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Group 4 Metallocene Difluoride/Palladium Bimetallic Catalysts for the Reductive Cross-Coupling of Alkynes with Aryl Iodides and Bromides

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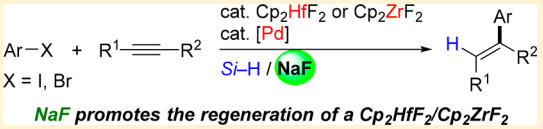
Supporting Information

ABSTRACT: A novel protocol has been developed for the selective synthesis of (*E*)-alkenes via the reductive cross-coupling of alkynes and aryl halides using a bimetallic catalyst system composed of a group 4 metallocene difluoride ($Cp_2[M]F_2$; [M] = Hf or Zr; Cp = cyclopentadienide) and palladium dichloride. This reaction proceeds via a coupling between an aryl halide and an *in situ* generated alkenyl metallocene intermediate derived from the group 4 metallocene difluoride, a hydrosilane, and an alkyne. For a catalytic reductive coupling, the addition of sodium fluoride (NaF) to the reaction system is required. Moreover, in the presence of NaF, a ligand exchange was observed by NMR spectroscopy in hafnocene diiodide (Cp_2HfI_2) to afford hafnocene difluoride (Cp_2HfF_2).

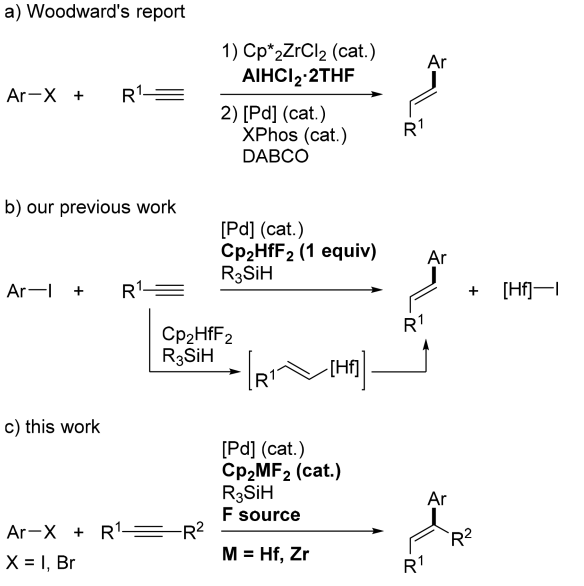


INTRODUCTION

Transition-metal-catalyzed hydroarylation of alkynes represents useful and straightforward synthetic routes to polysubstituted alkenes.[1,2] In particular, the reductive cross-coupling of organohalides with alkenylzirconium species, obtained from the hydrozirconation of alkynes with Schwartz's reagent (Cp_2ZrHCl), has been used for the highly regio- and stereoselective synthesis of polysubstituted alkenes that can be used for the stereoselective synthesis of various natural products or their useful fragments.[3] However, these coupling reactions traditionally require a stoichiometric amount of an alkenyl species bound to a group 4 metal, i.e., a group 4 metal hydride species, given that the effective regeneration of group 4 metal hydrides via the reduction of *in situ* generated group 4 metal halides, which contain relatively strong metal−halogen bonds, with a hydride source is nontrivial. The development of a reductive cross-coupling method that comprises an efficiently catalytic hydrometalation of alkynes with a group 4 metal hydride should therefore be highly desirable.

Thus far, several reductive cross-coupling reactions between alkynes and aryl halides or alkyl pseudohalides have been reported to proceed via catalytic hydrostannylations and hydrocuprations.[4] Meanwhile, to the best of our knowledge, similar procedures that use a catalytic amount of a group 4 metal as the key catalyst have not yet been disclosed. Recently, Woodward et al. have reported a palladium/zirconium-catalyzed reductive cross-coupling between alkynes and aryl halides that affords (*E*)-alkenes.[5] However, to effectively drive the corresponding coupling forward in this reaction, the addition of an excess of the key alkenyl aluminum intermediate, which is generated from alkynes and a dichloroalane−tetrahydrofuran complex ($AlHCl_2$·2THF), is necessary (Scheme 1a).

Scheme 1. Palladium-Catalyzed Reductive Cross-Coupling of Alkynes with Aryl Halides Using Either a Hafnocene Halide or a Zirconocene Halide



On the other hand, our group has recently reported a Pd-catalyzed reductive cross-coupling between aryl iodides and an alkenyl hafnium intermediate, which is prepared via the hydrohafnation of an alkyne with a hafnium hydride derived from Cp_2HfF_2 and a hydrosilane and leads to the highly stereoselective generation of (*E*)-alkenes (Scheme 1b).[6] To

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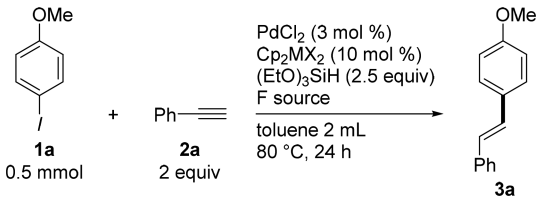
generate a hafnium hydride from a hafnium halide, a strong reducing agent such as lithium aluminum hydride is generally required.[7] In contrast, recent developments and our approach involve the *in situ* generation of the group 4 metallocene hydride from the fluoride complex and a mild reducing agent (hydrosilane), which suppress the side reactions typically observed when using strong reducing agents.[8] However, similar to other conventional studies using group 4 metallocene derivatives, our procedure also contained a serious drawback: to complete the desired reductive coupling, a stoichiometric amount (1 equiv) of Cp_2HfF_2 is required, which reduces the practicality and utility of this protocol. In order to suppress the Cp_2HfF_2 loading, we were interested to find an appropriate additive to regenerate Cp_2HfF_2 *in situ*. Eventually, we discovered that the addition of an excess of sodium fluoride (NaF) successfully promotes the catalytic reductive coupling of alkynes and aryl halides using a $Cp_2[M]F_2$/Pd(II) catalytic system ([M] = Hf(IV) or Zr(IV)) (Scheme 1c). In this paper, we report the full details involving scope and limitations of this reaction.

RESULTS AND DISCUSSION

To find the optimal fluoride source for the regeneration of the Cp_2HfF_2 catalyst, the reductive cross-coupling of 4-iodoanisole (**1a**) and phenylacetylene (**2a**) was initially performed in toluene at 80 °C in the presence of 3 mol % $PdCl_2$, 10 mol % Cp_2HfF_2, 2.5 equiv of $(EtO)_3SiH$, and various fluorine salts (1 equiv) (Table 1). Initially, although we were concerned that an addition of a fluoride source might deactivate the reducing agent, i.e., the hydrosilane, we added several metal fluorides to our catalytic system. When LiF, KF, CsF, or CaF_2 was used as the fluoride source, the desired reaction did not occur (entries 1−4). However, it should be noted that, among these reactions, the addition of NaF afforded the desired coupling product *trans*-alkene **3a** in a 19% GC yield (entry 5).[9] Also, $^nBu_4NF$ as a soluble fluoride source did not work effectively in this reductive coupling (entry 6). Therefore, when the amount of NaF was gradually increased to 5 equiv relative to **1a**, the yield of **3a** improved to a 75% GC yield (entries 7 and 8). This result implies that even though NaF itself is hardly soluble in the reaction system, it may exactly be the low solubility of NaF that effectively regenerates the Cp_2HfF_2 catalyst *in situ* without deactivating the hydrosilane. Furthermore, when the loading of $PdCl_2$ was decreased to 1 mol %, the desired reductive coupling proceeded cleanly to yield alkene **3a** in an 81% isolated yield (entry 9). On the other hand, reactions using Cp_2HfCl_2 or Cp_2TiF_2 did not realize the targeted coupling (entries 10 and 11). Moreover, in the absence of Cp_2HfF_2, the coupling did not proceed (entry 12). These results demonstrate that both Cp_2HfF_2 and the palladium catalyst are indispensable to drive the reaction. Although, the use of Cp_2ZrF_2 also furnished the desired alkene **3a** in a 76% yield, the yield was slightly reduced compared to that obtained from Cp_2HfF_2 (entry 13). However, it was found that Cp_2ZrF_2 also displays a relatively high catalytic activity to the reductive coupling.

