

Iron-Catalyzed Cross-Coupling Reactions between Arylzinc Reagents and Alkyl Halides Bearing β -Fluorines

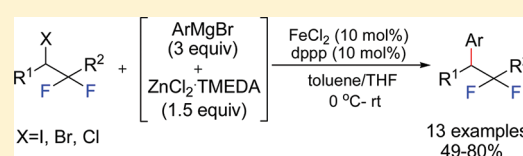
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S Supporting Information

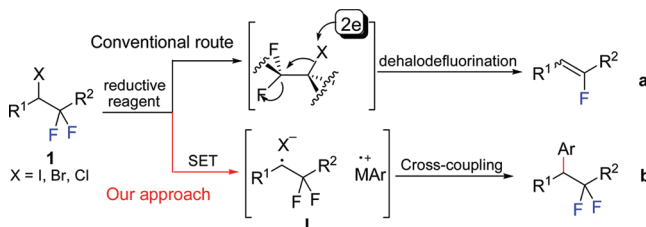
ABSTRACT: We report the first example of iron-catalyzed cross-coupling of α -halo- β,β -difluoroethylene-containing compounds with arylzinc reagents using TMEDA and dppp as coligands. The reaction affords a wide range of functional group tolerant *gem*-difluoromethylenated compounds in moderate to good yields. The facile dehalodefluorination of α -halo- β,β -difluoroethylene-containing compounds upon treatment of reductive metal reagents was mostly inhibited. Mechanistic studies indicated that the cross-coupling reaction could involve a single-electron-transfer process.



Transition-metal-catalyzed reactions are widely used for carbon–carbon bond formation. The past few years have seen huge advances in methodologies for transition-metal-catalyzed coupling of sp^3 -hybridized carbon electrophiles ($\text{C}(\text{sp}^3)\text{--X}$, $\text{X} = \text{I}, \text{Br}, \text{Cl}$) with arylmetal nucleophiles ($\text{C}(\text{sp}^2)\text{--M}$).¹ However, to the best of our knowledge, the cross-coupling of alkyl halides bearing β -fluorine(s) with arylmetal reagents has not been reported yet. We reasoned that two problems might make the coupling of alkyl halides bearing β -fluorine(s) challenging: (1) the vicinal halo fluorides mostly undergo dehalodefluorination to form fluoroalkenes upon treatment with reductive metal reagents (Scheme 1a);² (2) the strongly electron-withdrawing β -fluorinated group may stabilize the formed transition-metal complex, which undergoes reductive elimination slowly even under harsh conditions.³ In contrast to carbanions, it is well-known that carbon radicals are not subject to β -elimination of functional groups (e.g., OR, NR₂, F).⁴ In addition, an alkyl radical could also be inductively destabilized by β -fluorine substitutions, which result in a more active species.⁵ Therefore, we envisioned that compounds with vicinal halo fluorides moieties such as α -halo- β,β -difluoroethylene derivatives may readily react with reductive arylmetal reagents to give the corresponding coupling products, if the reaction occurs through a β -fluoroalkyl radical intermediate (Scheme 1b).

Recently, nickel,⁶ iron,^{7–10} cobalt,¹¹ and palladium¹² complexes have been used as efficient catalysts for the coupling of alkyl electrophiles with nucleophilic metal reagents. Among them, iron salts are particularly attractive catalysts, owing to their low cost, environmental friendliness, and lack of toxicity. From a mechanistic point of view, although the detailed mechanisms concerned with the iron-catalyzed coupling reactions were still unclear, extensive studies indicated that single-electron-transfer (SET) processes may be involved in these reactions.^{7e,8a,8b,8d,8e,8h,8f,13} With this notion in mind, we studied the iron-catalyzed coupling of α -halo- $\beta,$

Scheme 1. Reductive Dehalodefluorination (Conventional Route) and Our Approach to Cross-Coupling Reaction of Vicinal Halo Difluorides



β -difluoroethylene-containing compounds with arylzinc reagents. Herein, we report that a FeCl_2 /TMEDA/dppp combination is an efficient catalyst system for the coupling of α -halo- β,β -difluoroethylene-containing compounds with arylzinc reagents. The resulted *gem*-difluoromethylenated compounds have wide applications in pharmaceuticals, agrochemicals, and materials due to their special physical and chemical properties.¹⁴

