# ORGANOMETALLICS

### Copper- and Nickel-Catalyzed Cross-Coupling Reaction of Monofluoroalkenes with Tertiary, Secondary, and Primary Alkyl and **Aryl Grignard Reagents**

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**S** Supporting Information

ABSTRACT: A highly efficient cross-coupling reaction of monofluoroalkenes with tertiary, secondary, and primary alkyl and aryl Grignard reagents in the presence of a catalytic amount of copper or nickel catalyst, respectively, has been R = secondary, primary alkyl and aryl groups developed. The reactions proceeded smoothly at room



temperature, providing (E)-alkene isomers in moderate to high yields. Plausible mechanisms of the Ni-catalyzed coupling reaction of monofluoroalkene with Grignard reagents are suggested.

#### INTRODUCTION

Monofluoroalkenes are important structural motifs in biologically active molecules, and numerous methods for the synthesis of monofluoroalkenes have been developed.<sup>1</sup> Despite their wide applications in medicinal and peptide chemistry,<sup>2</sup> the synthetic utility of monofluoroalkenes in organic synthesis is still underdeveloped.<sup>3</sup> The breaking, activation, and functionalization of the inert C-F bonds are particularly challenging synthetic problems in fluorine chemistry and organic synthesis and, therefore, continue to attract significant attention from synthetic chemists.<sup>4</sup> However, most of the present work involves the activation or cleavage of C-F bonds of fluoroarenes and gem-difluoroalkenes.<sup>5</sup> The cleavage and activation of C-F bonds of nonactivated monofluoroalkenes remain largely unexplored; only sporadic examples have been reported.<sup>6</sup> Generally, monofluoroalkenes are assumed to be less reactive toward nucleophilic substitution than gem-difluoroalkenes due to the relatively lower polarization of the carboncarbon double bond of monofluoroalkenes.<sup>7</sup> However, several examples have demonstrated that the second C-F bond of gem-difluoroalkenes is also reactive and can be cleaved readily.<sup>8</sup>

The transition-metal-catalyzed Kumada-Tamao-Corriu cross-coupling of aryl or alkenyl halides with Grignard reagents is one of the most valuable methods for the construction of carbon-carbon bonds.9 With the development of the Kumada cross-coupling reaction, the less reactive aryl fluorides,<sup>1</sup> unactivated fluoroalkanes,<sup>11</sup> and more reactive gem-difluor-oalkenes have also been successfully used as coupling partners.<sup>8d,12</sup> However, cross-coupling reactions of monofluoroalkenes with Grignard reagents have been much less studied. In this paper, we report a novel cross-coupling reaction of monofluoroalkenes with tertiary, secondary, and primary alkyl and aryl Grignard reagents in the presence of a catalytic amount

of copper or nickel catalyst, respectively, which affords the Eisomer of alkylated or arylated olefins depending on the Grignard reagents and catalysts used (Scheme 1).

Scheme 1. Coupling Reactions of Monofluoroalkenes with Various Grignard Reagents



#### RESULTS AND DISCUSSION

Inspired by our recently developed palladium- and nickelcatalyzed or copper-mediated coupling reactions of gemdifluoroalkenes with various Grignard reagents, herein we focused our efforts on the coupling reactions of monofluoroalkenes with various Grignard reagents in the presence of different metal catalysts. We first chose 1-(2-fluorovinyl)-4methoxybenzene (1a) and tBuMgCl (2a) as the model substrates to optimize the reaction conditions, and the results are summarized in Table 1. Initially, the effect of the catalyst on the reaction was examined. Among the various transition-metal catalysts examined, CuCN and CuI were the most suitable for the reaction, affording the expected product E-3aa in 99% and 95% yields, respectively (entries 7 and 8), while other metal salts such as Pd(PPh<sub>3</sub>)<sub>4</sub>, Cu(OAc)<sub>2</sub>, Cu(OAc), CuBr, and CuCl gave low yields (entries 2–6). NiCl<sub>2</sub>(dppe) and NiCl<sub>2</sub>(dppp) were also effective for this transformation, but they are more expensive than copper catalysts (entries 9 and 10).