Subsequently, we investigated the substrate scope for the reductive coupling with this Hf/Pd catalytic system. Initially, couplings of phenylacetylene (**2a**) with various aryl iodides were tested (Table 2). Iodobenzene and aryl iodides that contain electron-donating substituents, such as a methyl or *tert*-butyl groups, were compatible with this catalytic system, giving the corresponding alkenes **3b**−**3d** and **3f** in high yields except for an *o*-methyl substituent on the aryl iodide. The substrate bonding with an *o*-methyl substituent slightly reduced the yield (**3e**), probably due to the steric hindrance arising from an *ortho* effect between the substrates. Iodoarenes

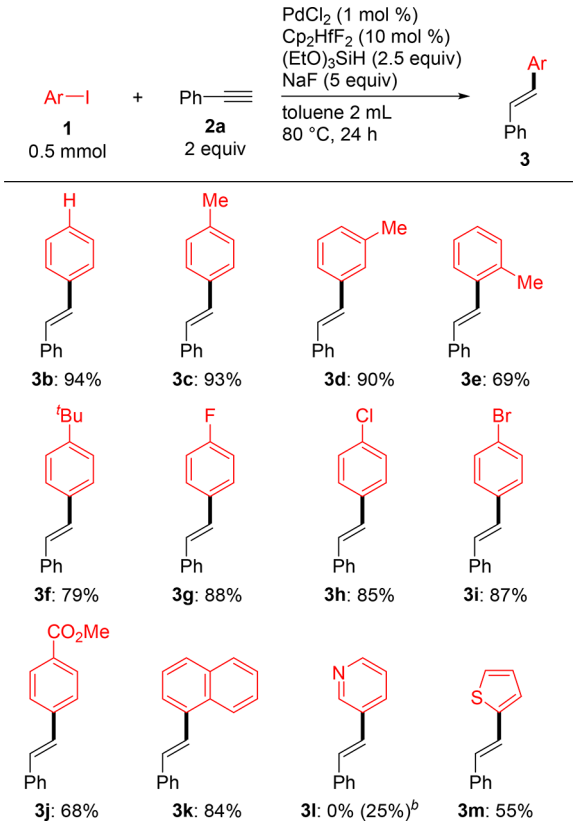
Table 1. Optimization of the Reaction Conditions



entry	F source (equiv)	Cp_2MX_2	GC yield (%)
1	LiF (1)	Cp_2HfF_2	0
2	KF (1)	Cp_2HfF_2	0
3	CsF (1)	Cp_2HfF_2	0
4	CaF_2 (1)	Cp_2HfF_2	0
5	NaF (1)	Cp_2HfF_2	19
6	$^nBu_4NF$ (1)[a]	Cp_2HfF_2	0
7	NaF (3)	Cp_2HfF_2	42
8	NaF (5)	Cp_2HfF_2	75
9[b,c]	NaF (5)	Cp_2HfF_2	83 (81)[d]
10[b]	NaF (5)	Cp_2HfCl_2	0
11[b]	NaF (5)	Cp_2TiF_2	0
12[b]	NaF (5)	–	0
13[b]	NaF (5)	Cp_2ZrF_2	76

[a]1 M in THF. [b]$PdCl_2$ (1 mol %). [c]16 h. [d]Isolated yield.

Table 2. Substrate Scope with Respect to Aryl Iodides[a]



[a]Isolated yield. [b]Cp_2ZrF_2 was used instead of Cp_2HfF_2.

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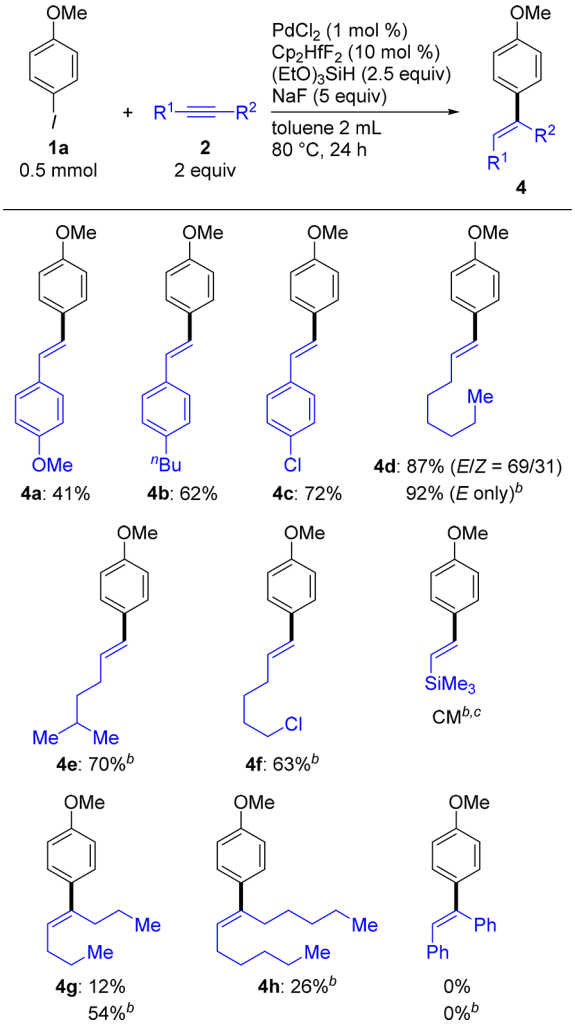
with electron-withdrawing substituents such as a fluorine, chlorine, and bromine also provided the expected alkenes **3g**–**3i** in good yields. A reducible ester group was tolerated under the applied reducing conditions and furnished alkene **3j** in a relatively good yield. Moreover, 1-iodonaphthalene afforded alkene **3k** in an 84% yield. In contrast, the heterocyclic iodoarene 3-iodopyridine, which contains a basic nitrogen atom, was ineffective under standard conditions involving Cp_2HfF_2. However, when Cp_2ZrF_2 was employed instead of Cp_2HfF_2, the expected coupling generated the desired alkene **3l** in a 25% yield. Meanwhile, 2-iodothiophene, which does not contain any basic sites in the ring skeleton, was coupled well with **2a** under standard conditions involving Cp_2HfF_2 to give the coupling product **3m** in a 55% yield. In most cases, the formation of a small amount of the corresponding alkene dimer derived from the alkynes was observed, which implies the *in situ* generation of a Pd(0) catalyst. Also, the stereochemistry of the formed *trans*-alkenes, which are formed exclusively, suggests the *in situ* generation of either a hafnium hydride or a zirconium hydride that selectively add toward the alkyne in a *syn* fashion.