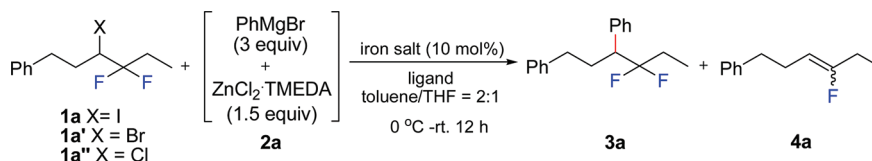
RESULTS AND DISCUSSION

To probe the hypothesis, we chose the reaction outlined in Table 1 to screen the catalyst system. Nakamura and co-workers demonstrated that FeCl_3 /*N,N,N',N'*-tetramethylethylenediamine (TMEDA)^{9a,d,e} and FeCl_2 /TMEDA^{9d} can be used effectively in the coupling of $\text{C}(\text{sp}^2)\text{--Zn}$ reagents with alkyl halides. Accordingly, the coupling of 3,3-difluoro-4-iodo-6-phenylhexane

Special Issue: Fluorine in Organometallic Chemistry

Received: July 4, 2011

Published: September 07, 2011

Table 1. Optimization of the Iron-Catalyzed Cross-Coupling of Phenylzinc Reagent with 3,3-Difluoro-4-halo-6-phenylhexane (**1**)^a

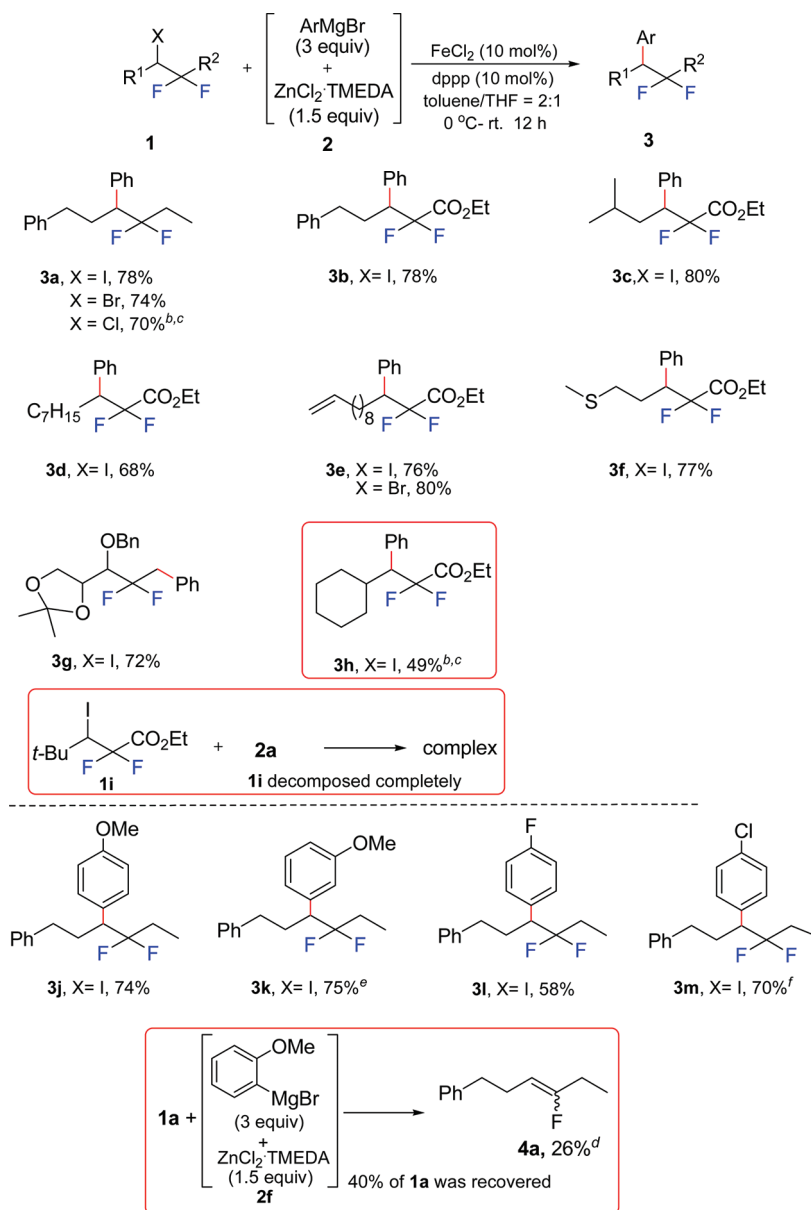
entry	RX	Fe salt	ligand ^b	conversion (%) ^c	yield 3a/4a (%) ^c
1	1a	FeCl ₃	TMEDA	100	68/12
2	1a	FeCl ₂	TMEDA	100	72/8
3	1a'	FeCl ₂	TMEDA	90	58/10
4	1a''	FeCl ₂	TMEDA	50	25 ^{d,e} /7
5 ^f	1a	FeCl ₂	dppp	60	18/6
6	1a	FeCl ₂	TMEDA/dppp	100	78/5
7	1a'	FeCl ₂	TMEDA/dppp	100	76/4
8	1a''	FeCl ₂	TMEDA/dppp	90	70 ^{d,e} /5
9	1a	FeCl ₂	TMEDA/dppe	100	50/5
10	1a	FeCl ₂	TMEDA/dppb	100	55/7
11	1a	FeCl ₂	TMEDA/dpppen	100	70/6
12	1a	FeCl ₃	TMEDA/dppp	100	73/8
13	1a		TMEDA/dppp	0	0 ^g
14 ^h	1a	FeCl ₂	TMEDA/dppp	100	0/8