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Table 1. Optimization of the Reaction Conditions $^{a,b}$ 

	$H = \frac{1}{2} $					
	<b>1a</b> , <i>E/Z</i> = 93	7 2a	E-3aa	—0 <b>Z-3aa</b>		
entry	catalyst (amt (mol %))	2a (equiv)	yield of E-3aa (%)	yield of Z-3aa (%)	E-1a	Z-1a
1	none	4.0	60	0	38	2
2	$Pd(PPh_3)_4$ (4)	4.0	62	0	37	1
3	$Cu(OAc)_2$ (25)	4.0	43	0	50	4
4	Cu(OAc) (25)	4.0	30	0	65	5
5	CuBr (25)	4.0	67	0	8	2
6	CuCl (25)	4.0	81	0	18	0
7	CuI (25)	4.0	95	0	0	0
8	CuCN (25)	4.0	99	0	0	0
9	NiCl <sub>2</sub> (dppe) (4)	4.0	92	0	0	0
10	$NiCl_2(dppp)$ (4)	4.0	80	9	0	0
11	CuCN (25)	2.0	19	0	75	6
12	CuCN (25)	3.0	47	0	49	4
13	CuCN (15)	4.0	42	0	54	4
14	CuCN (35)	4.0	60	0	37	3
<sup>4</sup> Reaction con	ditions: 1a (1.0 mmol), THF (2	2 mL), room temp	erature, 2 h, Ar. <sup>b</sup> Yields det	termined by GC-MS or G	C analysis and	based on 1a

To our surprise, the reaction gave *E*-3aa in moderate yield in absence of metal catalyst (Table 1, entry 1), whereas the reaction of a *gem*-difluoroalkene such as 1-(2,2-difluorovinyl)-4-methoxybenzene with *t*BuMgCl (2a; 4.0 equiv) in the absence of metal catalyst gave only 5% of the tertiary alkylation product (2.0 equiv of 2a gave only a trace amount of product in our previous result).<sup>8g</sup> The results indicated that the C–F bond of the monofluoroalkene was more reactive than the C–F bond of the *gem*-difluoroalkene in tertiary alkylation under transition-metal-free conditions.

Finally, the influence of the amounts of CuCN and *t*BuMgCl on the reaction was also examined (Table 1, entries 11-14). It was found that 0.25 equiv of CuCN and 4.0 equiv of *t*BuMgCl (2a) gave the best results (entry 8). Decreasing or increasing the amounts of CuCN and 2a obviously diminished the yields of product *E*-3aa. GC-MS and GC analysis of the crude reaction mixtures indicated that no *Z*-isomeric products were detected in most cases, except for entry 10. Under the optimal reaction conditions (entry 8), the *E* isomer 3aa was obtained exclusively and neither *Z* isomer 3aa nor starting materials *E*-1a and *Z*-1a were detected after the completion of the reaction (GC, GC-MS, and <sup>19</sup>F NMR). These results indicated that the *Z* isomer starting material 1a also could be converted to *E*-3aa.

With the optimized conditions in hand (Table 1, entry 8), we next examined the scope of the novel copper-catalyzed tertiary alkylation of various monofluoroalkenes with tertiary alkyl Grignard reagents (2a,b) (Table 2). The results indicated that both electron-rich and -poor monofluoroalkenes could afford tertiary alkylation products in moderate to high yields and the E isomers 3aa-ab were obtained as the sole products, with the exception of 3ga. This reaction displayed good functional group compatibility, and various functional groups such as alkoxy, methylthio, halo, acetamido, and cyano were well tolerated. The tolerance of the Br, Cl, and CN groups is important (1j-1), which are useful for further synthetic transformation. N-(4-(2-Fluorovinyl) phenyl)acetamide (1g) was a poor substrate and furnished the expected product E-3ga in only 42% yield along with 30% of unreacted E-1g. 1-(2-Fluorovinyl)naphthalene was a good substrate for this reaction, the

Table 2. Cu-Catalyzed Tertiary Alkylation of Monofluoroalkenes $^{a,b}$ 



<sup>a</sup>Reaction conditions: 1a-l (1.0 mmol), 2a,b (4.0 mmol), CuCN (25 mol %), THF (2 mL), room temperature, 2 h, Ar. <sup>b</sup>Isolated yields. <sup>c</sup>E:Z ratios of 1a-l: 1a (93:7), 1b (93:7), 1c (95:5), 1d (90:10), 1e (94:6), 1f (95:5), 1g (97:3), 1h (92:8), 1i (90:10), 1j (95:5), 1k (92:8), 1l (85:15).

corresponding product E-3ia being obtained in high yield. The reaction of monofluoroalkene 1a with *tert*-pentylmagnesium chloride (2b) also proceeded efficiently and afforded tertiary alkylated alkene E-3ab in good yield.