Subsequently, the substrate range of terminal/internal alkynes was surveyed in the coupling with 4-iodoanisole (**1a**), and the results are summarized in Table 3. Both electron-rich aromatic alkynes bearing methoxy or *n*-butyl groups and electron-poor aromatic alkynes bearing a chloro group could be incorporated into the products, affording the desired alkenes **4a**–**4c** in moderate to good yields. To our delight, aliphatic alkynes, which were an unsuitable substrate in our previous study using a stoichiometric amount of Cp_2HfF_2, could be used effectively in the present catalytic system. For instance, 1-octyne provided a mixture of (*E*)-**4d** and (*Z*)-**4d** in an 87% yield (*trans*/*cis* = 69/31). Interestingly, when the same reaction was conducted with Cp_2ZrF_2, (*E*)-**4d** was obtained as the sole product in an excellent yield. Similarly, when 5-methyl-1-hexyne and 6-chloro-1-hexyne were treated with Cp_2ZrF_2, the corresponding products **4e** and **4f** were obtained in 70% and 63% yields, respectively. Using trimethylsilylacetylene afforded an inseparable mixture of the corresponding alkene and the desilylated product, 4-methoxystyrene, which is due to a desilylation of a silyl group of the alkene with remaining NaF.[10] Moreover, the internal alkynes 4-octyne could be successfully employed as a coupling partner, especially for reactions involving Cp_2ZrF_2, which afforded alkene **4g** in a practical yield. When 6-dodecyne with a longer alkyl chain was used, the yield decreased and the coupling product **4h** was obtained in a 26% yield. Conversely, the reaction of **1a** with diphenylacetylene as an aromatic internal alkyne did not proceed and only the starting alkyne was recovered.

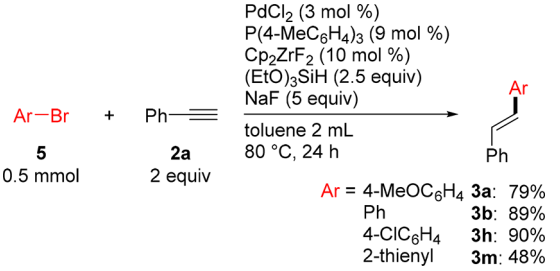
Moreover, a catalytic reductive cross-coupling using aryl bromides as a counterpart was efficiently achieved by a combination of Cp_2ZrF_2 and a phosphine ligand (Scheme 2). For example, when the reaction of acetylene **2a** with 4-bromoanisole was conducted using the Zr/Pd catalytic system and tris(4-methylphenyl)phosphine as a ligand, the corresponding (*E*)-alkene **3a** was obtained in a 79% yield. Bromobenzene also reacted, readily affording coupling product **3b** in an 89% yield.[11] Moreover, a chlorine-substituted aryl bromide could be used in this catalytic system to selectively provide (*E*)-alkene **3h** in a high yield under preservation of the chlorine group. 2-Bromothiophene was converted into the corresponding alkene **3m** in a moderate yield.

Table 3. Substrate Scope with Respect to Alkynes[a]



[a]Isolated yield. [b]Cp_2ZrF_2 was used instead of Cp_2HfF_2. [c]An inseparable mixture of *trans*-(4-methoxystyryl)trimethylsilane and 4-methoxystyrene was obtained.

Scheme 2. Cp_2ZrF_2/Pd-Catalyzed Reductive Cross-Coupling of Aryl Bromides with Phenylacetylene



To investigate the regeneration of Cp_2HfF_2 during this coupling reaction, we initially examined the reaction of Cp_2HfI_2 with 5 equiv of NaF at 80 °C for 13 h (eq 1 in Scheme 3). Although the exchange to Cp_2HfF_2 was lower than expected (5% NMR yield), the formation of Cp_2HfF_2 was confirmed by NMR spectroscopy (see Figure S1 in SI).[12] Given that the *in situ* molar ratio of fluoride anions (*cf.* eq 1) is lower than that in the actual reaction system, the content of NaF was then increased to 50 equiv, which should be closer to

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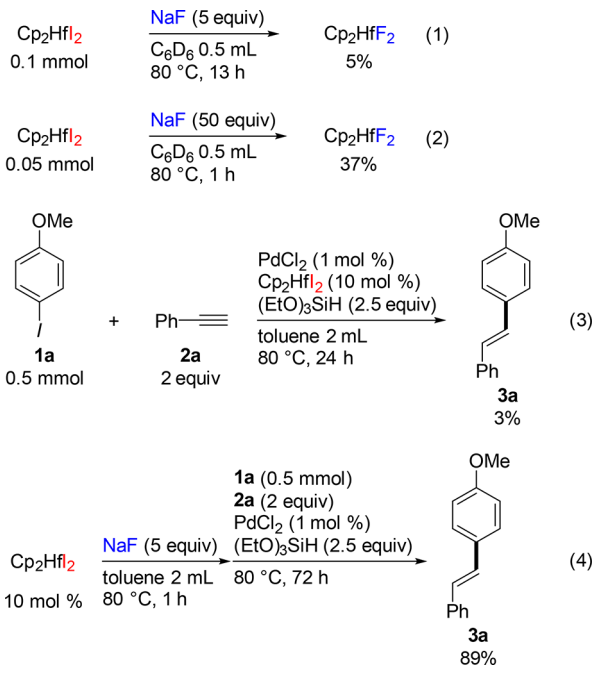
Scheme 3. Mechanistic Aspects for Conversion of Cp_2HfI_2 to Cp_2HfF_2 in the Presence of NaF



the actual molar ratio. Consequently, the formation of Cp_2HfF_2 increased to a 37% NMR yield (eq 2 in Scheme 3 and Figure S2 in SI). Moreover, monitoring the direct conversion of Cp_2HfI_2 to Cp_2HfF_2 in C_6D_6 in the presence of 25 equiv of NaF by ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectroscopy was carried out, and the time-course plots of each conversion are shown in Figures 1 and 2 (see also Figure S3 in SI). The ^{1}H NMR spectra show the gradual formation of the peak corresponding to Cp_2HfF_2 (5.914 ppm) under concomitant disappearance of the peak associated with Cp_2HfI_2 (5.854 ppm) (Figure 1). The ^{19}F NMR showed an emergence of the peak corresponding to Cp_2HfF_2 (−14.66 ppm) with progressing reaction time (Figure 2). Also, we examined the applicability of Cp_2HfI_2 as a catalyst precursor for the present reductive cross-coupling. When the coupling of aryl iodide **1a** and acetylene **2a** with a catalytic amount of Cp_2HfI_2 in the absence of NaF was conducted, the desired coupling hardly proceeded (eq 3 in Scheme 3). Conversely, the same reaction using an *in situ* generated catalytic amount of Cp_2HfF_2 derived from Cp_2HfI_2 and NaF provided the expected coupling product **3a** in an 89% GC yield (eq 4 in Scheme 3). Consequently, these results strongly imply the regeneration of a hafnocene fluoride species from a hafnocene iodide species, which could be formed *in situ* after the reductive coupling of alkynes and aryl iodides, and an excess of NaF.

On the basis of this mechanistic study and our previous work,[6] we propose a plausible reaction mechanism for the $Cp_2[M]F_2$/Pd-catalyzed ([M] = Hf, Zr) reductive coupling of alkynes with aryl halides in Scheme 4. Initially, the group 4 metallocene fluoride ([M]−F) should react with the reducing agent triethoxysilane to generate *in situ* a group 4 metallocene hydride ([M]−H), followed by a stereo- and regioselective hydrometalation of the hydride toward an alkyne to form alkenyl metallocene intermediate **A**. Subsequently, a transmetalation of intermediate **A** toward aryl palladium intermediate **B**, which is derived from the oxidative addition of aryl halides to a Pd^0 catalyst, should occur to produce alkenyl aryl palladium species **C** and metallocene halide **D** ([M]−X). Under conventional conditions, it is relatively difficult to return byproduct metallocene halide **D** to the catalytic cycle. However, using the present system, the addition of NaF to the reaction system regenerates a metallocene fluoride ([M]−F) from the metallocene halide ([M]−X), to successfully construct a catalytic cycle. Finally, the reductive elimination of intermediate **C** provides the desired alkene.

