99
L = cod, $ZnCl_2$ (2 equiv): **5ba**:**6ba** = 1:99

From **4ba** L = binap, $ZnCl_2$ (0 equiv): **5ba**:**6ba** = <1:99
L = binap, $ZnCl_2$ (2 equiv): **5ba**:**6ba** = <1:99
L = cod, $ZnCl_2$ (2 equiv): **5ba**:**6ba** = <1:99

In summary, we have disclosed that the addition of arylzinc reagents ArZnCl to unfunctionalized alkynes is efficiently catalyzed by rhodium complexes in the presence of a catalytic amount of zinc chloride. One of the divergent pathways in giving 2-arylalkenylzincs or *ortho*-alkenylarylzincs, the latter of which are generated through 1,4-Rh migration from alkenyl to aryl in the catalytic cycle, is chosen by use of the appropriate ligands on rhodium.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02668.

Experimental procedures, compound characterization data, and crystallographic data (PDF)

### Accession Codes

CCDC 1813165 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.

## ■ ACKNOWLEDGMENTS

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