To our delight, *E* isomers **3** were isolated as the sole isomeric products in all cases. Further analysis of the reaction mixtures by <sup>19</sup>F NMR spectroscopy and GC-MS revealed that both starting materials *E*- and **Z**-1**a**-1 were completely consumed; no *Z* products **3** were detected. These results suggested that the cleavage of the carbon–carbon double bond might be involved in this transformation. This phenomenon is consistent with our previous report on the Cu-catalyzed tertiary alkylation of *gem*-difluoroalkenes.<sup>8g</sup>

To further extend the scope and utility of the Kumada crosscoupling reaction of monofluoroalkenes with Grignard reagents, secondary and primary alkyl and aryl Grignard reagents were used as substrates to react with monofluoroalkenes. Unfortunately, only trace amounts of the expected secondary and primary alkylation and arylation products were observed in the presence of 25 mol % of CuCN; instead, large amounts of defluorinated alkenes were detected. After reexamining the reaction conditions, we found that 4 mol % of NiCl<sub>2</sub>(dppe) could efficiently catalyze the coupling reactions between monofluoroalkenes and secondary and primary alkyl and aryl Grignard reagents. Thus, a variety of secondary and primary alkyl and aryl Grignard reagents were subjected to cross-coupling with monofluoroalkenes in the presence of NiCl<sub>2</sub>(dppe). As shown in Tables 3–5, the coupling reactions

### Table 3. Ni-Catalyzed Secondary Alkylation of Monofluoroalkenes $^{a-c}$



<sup>*a*</sup>Reaction conditions: 1a-e,h,j,k,m (1.0 mmol), 2c-f (4.0 mmol), NiCl<sub>2</sub>(dppe) (4 mol %), THF (2 mL), room temperature, 2 h, Ar. <sup>*b*</sup>Isolated yields. <sup>*c*</sup>The *E*:*Z* ratios of 1a-e,h,j,k are the same as in Table 2. <sup>*d*</sup>The *E*:*Z* ratio of 1m was 95:5.

## Table 4. Ni-Catalyzed Primary Alkylation of Monofluoroalkenes $^{a-c}$



<sup>a</sup>Reaction conditions: 1a,b,g,j,l,m (1.0 mmol), 2g-j (4.0 mmol), NiCl<sub>2</sub>(dppe) (4 mol %), THF (2 mL), room temperature, 2 h, Ar. <sup>b</sup>Isolated yields. <sup>c</sup>The *E:Z* ratios of 1a,b,g,j,l,m are the same as in Tables 2 and 3. <sup>d</sup>Two equivalents of 2i was used.

Table 5. Ni-Catalyzed Arylation of Monofluoroalkenes<sup>a-c</sup>



<sup>a</sup>Reaction conditions: **1a,h,j,m** (1.0 mmol), **2k** (2.0 mmol), NiCl<sub>2</sub>(dppe) (4 mol %), THF (2 mL), room temperature, 2 h, Ar. <sup>b</sup>Isolated yields. <sup>c</sup>The E:Z ratios of **1a,h,j,m** are the same as in Tables 2 and 3.

of monofluoroalkenes with secondary and primary alkyl and aryl Grignard reagents proceeded smoothly, affording the desired products in moderate to good yields.

Although *E* products **3** were isolated as the only products in most cases (except for **3ae,de,ee**, which were isolated as a mixture of isomers; Tables 3-5), analysis of the crude reaction mixtures by GC and GC-MS showed that small or trace amounts of *Z* products **3** were also detected in some cases. We assumed that some of the starting material *Z* isomers **1** could convert to *Z*-products, whereas some other *Z* isomers **1** could be transformed to *E* products (these assumptions were confirmed in Scheme 2). However, most of the *Z* products were presumably lost in the workup procedure.

#### Scheme 2. Alkylation and Arylation of (Z)-Monofluoroalkene Z-1a



To gain further insights into the mechanism of these transformations, some control experiments were performed under the standard conditions. Cu-catalyzed tertiary alkylation of pure monofluoroalkene Z-1a with tBuMgCl only afforded the E isomer of 3aa and no Z isomer of 3aa was detected (Scheme 2, eq I). The result of this experiment indicated that the double bond was cleaved to form the more stable *E* isomer. However, Ni-catalyzed secondary and primary alkylation and arylation of pure monofluoroalkene Z-1a furnished a mixture of E and Z isomers of products (E:Z ratios were determined by GC-MS, and Z-3ac and Z-3ak could be isolated). The reaction proceeded only with partial retention of configuration of the C-C double bond, and substantial isomerization to the more thermodynamically stable E isomer was observed (Scheme 2, eqs II-IV). These observations implied that Z-1a might be consumed by two different pathways.