CONCLUSIONS

We have developed a novel catalytic system composed of hafnocene difluoride or zirconocene difluoride and a hydrosilane that has been especially useful for the Pd-catalyzed reductive cross-coupling of alkynes and aryl halides, leading to the stereoselective preparation of a variety of alkene derivatives. It is particularly noteworthy that the addition of NaF successfully promotes the regeneration of a hafnocene/zirconocene fluoride species from the corresponding metallocene halide, which is crucial for the catalytic cycle. We have moreover observed the direct conversion of Cp_2HfI_2 to Cp_2HfF_2 in the presence of NaF by NMR spectroscopy. Ongoing efforts in our group are focused on other substrates to further investigate this catalyst system.

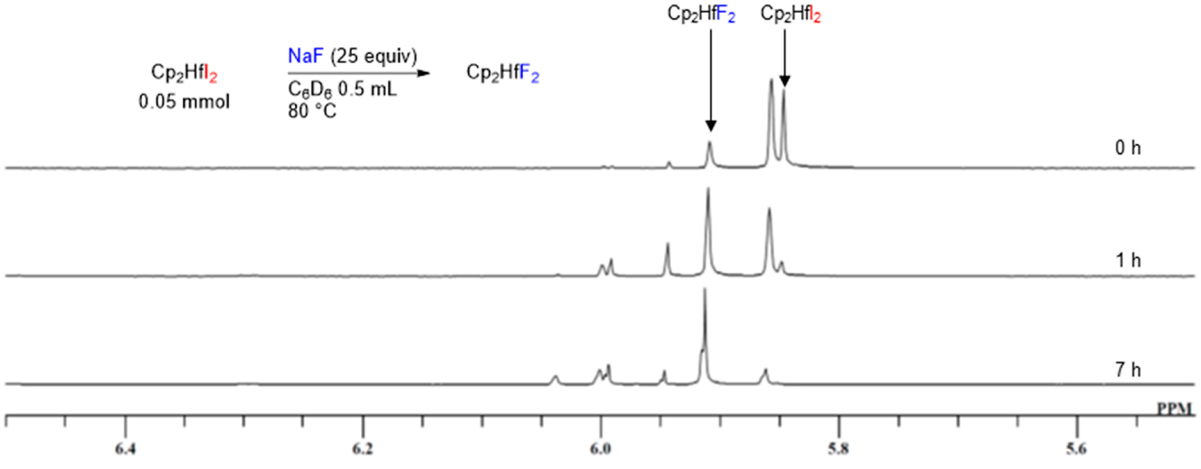


Figure 1. Monitoring of the time-dependent conversion of Cp_2HfI_2 to Cp_2HfF_2 by ^{1}H NMR spectroscopy.

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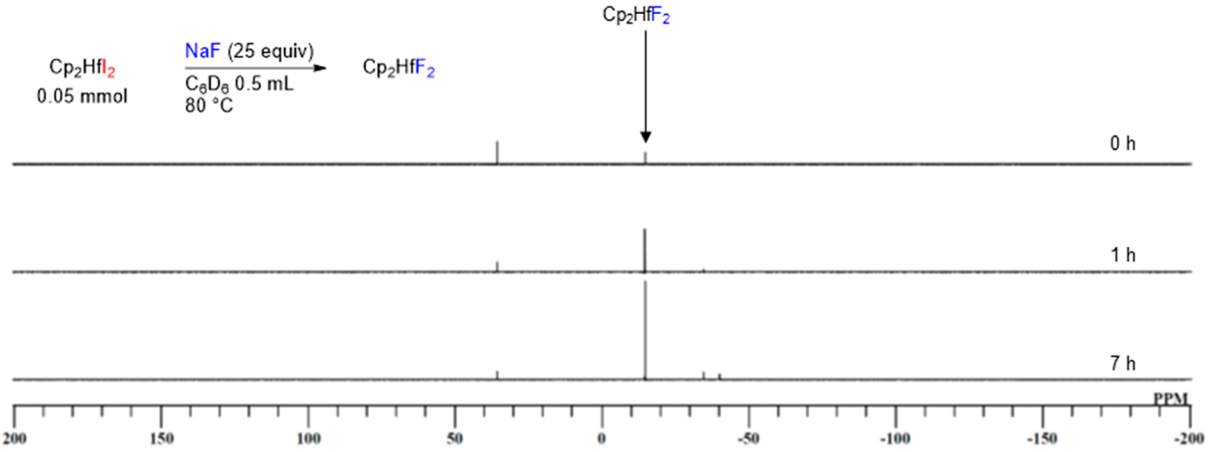
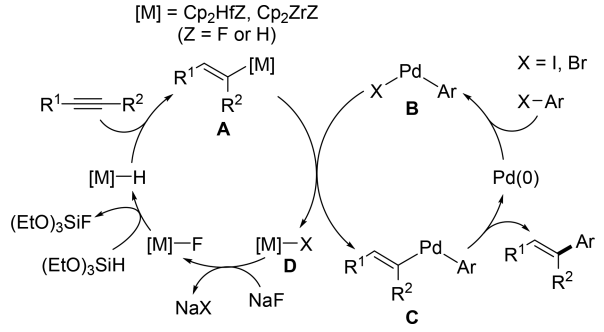


Figure 2. Monitoring of the time-dependent conversion of Cp_2HfI_2 to Cp_2HfF_2 by ^{19}F NMR spectroscopy.

Scheme 4. A Plausible Catalytic Cycle for the $Cp_2[M]F_2$/Pd-Catalyzed ([M] = Hf, Zr) Reductive Coupling of Alkynes with Aryl Halides



EXPERIMENTAL SECTION

General Information. All reactions were carried out under a N_2 atmosphere, unless otherwise noted. Toluene and hexane were freshly distilled over Na-benzophenone prior to use. Dichloromethane (CH_2Cl_2) was dried over P_2O_5 and was then distilled. Palladium dichloride, fluoride salts, such as LiF, NaF, KF, CsF, and CaF_2, boron triiodide, tris(4-methylphenyl)phosphine, diphenylacetylene, aryl iodides **1a**, **1c**, **1h**, **1i**, **1j**, and **1l**, aryl bromides, and hydrosilanes were commercially available and were used without further purification, unless otherwise noted. Alkynes, except for diphenylacetylene, 4-methoxyphenylacetylene, and 4-chlorophenylacetylene, and aryl iodides **1b**, **1d**, **1e**, **1f**, **1g**, **1k**, and **1m** were commercially available and were purified by distillation under reduced pressure prior to use. Column chromatography was performed using a silica gel. ^1H NMR spectra were measured at 500 MHz, and ^{13}C NMR spectra were measured at 125 MHz. Chemical shifts in ^1H and ^{13}C NMR spectra were reported in ppm relative to residual solvent peaks such as those of chloroform (δ 7.26 for ^1H, and δ 77.0 for ^{13}C) and C_6D_6 (δ 7.16 for ^1H, and δ 128.0 for ^{13}C) or of the internal reference tetramethylsilane (δ 0.00 for ^1H). ^{19}F NMR spectra were measured at 470 MHz using the center peak of $CF^{35}Cl_3$ (0.00 ppm). High-resolution mass spectra (HRMS) were measured using NBA (3-nitrobenzylalcohol) as a matrix. Starting materials involving 4-methoxyphenylacetylene,[13] 4-chlorophenylacetylene,[13] Cp_2HfF_2,[6] Cp_2HfCl_2,[6] Cp_2ZrF_2,[6] and Cp_2TiF_2[6] were prepared via a procedure described in the literature, and the spectra obtained agreed with the authentic samples. Cp_2HfI_2 was prepared using a similar procedure described in the literature.[14]