^a Reactions were carried out on a 0.2 mmol scale. TMEDA = *N,N,N',N'*-tetramethylethylenediamine; Ph₂P(CH₂)_{*n*}PPh₂ = dppe (*n* = 2), dppp (*n* = 3), dppb (*n* = 4), dpppen (*n* = 5). ^b ZnCl₂·TMEDA¹⁶ was used as the source of TMEDA ligand. Diphosphine ligand (10 mol %) was used. ^c Yield and conversion relative to benzotrifluoride as an internal standard were determined by ¹⁹F NMR. ^d Phenylzinc reagent (3 equiv) was used. ^e The reaction time was 24 h. ^f ZnCl₂ instead of ZnCl₂·TMEDA was used. ^g **1a** was recovered completely. ^h TMEDA instead of ZnCl₂·TMEDA was used.

(**1a**) (for the preparation of compounds **1a–i**, **1a'**, and **1a''** see the Supporting Information) with phenylzinc reagent **2a** using FeCl₃/TMEDA or FeCl₂/TMEDA as catalyst proceeded smoothly to afford the desired product **3a** together with a small amount of the deiododefluorination product **4a**¹⁵ (entries 1 and 2). The FeCl₂/TMEDA catalysts were more effective than FeCl₃/TMEDA (entries 1 and 2), in terms of both conversion to the desired product and relative amounts of side products. However, when the less reactive β,β-difluorinated bromide **1a'** and chloride **1a''** were employed in the coupling with **2a** using FeCl₂/TMEDA as catalyst, the yields and selectivities with respect to side product **4a** were much lower than those obtained with **1a** (entries 3 and 4). Very recently, Nakamura's group^{9c} and Bedford's group^{9b} reported independently that iron diphosphine catalyst systems, such as FeCl₂/1,3-bis(diphenylphosphino)propane (dppp) and FeCl₂/1,2-bis(diphenylphosphino)benzene, showed excellent activity in the cross-coupling reactions of arylzinc reagents with alkyl halides, which had not been achieved by using iron TMEDA catalysts. Unfortunately, when we attempted the coupling of the relatively reactive **1a** with **2a** using FeCl₂/dppp catalysts, the yield and selectivity obtained were very poor (entry 5). Since both of the iron/TMEDA and iron/diphosphine catalysts could be utilized effectively in the coupling of arylzinc reagents with nonfluorinated alkyl halides, we were interested to see whether the combination of these two kinds of iron-based catalysts (iron/TMEDA/diphosphine) could be used to fabricate the desired α-aryl-β,β-difluoroethylene-containing compounds. It was found that **1a** coupled with **2a** smoothly in the presence of the catalyst combination FeCl₂/TMEDA/dppp to give **3a** in an improved yield and with a better selectivity than those obtained with FeCl₂/TMEDA as catalysts (entry 6). Much to our delight, when the catalyst combination FeCl₂/TMEDA/dppp was