Up to now, two mechanisms have been proposed for the Pdor Ni-catalyzed cross-coupling of fluoroalkenes with organometallic reagents. The first mechanism, reported by Ogoshi et al., involved the oxidative addition of the alkene C–F bond, followed by cross-coupling with organometallic reagents.<sup>12c,13</sup> Another mechanism was proposed by Toste and Ichikawa et al., which involved the *syn* addition of the C–Pd to the double bond and subsequent  $\beta$ -fluoride elimination.<sup>14</sup> In our case, the Cu-catalyzed tertiary alkylation of monofluoroalkenes proceeded via addition of R<sub>2</sub>CuMgX to monofluoroalkenes and  $\beta$ elimination of fluoride ion, which is analogous to our previous report on the Cu-catalyzed tertiary alkylation of *gem*difluoroalkenes.<sup>8g</sup> However, the mechanism of the Ni-catalyzed secondary and primary alkylation and arylation of monofluoroalkenes is still unclear and needs to be elucidated.

On the basis of the above experimental results and related literatures, two plausible mechanisms of the present Nicatalyzed cross-coupling of primary and secondary alkylation and arylation of monofluoroalkenes are proposed in Schemes 3

Scheme 3. Proposed Mechanism of the Ni-Catalyzed Alkylation and Arylation of (E)-/(Z)-Monofluoroalkene (Path A)



Scheme 4. Proposed Mechanism of the Ni-Catalyzed Alkylation and Arylation of (E)-/(Z)-Monofluoroalkene (Path B)



and 4. The first is supposed to proceed through the initial activation of the C-F bond and subsequent transmetalation and reductive elimination (Scheme 3, path A). The second involves three elementary steps: transmetalation with RMgX, insertion of fluoroalkene into the Ni–C bond, and  $\beta$ -fluoride elimination (Scheme 4, path B). However, neither path A nor path B can be ruled out on the basis of our control experiments. The concurrent formation of *E* products in control experiments clearly demonstrated that the cleavage of the double bond was also involved in these reactions, leading to the formation of a mixture of E and Z products starting from pure Z-1a. Retaining mainly the Z configuration of 1a in these transformations (Scheme 2, eqs II-IV) suggested that the oxidative addition of the alkene C-F bond (path A) is highly preferred over a competing addition-elimination process (path B) under the Ni-catalyzed reaction conditions.

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In summary, we have reported a highly efficient coupling reaction of monofluoroalkenes with tertiary, secondary, and primary alkyl and aryl Grignard reagents in the presence of copper or nickel catalysts. The reactions proceeded smoothly at room temperature, providing (E)-alkene isomers in moderate to high yields. Preliminary mechanistic experiments suggest that the Ni-catalyzed coupling reaction of primary and secondary alkylation and arylation of monofluoroalkenes might proceed via two pathways: oxidative addition and addition-elimination. However, whether the reaction proceeds via an oxidative addition first or addition-elimination first remains unclear. The dominant mechanism might involve oxidative addition of the C-F bond to the nickel(0) complex. The mechanisms we proposed in this paper are different from the mechanisms suggested by Ogoshi and Toste. Our investigation provides a better understanding of the mechanism of the transition-metalcatalyzed coupling reaction of fluoroalkene with organometallic reagents.

#### EXPERIMENTAL SECTION

**General Information.** All reagents were analytical grade, obtained from commercial suppliers, and were used without further purification. THF was dried by standard methods prior to use and degassed. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a 400 spectrometer (400 MHz for <sup>1</sup>H NMR and 100 MHz for <sup>13</sup>C NMR) using TMS as internal standard. The <sup>19</sup>F NMR spectra were obtained using a 400 spectrometer (376 MHz). CDCl<sub>3</sub> was used as the NMR solvent in all cases. The GC and GC-MS measurements were calibrated by authentic standards. High-resolution mass spectra (HRMS) were acquired in the electron-impact mode (EI) using a TOF mass analyzer.

Substrates 1a-f,h-k,m were synthesized according to previously reported procedures.<sup>15</sup> Substrates 1g,l were synthesized according to methods in the literature.<sup>16</sup> Substrate Z-1a was prepared according to reported methods.<sup>6g</sup>

General Procedure for the Synthesis of Target Compounds. A 25 mL oven-dried round-bottom flask, equipped with a magnetic stirrer bar, was charged with the monofluoroalkene (1.0 mmol) and CuCN (22.5 mg, 0.25 mmol) or NiCl<sub>2</sub>(dppe) (21.2 mg, 0.04 mmol) in 2 mL of dry THF at room temperature under an argon atmosphere. To this mixture was added a solution of a Grignard reagent in THF (4.0 mmol) dropwise via a syringe. After it was stirred for 2 h, the reaction mixture was quenched with 2 mL of a saturated aqueous solution of NH<sub>4</sub>Cl and extracted with ethyl acetate ( $3 \times 10$  mL). The organic layer was separated and then dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated under vacuum. The crude product was purified by column chromatography on silica gel using *n*-hexane as eluent to afford pure target compounds.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00859.

Experimental details and <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>19</sup>F NMR, and HRMS spectral data for all products (PDF)

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The authors declare no competing financial interest.

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