General Procedure for the Reductive Cross-Coupling of Alkynes and Aryl Iodides Leading to (*E*)-Alkenes. To a screw-capped vial in a glovebox, Cp_2HfF_2 (17.3 mg, 0.0500 mmol) or Cp_2ZrF_2 (13.0 mg, 0.0500 mmol), $PdCl_2$ (0.9 mg, 5×10^{-3} mmol), and NaF (105 mg, 2.50 mmol) were successively added. The vial was sealed and removed from the glovebox, and then toluene (2 mL), an aryl iodide (**1**: 0.50 mmol), an alkyne (**2**: 1.0 mmol) and $(EtO)_3SiH$ (205.4 mg, 1.250 mmol) were successively added to the vial. The mixture was heated at 80 °C for 24 h. After the reaction, H_2O (3 mL) was added to the mixture, and the organic layer was extracted with EtOAc (3 mL × 3). The combined organic layer was evaporated under reduced pressure. The crude material was purified via silica gel column chromatography (hexane/EtOAc) to give the corresponding alkene **3** or **4**.

***trans*-4-Methoxystilbene (3a).**[6] The general procedure was followed with phenylacetylene (102.2 mg, 1.000 mmol) and 4-iodoanisole (117.1 mg, 0.5000 mmol) for 16 h. Column chromatography (99/1 = hexane/EtOAc) afforded **3a** as a colorless solid (85.2 mg, 81%): mp 130−133 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 3.83 (s, 3 H, CH_3), 6.90 (d, J = 8.0 Hz, 2 H, Ar*H*), 6.97 (d, J = 16.5 Hz, 1 H, C*H*), 7.07 (d, J = 16.5 Hz, 1 H, C*H*), 7.23 (d, J = 8.0 Hz, 1 H, Ar*H*), 7.34 (t, J = 8.0 Hz, 2 H, Ar*H*), 7.46 (d, J = 8.0 Hz, 2 H, Ar*H*), 7.48 (d, J = 8.0 Hz, 2 H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3, 114.1, 126.2, 126.6, 127.2, 127.7, 128.2, 128.6, 130.1, 137.6, 159.3; LRMS (EI) m/z (% relative intensity) 210 (M^+, 100), 195 (17), 165 (28), 152 (17), 89 (14).

***trans*-Stilbene (3b).**[6] The general procedure was followed with phenylacetylene (102.2 mg, 1.000 mmol) and iodobenzene (102.1 mg, 0.5000 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded **3b** as a colorless solid (84.7 mg, 94%): mp 120−121 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.11 (s, 2 H, C*H*), 7.26 (t, J = 7.5 Hz, 2 H, Ar*H*), 7.36 (t, J = 7.5 Hz, 4 H, Ar*H*), 7.52 (d, J = 7.5 Hz, 4 H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 126.5, 127.6, 128.67, 128.69, 137.3; LRMS (EI) m/z (% relative intensity) 180 (M^+, 100), 165 (33), 102 (41), 90 (17), 76 (18).

***trans*-4-Methylstilbene (3c).**[6] The general procedure was followed with phenylacetylene (102.2 mg, 1.000 mmol) and 4-iodotoluene (109 mg, 0.500 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded **3c** as a colorless solid (90.3 mg, 93%): mp 117−118 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 2.36 (s, 3 H, CH_3), 7.05 (d, J = 16.5 Hz, 1 H, C*H*), 7.09 (d, J = 16.5 Hz, 1 H, C*H*), 7.16 (d, J = 8.0 Hz, 2 H, Ar*H*), 7.24 (t, J = 7.5 Hz, 1 H, Ar*H*), 7.35 (t, J = 7.5 Hz, 2 H, Ar*H*), 7.41 (d, J = 8.0 Hz, 2 H, Ar*H*), 7.50 (d, J = 7.5 Hz, 2 H, Ar*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2, 126.37, 126.4, 127.4, 127.7, 128.58, 128.63, 129.4, 134.5, 137.48, 137.5; LRMS (EI) m/z (% relative intensity) 194 (M^+, 100), 179 (79), 165 (33), 152 (26), 115 (56), 96 (63), 76 (28).

***trans*-3-Methylstilbene (3d).**[6] The general procedure was followed with phenylacetylene (102.2 mg, 1.000 mmol) and 3-iodotoluene (109.1 mg, 0.5000 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded **3d** as a colorless solid (87.4 mg, 90%): mp 42−43 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 2.37 (s, 3 H, CH_3), 7.07−7.09 (m, 3 H), 7.24 (t, J = 7.5 Hz, 2 H, Ar*H*), 7.31−7.36 (m, 4 H), 7.50 (d, J = 7.5 Hz, 2 H, Ar*H*); ^{13}C NMR

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(125 MHz, $CDCl_3$) δ 21.4, 123.7, 126.5, 127.2, 127.5, 128.4, 128.55, 128.6, 128.8, 137.2, 137.4, 138.2; LRMS (EI) m/z (% relative intensity) 194 (M^+, 100), 179 (77), 115 (11), 96 (11), 89 (10).

***trans*-2-Methylstilbene (3e).**[6] The general procedure was followed with phenylacetylene (102.2 mg, 1.000 mmol) and 2-iodotoluene (109.2 mg, 0.5000 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded **3e** as a colorless oil (67.0 mg, 69%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.43 (s, 3 H, CH_3), 6.99 (d, J = 16.0 Hz, 1 H, ArH), 7.17 (d, J = 3.5 Hz, 2 H, ArH), 7.19−7.22 (m, 1 H), 7.26 (t, J = 7.5 Hz, 1 H, ArH), 7.31−7.37 (m, 3 H), 7.51 (d, J = 7.5 Hz, 2 H, ArH), 7.58 (d, J = 7.5 Hz, 1 H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.9, 125.3, 126.2, 126.49, 126.53, 127.52, 127.56, 128.7, 130.0, 130.4, 135.8, 136.4, 137.6; LRMS (EI) m/z (% relative intensity) 194 (M^+, 100), 179 (98), 165 (13), 115 (26), 96 (11), 89 (10).

***trans*-4-*tert*-Butylstilbene (3f).**[6] The general procedure was followed with phenylacetylene (102.2 mg, 1.000 mmol) and 4-*tert*-butyliodobenzene (130.1 mg, 0.5000 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded **3f** as a colorless solid (93.4 mg, 79%): mp 95−97 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33 (s, 9 H, CH_3), 7.06 (d, J = 16.5 Hz, 1 H, CH), 7.10 (d, J = 16.5 Hz, 1 H, CH), 7.24 (t, J = 7.5 Hz, 1 H, ArH), 7.34 (t, J = 7.5 Hz, 2 H, ArH), 7.38 (d, J = 8.5 Hz, 2 H, ArH), 7.45 (d, J = 8.5 Hz, 2 H, ArH), 7.50 (d, J = 7.5 Hz, 2 H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.3, 34.6, 125.6, 126.2, 126.4, 127.4, 127.9, 128.5, 128.6, 134.5, 137.5, 150.8; LRMS (EI) m/z (% relative intensity) 236 (M^+, 44), 221 (100), 178 (16), 103 (17), 91 (64), 77 (20).