applied to the coupling of the less reactive β,β-difluorinated bromide **1a'** with **2a**, the desired product **3a** was obtained with much better yield and selectivity (entry 7). The β,β-difluorinated chloride **1a''** also took part in the coupling reaction using FeCl₂/TMEDA/dppp with a slightly lower reaction rate (entry 8), and the yield and selectivity of product **3a** improved significantly in comparison with those observed using FeCl₂/TMEDA. It seemed that the diphosphine ligands enhanced the catalytic activity of the iron/TMEDA species in the coupling. Thus, a series of diphosphine ligands were then examined. As can be seen, increasing the chain length of the alkyl spacer in the biphosphines Ph₂P(CH₂)_{*n*}PPh₂ (*n* = 2–5) led to a general increase in the yield of the desired coupled product (entry 6, entries 9–11), although dppp (*n* = 3) showed activity higher than anticipated from the trend. A similar activity trend of the biphosphines was observed by Bedford et al. in the iron-catalyzed coupling of alkyl halides with aryl Grignard reagents.^{8h} The coupling reaction of **1a** with **2a** using FeCl₃/TMEDA/dppp as catalyst also afforded the desired product **3a** in yield and selectivity slightly lower than those with FeCl₂/TMEDA/dppp but higher than those with FeCl₃/TMEDA (entry 12). No coupled product **3a** was detected when the iron catalyst was omitted, and the starting material **1a** remained unchanged (entry 13). The coupling of **1a** with phenylmagnesium bromide in the absence of ZnCl₂ failed to give the coupled product **3a** (entry 14). This result showed that transmetalation from magnesium to zinc was essential for the coupling reaction.

With the optimized conditions in hand (Table 1, entry 6), the scopes of α-halo-β,β-difluoroethylene-containing electrophiles and arylzinc reagents were then examined, as depicted in Table 2. The secondary β,β-difluorinated iodide **1a**, bromide **1a'**, and chloride **1a''** coupled with phenylzinc reagent **2a** smoothly to

Table 2. Iron-Catalyzed Cross-Coupling of Arylzinc Reagents with α -Halo- β,β -difluoroethylene-Containing Compounds^a

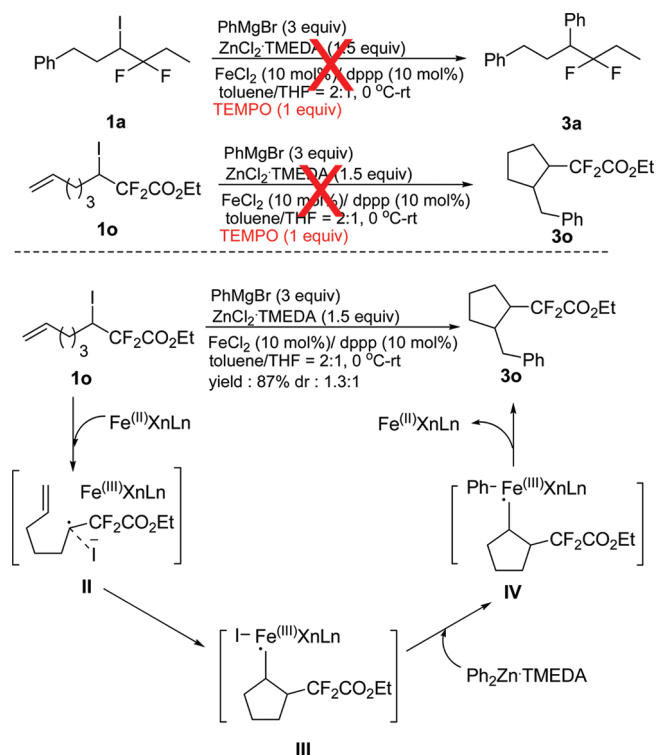
^a Reactions were performed using **1** (0.2 mmol), ArMgBr (1 M in THF, 3.0 equiv), $\text{ZnCl}_2 \cdot \text{TMEDA}$ (1.5 equiv), FeCl_2 (10 mol %), and dppp (10 mol %) in toluene/THF (1.8 mL). Isolated yield. ^b Phenylzinc reagent (3 equiv) was used. The reaction time was 24 h. ^c The conversion of **1a** and **1h** was 90%. ^d Yield relative to benzotrifluoride as an internal standard was determined by ^{19}F NMR. ^e 3-MeO-PhMgBr (1 M in THF/toluene) was used. ^f 4-Cl-PhMgBr (0.8 M in diethyl ether, 6 equiv) was used, and an additional volume of THF (0.6 mL) was added into the reaction mixture.