***trans*-4-Fluorostilbene (3g).**[6] The general procedure was followed with phenylacetylene (102.2 mg, 1.000 mmol) and 1-fluoro-4-iodobenzene (111 mg, 0.500 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded **3g** as a colorless solid (87.2 mg, 88%): mp 117−120 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99−7.08 (m, 4 H), 7.26 (t, J = 7.5 Hz, 1 H, ArH), 7.35 (t, J = 7.5 Hz, 2 H, ArH), 7.45−7.50 (m, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 115.6 (d, J = 21.3 Hz), 126.4, 127.4, 127.7, 127.9 (d, J = 8.8 Hz), 128.5 (d, J = 2.5 Hz), 128.7, 133.5 (d, J = 3.8 Hz), 137.1, 162.3 (d, J = 246 Hz); LRMS (EI) m/z (% relative intensity) 198 (M^+, 100), 183 (30), 177 (16), 98 (15), 77 (10).

***trans*-4-Chlorostilbene (3h).**[6] The general procedure was followed with phenylacetylene (102.2 mg, 1.000 mmol) and 1-chloro-4-iodobenzene (119.3 mg, 0.5000 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded **3h** as a colorless solid (91.2 mg, 85%): mp 118−120 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (d, J = 16.5 Hz, 1 H, CH), 7.08 (d, J = 16.5 Hz, 1 H, CH), 7.27 (d, J = 7.5 Hz, 1 H, ArH), 7.31 (d, J = 8.0 Hz, 2 H, ArH), 7.36 (t, J = 7.5 Hz, 2 H, ArH), 7.42 (d, J = 8.0 Hz, 2 H, ArH), 7.50 (d, J = 7.5 Hz, 2 H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 126.5, 127.3, 127.6, 127.9, 128.7, 128.8, 129.3, 133.1, 135.8, 136.9; LRMS (EI) m/z (% relative intensity) 216 ([M + 2]$^+$, 34), 214 (M^+, 100), 178 (94), 89 (25), 76 (18).

***trans*-4-Bromostilbene (3i).**[6] The general procedure was followed with phenylacetylene (102.2 mg, 1.000 mmol) and 1-bromo-4-iodobenzene (141.5 mg, 0.5000 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded **3i** as a colorless solid (110.1 mg, 85%): mp 135−137 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (d, J = 16.5 Hz, 1 H, CH), 7.09 (d, J = 16.5 Hz, 1 H, CH), 7.27 (t, J = 7.5 Hz, 1 H, ArH), 7.36 (t, J = 8.0 Hz, 4 H, ArH), 7.47 (d, J = 8.0 Hz, 2 H, ArH), 7.50 (d, J = 7.5 Hz, 2 H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 121.3, 126.5, 127.4, 127.9, 128.0, 128.7, 129.4, 131.8, 136.2, 136.9; LRMS (EI) m/z (% relative intensity) 260 ([M + 2]$^+$, 65), 258 (M^+, 70), 178 (100), 152 (11), 89 (25), 76 (18).

***trans*-4-Methoxycarbonylstilbene (3j).**[15] The general procedure was followed with phenylacetylene (102.2 mg, 1.000 mmol) and methyl 4-iodobenzoate (133 mg, 0.500 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded **3j** as a colorless solid (81.0 mg, 68%): mp 158−160 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.92 (s, 3 H, CH_3), 7.12 (d, J = 16.5 Hz, 1 H, CH), 7.22 (d, J = 16.5 Hz, 1 H, CH), 7.30 (t, J = 7.5 Hz, 1 H, ArH), 7.38 (t, J = 7.5 Hz, 2 H, ArH), 7.53 (d, J = 7.5 Hz, 2 H, ArH), 7.56 (d, J = 8.5 Hz, 2 H, ArH), 8.02 (d, J = 8.5 Hz, 2 H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.1, 126.3, 126.8, 127.5, 128.2, 128.8, 128.9, 130.0, 131.2, 136.7, 141.8, 166.9; LRMS (EI) m/z (% relative intensity) 238 (M^+, 100), 207 (52), 179 (61), 89 (19).

***trans*-1-Styrylnaphthalene (3k).**[6] The general procedure was followed with phenylacetylene (102.2 mg, 1.000 mmol) and 1-iodonaphthalene (127 mg, 0.500 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded **3k** as a colorless solid (96.7 mg, 84%): mp 64−66 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, J = 16.5 Hz, 1 H, CH), 7.28 (t, J = 7.5 Hz, 1 H, ArH), 7.38 (t, J = 7.5 Hz, 2 H, ArH), 7.44−7.52 (m, 3 H), 7.58 (d, J = 7.5 Hz, 2 H, ArH), 7.71 (d, J = 7.5 Hz, 1 H, ArH), 7.78 (d, J = 7.5 Hz, 1 H, ArH), 7.83−7.88 (m, 2 H), 8.20 (d, J = 7.5 Hz, 1 H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 123.6, 123.7, 125.66, 125.75, 125.8, 126.1, 126.7, 127.7, 128.0, 128.6, 128.7, 131.4, 131.7, 133.7, 135.0, 137.6; LRMS (EI) m/z (% relative intensity) 230 (M^+, 100), 215 (16), 202 (15), 152 (54), 135 (44), 101 (17), 77 (12).

***trans*-3-Styrylpyridine (3l).**[6] The general procedure was followed with Cp_2ZrF_2 (13.0 mg, 0.0500 mmol), phenylacetylene (102.2 mg, 1.000 mmol), and 3-iodopyridine (102.5 mg, 0.5000 mmol) for 24 h. Column chromatography (eluent as hexane) afforded **3l** as a colorless solid (22.7 mg, 25%): mp 69−72 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (d, J = 16.5 Hz, 1 H, CH), 7.17 (d, J = 16.5 Hz, 1 H, CH), 7.26−7.32 (m, 2 H, ArH), 7.39 (t, J = 8.0 Hz, 2 H, ArH), 7.53 (d, J = 8.0 Hz, 2 H, ArH), 7.84 (d, J = 8.0 Hz, 1 H, ArH), 8.49 (d, J = 4.5 Hz,1 H, ArH), 8.73 (d, J = 2.0 Hz, 1 H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 123.5, 124.8, 126.6, 128.2, 128.8, 130.8, 132.6, 132.9, 136.6, 148.5; LRMS (EI) m/z (% relative intensity) 181 (M^+, 100), 166 (24), 152 (100), 127 (50), 102 (41), 89 (35).

***trans*-2-Styrylthiophene (3m).**[6] The general procedure was followed with phenylacetylene (102.2 mg, 1.000 mmol) and 2-iodothiophene (105.0 mg, 0.5000 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded **3m** as a colorless solid (51.2 mg, 55%): mp 102−103 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (d, J = 16.0 Hz, 1 H, CH), 7.00 (t, J = 4.0 Hz, 1 H, ArH), 7.06 (s, 1 H, ArH), 7.18−7.26 (m, 3 H), 7.34 (t, J = 7.5 Hz, 2 H, ArH), 7.46 (d, J = 7.5 Hz, 2 H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 121.8, 124.3, 126.1, 126.3, 127.6, 128.3, 128.7, 136.9, 142.9; LRMS (EI) m/z (% relative intensity) 186 (M^+, 100), 171 (13), 153 (19), 141 (19), 115 (13), 92 (10), 77 (10).

***trans*-4,4′-Dimethoxystilbene (4a).**[6] The general procedure was followed with 4-methoxyphenylacetylene (133.2 mg, 1.000 mmol) and 4-iodoanisole (117 mg, 0.5000 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded **4a** as a colorless solid (49.3 mg, 41%): mp 207−208 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.82 (s, 6 H, CH_3), 6.89 (d, J = 9.0 Hz, 4 H, ArH), 6.93 (s, 2 H, ArH), 7.42 (d, J = 9.0 Hz, 4 H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3, 114.1, 126.2, 127.4, 130.5, 159.0; LRMS (EI) m/z (% relative intensity) 240 (M^+, 100), 225 (50), 180 (50), 121 (80).

***trans*-4-Butyl-4′-methoxystilbene (4b).**[16] The general procedure was followed with 4-butylphenylacetylene (158.2 mg, 1.000 mmol) and 4-iodoanisole (118.0 mg, 0.5000 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded **4b** as a pale yellow solid (82.6 mg, 62%): mp 110−112 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.93 (t, J = 7.5 Hz, 3 H, CH_3), 1.36 (sext, J = 7.7 Hz, 2 H, CH_2), 1.59 (sext, J = 7.7 Hz, 2 H, CH_2), 2.61 (t, J = 7.5 Hz, 2 H, CH_2), 3.83 (s, 3 H, OCH_3), 6.89 (d, J = 8.0 Hz, 2 H, ArH), 6.95 (d, J = 16.0 Hz, 1 H, CH), 7.02 (d, J = 16.0 Hz, 1 H, CH), 7.16 (d, J = 8.0 Hz, 2 H, ArH), 7.40 (d, J = 8.0 Hz, 2 H, ArH), 7.44 (d, J = 8.0 Hz, 2 H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.4, 33.6, 35.4, 55.3, 114.1, 126.1, 126.6, 127.2, 127.6, 128.7, 130.4, 135.0, 142.2, 159.1; LRMS (EI) m/z (% relative intensity) 266 (M^+, 100), 223 (100), 208 (10), 165 (15), 135 (11), 73 (13); HRMS (FAB-Magnetic Sector) calcd for [M]$^+$ ($C_{19}H_{22}O$) m/z 266.1671, found 266.1674.

***trans*-4-Chloro-4′-methoxystilbene (4c).**[6] The general procedure was followed with 4-chlorophenylacetylene (136.6 mg, 1.000 mmol) and 4-iodoanisole (117 mg, 0.500 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded **4c** as a colorless solid (88.1 mg, 72%): mp 170−172 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.83 (s, 3 H, CH_3), 6.89−6.93 (m, 3 H), 7.03 (d, J = 16.0 Hz, 1 H, CH), 7.30 (d, J = 8.5 Hz, 2 H, ArH), 7.40 (d, J = 8.5 Hz, 2 H, ArH),

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7.44 (d, J = 8.5 Hz, 2 H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3, 114.2, 125.2, 127.4, 127.8, 128.76, 128.79, 129.7, 132.7, 136.1, 159.5; LRMS (EI) m/z (% relative intensity) 246 ([M + 2]$^+$, 34), 244 (M$^+$, 100), 229 (20), 207 (26), 165 (38), 91 (17).

***trans*-1-(4-Methoxyphenyl)-1-octene ((*E*)-4d).**[17] The general procedure was followed with Cp_2ZrF_2 (13.0 mg, 0.0500 mmol), 1-octyne (117 mg, 1.00 mmol), and 4-iodoanisole (117 mg, 0.500 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded (*E*)-**4d** as a colorless oil (100.4 mg, 92%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, J = 6.5 Hz, 3 H, CH_3), 1.27−1.36 (m, 6 H, CH_2), 1.42−1.47 (m, 2 H, CH_2), 2.17 (q, J = 7.3 Hz, 2 H, CH_2), 3.79 (s, 3 H, OCH_3), 6.08 (dt, J = 15.5, 7.0 Hz, 1 H, CH), 6.31 (d, J = 15.5 Hz, 1 H, CH), 6.83 (d, J = 8.5 Hz, 2 H, ArH), 7.27 (d, J = 8.5 Hz, 2 H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.6, 28.9, 29.5, 31.8, 33.0, 55.2, 113.9, 126.9, 129.0, 129.1, 130.8, 158.6; LRMS (EI) m/z (% relative intensity) 218 (M$^+$, 36), 147 (100), 134 (29), 115 (11), 91 (28). 77 (15).

***cis*-1-(4-Methoxyphenyl)-1-octene ((*Z*)-4d).**[18] The general procedure was followed with Cp_2HfF_2 (17.3 mg, 0.0500 mmol), 1-octyne (117 mg, 1.00 mmol), and 4-iodoanisole (117 mg, 0.500 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded a mixture of (*E*)-**4d** and (*Z*)-**4d** (*trans*/*cis* = 69/31) as a colorless oil (95.0 mg, 87%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88−0.90 (m, 3 H, CH_3), 1.27−1.35 (m, 6 H, CH_2), 1.42−1.47 (m, 2 H, CH_2), 2.15−2.19 (m, 2 H, CH_2), 3.80 (s, 3 H, OCH_3), 5.71 (dt, J = 8.0, 1.5 Hz, 1 H, CH), 6.05−6.11 (m, 1 H, CH), 6.84 (d, J = 8.5 Hz, 2 H, ArH), 7.32 (d, J = 8.5 Hz, 2 H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 15.8, 22.6, 28.7, 29.4, 31.6, 55.2, 113.5, 126.5, 127.3, 129.0, 133.7, 158.3; LRMS (EI) m/z (% relative intensity) 218 (M$^+$, 27), 147 (100), 134 (29), 115 (11), 91 (17). 77 (15).

***trans*-1-(4-Methoxyphenyl)-5-methyl-1-hexene (4e).** The general procedure was followed with Cp_2ZrF_2 (13.0 mg, 0.0500 mmol), 5-methyl-1-hexyne (96.2 mg, 1.00 mmol), and 4-iodoanisole (117.0 mg, 0.5000 mmol) for 24 h. Column chromatography (eluent as hexane) afforded **4e** as a colorless oil (71.5 mg, 70%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.91 (d, J = 7.0 Hz, 6 H, CH_3), 1.34 (q, J = 7.0 Hz, 2 H, CH_2), 1.55−1.66 (m, 1 H, CH), 2.19 (q, J = 7.0 Hz, 2 H, CH_2), 3.80 (s, 3 H, OCH_3), 6.07 (dt, J = 7.0, 16.0 Hz, 1 H, CH), 6.32 (d, J = 16.0 Hz, 1 H, CH), 6.83 (d, J = 8.5 Hz, 2 H, ArH), 7.27 (d, J = 8.5 Hz, 2 H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.5, 27.5, 30.9, 38.7, 55.3, 113.9, 126.9, 128.8, 129.2, 130.8, 158.6; HRMS (FAB-Magnetic Sector): calcd for [M]$^+$ ($C_{14}H_{20}O$) m/z 204.1514, found 204.1515.