afford the corresponding product **3a** in good yields. Functional groups such as an ester (**3b**), terminal alkene (**3e**), thiomethyl (**3f**), and acetal (**3g**) were all compatible with the reaction conditions. Of particular note is that thiomethyl (**3f**), which is often regarded to poison the transition-metal catalysts,¹⁷ had little influence on the course of the reaction and a satisfactory 77% yield of **3f** was obtained. In addition, a primary alkyl iodide (**1g**) was also found to be a suitable substrate for the cross-coupling. Functionalized aryl zinc reagents with *p*- and *m*-methoxy groups and *p*-fluoro and *p*-chloro groups were competent coupling partners to give the desired products **3j**–**3m**, respectively, in moderate to good yields. Increasing the steric bulk of the α -halo- β,β -difluoride is deleterious to the reaction. For example,

reaction of ethyl 2,2-difluoro-3-iodo-4-cyclohexylbutanoate (**1h**) gave slightly reduced conversion to the coupled product **3h**. No cross-coupling product and the deiododefluorination side product were observed when the more hindered ethyl 2,2-difluoro-3-iodo-4,4-dimethylpentanoate (**1i**) was used. The starting material **1i** decomposed completely. Similarly, the reaction of the *o*-methoxyphenylzinc reagent **2f** with **1a** failed to give any of the coupled product; the deiododefluorination side product **4a** was formed in 26% yield. Compound **1a** decomposed partially and recovered in 40% yield. Compounds **1a**, **i** were stable to $\text{FeCl}_2/\text{TMEDA}/\text{dppp}$ in the absence of arylzinc reagents.

To gain some understanding of the mechanism, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 1 equiv), a typical radical

Scheme 2



scavenger, was added to the reaction system of **1a** and **2a**. The reaction was inhibited completely (Scheme 2). Furthermore, the δ,ϵ -unsaturated secondary alkyl iodide **1o** was designed and synthesized as a radical clock. Subjection of **1o** to the standard coupling conditions with **2a** afforded the 5-exo-trig cyclization product **3o** in 87% yield (dr = 1.3:1¹⁸); however, the cyclization was completely inhibited by TEMPO (Scheme 2), which suggested that a SET process occurred. A highly simplified representation of a possible radical-based coupling mechanism is shown in Scheme 2. The transfer of a single electron from the active iron species to the β,β -difluorinated iodide **1o** generated the radical anion intermediate **II** which might not be free but rather might be associated with the iron center.^{8d} Radical anion intermediate **II** underwent cyclization to the radical–iron complex **III**. Transmetalation with the in situ formed phenylzinc–TMEDA generated the radical–iron–aryl complex **IV**, which then underwent one-electron reductive elimination to give the product and active iron species.^{7e,8a,8b,8d,8e,8h,8f,13}

CONCLUSIONS

In summary, we have demonstrated an effective catalyst system composed of FeCl₂, TMEDA, and dppp for the cross-coupling of arylzinc reagents with α -halo- β,β -difluoroethylene-containing compounds. To the best of our knowledge, this is the first example of iron-catalyzed arylation of vicinal halo difluorides. The facile dehalodefluorination of vicinal halo difluorides upon treatment of reductive metal reagents was mostly inhibited. The cross-coupling reaction could involve a radical pathway.

EXPERIMENTAL SECTION

General Procedure for the Iron-Catalyzed Cross-Coupling Reaction of α -Halo- β,β -difluoroethylene-Containing Compounds with Arylzinc Reagents. In a dry reaction vessel, a mixture

of PhMgBr (0.6 mL of a 1.0 M THF solution, 0.6 mmol) and ZnCl₂·TMEDA (75.8 mg, 0.3 mmol) was stirred for 1 h. Then the resulting suspension was added to a mixture of (4,4-difluoro-3-iodohexyl)benzene (**1a**; 65.0 mg, 0.2 mmol), FeCl₂ (2.8 mg, 10 mol %), and 1,3-bis-(diphenylphosphino)propane (8.8 mg, 10 mol %) in toluene (1.2 mL) at 0 °C in one port. The reaction mixture was stirred at that temperature for 15 min after completion of the addition of phenylzinc reagent and stirred at room temperature for 12 h. A saturated aqueous solution of NH₄Cl (1.0 mL) was added to quench the reaction. The organic layer was separated, and the aqueous phase was extracted with ether (2 × 2 mL). The combined organic layers were concentrated in vacuo, and the residue was purified by column chromatography to give (4,4-difluorohexane-1,3-diyl) dibenzene (**3a**; 42.8 mg, 78% yield).

ASSOCIATED CONTENT

S Supporting Information. Text and figures giving full experimental details and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ACKNOWLEDGMENT

We thank Professor Qilong Shen and Professor Xingang Zhang of the Shanghai Institute of Organic Chemistry for insightful discussions. The National Natural Science Foundation of China (Nos. 21072018, 20632008) is greatly acknowledged for funding of this work.

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