***trans*-1-(4-Methoxyphenyl)-6-chloro-1-hexene (4f).**[19] The general procedure was followed with Cp_2ZrF_2 (13.0 mg, 0.0500 mmol), 6-chloro-1-hexyne (116.6 mg, 1.000 mmol), and 4-iodoanisole (117.0 mg, 0.5000 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded **4f** as a colorless oil (70.8 mg, 63%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.61 (quin, J = 7.5 Hz, 2 H, CH_2), 1.83 (quin, J = 7.5 Hz, 2 H, CH_2), 2.22 (q, J = 7.5 Hz, 2 H, CH_2), 3.56 (t, J = 7.5 Hz, 2 H, CH_2), 3.80 (s, 3 H, OCH_3), 6.50 (dt, J = 7.5 Hz, 16 Hz, 1 H, CH), 6.34 (d, J = 16 Hz, 1 H, CH), 6.83 (d, J = 8.5 Hz, 2 H, ArH), 7.27 (d, J = 8.5 Hz, 2 H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.7, 32.0, 32.2, 45.0, 55.3, 113.9, 127.0, 127.9, 129.7, 130.5, 158.7; LRMS (EI) m/z (% relative intensity) 226 ([M + 2]$^+$, 31), 224 (M$^+$, 100), 188 (79), 159 (71), 147 (95), 121 (65), 91 (58), 77 (46).

(*E*)-4-(4-Methoxyphenyl)-4-octene (4g).[20] The general procedure was followed with 4-octyne (110.2 mg, 1.000 mmol) and 4-iodoanisole (117.0 mg, 0.5000 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded **4g** as a colorless oil (Cp_2HfF_2 was used: 13.1 mg, 12%; Cp_2ZrF_2 was used: 59.0 mg, 54%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, J = 7.3 Hz, 3 H, CH_3), 0.95 (t, J = 7.3 Hz, 3 H, CH_3), 1.35 (sext, J = 7.3 Hz, 2 H, CH_2), 1.45 (sext, J = 7.3 Hz, 2 H, CH_2), 2.14 (q, J = 7.3 Hz, 2 H, CH_2), 2.44 (t, J = 7.3 Hz, 2 H, CH_2), 3.80 (s, 3 H, OCH_3), 5.59 (t, J = 7.5 Hz, 1 H, CH), 6.83 (d, J = 8.5 Hz, 2 H, ArH), 7.27 (d, J = 8.5 Hz, 2 H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 21.8, 23.1, 30.6, 31.7, 55.2, 113.5, 127.3, 127.8, 136.0, 139.3, 158.3; LRMS (EI) m/z (% relative intensity) 218 (M$^+$, 42), 189 (83), 175 (74), 147 (100), 121 (62), 91 (55), 77 (36).

(*E*)-6-(4-Methoxyphenyl)-6-dodecene (4h). The general procedure was followed with Cp_2ZrF_2 (13.0 mg, 0.0500 mmol), 6-dodecyne (166.3 mg, 1.000 mmol), and 4-iodoanisole (117.0 mg, 0.5000 mmol) for 24 h. Column chromatography (eluent as hexane) afforded **4h** as a colorless oil (35.7 mg, 26%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (t, J = 7.3 Hz, 3 H, CH_3), 0.90 (t, J = 7.3 Hz, 3 H, CH_3), 1.26−1.34 (m, 12 H, CH_2), 2.16 (q, J = 7.3 Hz, 2 H, CH_2), 2.44 (t, J = 7.3 Hz, 2 H, CH_2), 3.80 (s, 3 H, OCH_3), 5.57 (t, J = 7.3 Hz, 1 H, CH), 6.84 (d, J = 8.5 Hz, 2 H, ArH), 7.27 (d, J = 8.5 Hz, 2 H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.07, 14.09, 22.5, 22.6, 28.4, 28.5, 29.67, 29.70, 31.7, 31.9, 55.2, 113.5, 127.2, 127.9, 136.0, 139.4, 158.3; HRMS (EI-Quadrupole) calcd for [M]$^+$ ($C_{19}H_{30}O$) m/z 274.2297, found 274.2270.

General Procedure for the Reductive Cross-Coupling of Alkyne 2a and Aryl Bromides. To a screw-capped vial in a glovebox, Cp_2ZrF_2 (13.0 mg, 0.0500 mmol), $PdCl_2$ (2.7 mg, 0.015 mmol), tris(4-methylphenyl)phosphine (13.7 mg, 0.0450 mmol), and NaF (105 mg, 2.50 mmol) were added in succession. The vial was sealed and removed from the glovebox, and then toluene (2 mL), an aryl bromide (**5**: 0.50 mmol), phenylacetylene (**2a**: 102.2 mg, 1.000 mmol), and $(EtO)_3SiH$ (205.4 mg, 1.250 mmol) were added to the vial in succession. The mixture was heated at 80 °C for 24 h. After the reaction, H_2O (3 mL) was added to the mixture, which was then extracted with EtOAc (3 mL × 3). The combined organic layer was evaporated under reduced pressure. The crude material was purified via silica gel column chromatography (hexane/EtOAc) to give the corresponding alkene **3**.

***trans*-4-Methoxystilbene (3a).** The general procedure was followed with 4-bromoanisole (93.5 mg, 0.500 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded **3a** as a colorless solid (83.1 mg, 79%). The spectra obtained agreed with the above sample.

***trans*-Stilbene (3b).** The general procedure was followed with bromobenzene (78.5 mg, 0.500 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded **3b** as a colorless solid (80.2 mg, 89%). The spectra obtained agreed with the above sample.

***trans*-4-Chlorostilbene (3h).** The general procedure was followed with 1-bromo-4-chlorobenzene (95.7 mg, 0.500 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded **3h** as a colorless solid (96.6 mg, 90%). The spectra obtained agreed with the above sample.

***trans*-2-Styrylthiophene (3m).** The general procedure was followed with 2-bromothiophene (81.5 mg, 0.500 mmol) for 24 h. Column chromatography (99/1 = hexane/EtOAc) afforded **3m** as a colorless solid (44.7 mg, 48%). The spectra obtained agreed with the above sample.

Preparation of Cp_2HfI_2.[14] Borone triiodide (783 mg, 2.00 mmol) in CH_2Cl_2 (2 mL) was slowly added with stirring to Cp_2HfCl_2 (759 mg, 2.00 mmol) in CH_2Cl_2 (28 mL). The solution was stirred at room temperature for 1 h, and the color of the resultant mixture turned red. The solvent was removed by about one-third volume under reduced pressure. After the addition of hexane (40 mL), the solution was stirred slowly to precipitate a pale yellow solid. The solid was collected by filtration, washed with hexane three times, and dried in vacuo to afford Cp_2HfI_2 (619 mg, 55%) as a pale yellow solid: mp 280 °C (decomp.); ^{1}H NMR (500 MHz, C_6D_6) δ 5.86 (s, 10 H, CpH); ^{13}C NMR (125 MHz, C_6D_6) δ 113.6. LRMS (ESI): m/z (% relative intensity) 437 ([M − I]$^+$, 6).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b02055.

^{1}H and ^{13}C NMR charts of all alkene products prepared by the present method, ^{1}H and ^{13}C NMR charts of

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prepared Cp_2HfI_2, and ^1H and ^{13}C NMR time-course charts of control experiments (PDF)

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Notes

The authors declare no competing financial interest.

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(10) An inseparable mixture of *trans*-(4-methoxystyryl)trimethylsilane (14% NMR yield), 4-methoxystyrene (18% NMR yield), and other unidentified impurities was obtained.

(11) When Cp_2ZrF_2/Pd-catalyzed reductive cross-coupling of bromobenzene were examined with PPh_3, XPhos, and Xantphos, alkene **3b** was provided in 44%, 0%, and 11% yields, respectively.

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