

Carbon–carbon bond-forming reactions using alkyl fluorides*

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Abstract: This account summarizes our recent results on C–C bond formation reactions using alkyl fluorides mostly focusing on the transition-metal-catalyzed reactions. These reactions proceed efficiently under mild conditions by the combined use of Grignard reagents and transition-metal catalysts, such as Ni, Cu, and Zr. It is proposed that ate complex intermediates formed by the reaction of these transition metals with Grignard reagents play important roles as the active catalytic species. Organoaluminum reagents react directly with alkyl fluorides in nonpolar solvents at room temperature to form C–C bonds. These studies demonstrate the practical usefulness of alkyl fluorides in C–C bond formation reactions and provide a promising method for the construction of carbon frameworks employing alkyl fluorides. The scope and limitations, as well as reaction pathways, are discussed.

Keywords: bond formation; carbon–carbon bond; alkyl fluorides; transition-metal catalysts; organoaluminum.

INTRODUCTION

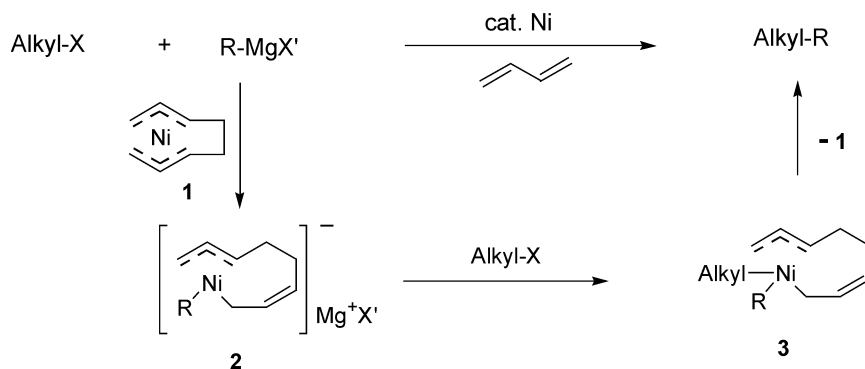
Recently, fluorine has become a key element in the fields of materials science and chemical biology due to the unique reactivities and properties arising from its high electronegativity. In terms of the synthetic application of organofluorides, however, fluorine chemistry is much less explored than those of the other halogens because of their strong C–F bonds. Therefore, developing reactions that replace fluorine atoms in organic molecules with other atoms or functional groups is a challenging theme in organic chemistry. During the past decade, it has become clear that C–F bonds can be cleaved by some typical or transition-metal reagents under mild conditions [1]. As for the transition-metal-mediated transformations involving cleavage of (sp²)C–F bonds, several reactions using fluoroarenes have already been developed, employing catalytic [2] or stoichiometric [3] amounts of metal complexes. On the other hand, examples of aliphatic (sp³)C–F bond fission by use of transition-metal complexes are very rare [4–6]. With these backgrounds, our attention was focused on developing new reactions of non-activated alkyl fluorides using transition- and/or non-transition-metal reagents. This article describes our recent results of C–C bond formation reactions using alkyl fluorides.

*Paper based on a presentation at the 14th International Symposium on Organometallic Chemistry Directed Towards Organic Synthesis (OMCOS-14), 2–6 August 2007, Nara, Japan. Other presentations are published in this issue, pp. 807–1194.

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NI-CATALYZED CROSS-COUPLING REACTION OF ALKYL FLUORIDES WITH GRIGNARD REAGENTS

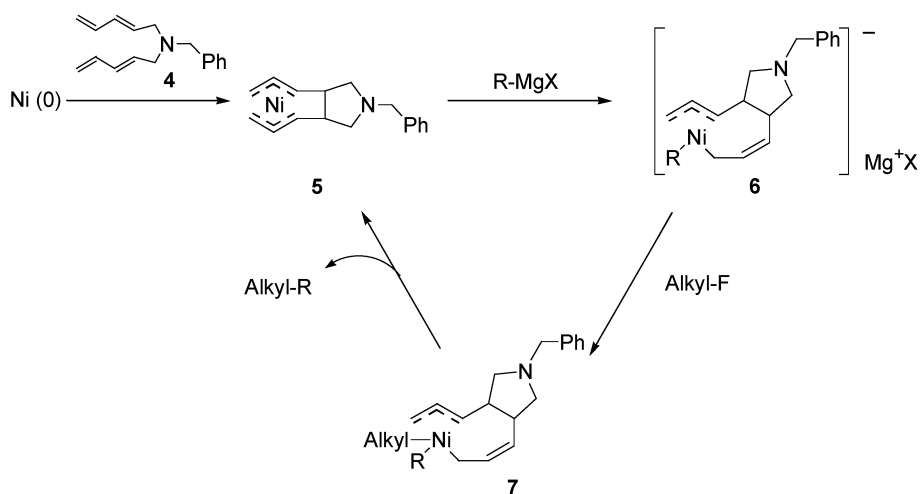
In 2002, we reported that Ni catalyzes cross-coupling reactions of alkyl chlorides, bromides, and tosylates with Grignard reagents in the presence of 1,3-butadienes under mild conditions (Scheme 1) [7]. We proposed a new catalytic pathway via bis- π -allyl nickel complex **1** and its ate complex **2**. This pathway is in large contrast to conventional cross-coupling reactions using phosphine ligands where low valent metal catalysts react first with organic halides and then with organometallic reagents leading to reductive elimination [8].



Scheme 1 A plausible reaction pathway.

During the course of this study, we have recently developed Ni-catalyzed cross-coupling reaction using non-activated alkyl fluorides [9]. For example, a reaction of *n*-octyl fluoride (2 mmol) with *n*-propylmagnesium bromide (0.93 M, 4.3 mL, 2.0 equiv) in the presence of 1,3-butadiene and Ni catalysts (3 mol %) at 25 °C for 6 h gave undecane. As expected, octyl fluoride did not react at all without 1,3-butadiene, whereas addition of 0.1 molar amount of 1,3-butadiene based on octyl fluoride enabled cross-coupling to proceed, giving a 9 % yield of undecane accompanied by a small amount of octane (entries 1–4). On increasing the amount of 1,3-butadiene up to 1 molar amount, the yield of undecane improved to 64 % (entry 6). When 1 molar amount of isoprene was employed instead of 1,3-butadiene, undecane was obtained in 47 % yield (entry 7). However, 2,3-dimethyl-1,3-butadiene and 1,5-cyclooctadiene did not promote this coupling reaction (entries 8 and 9). Ni complexes bearing phosphine ligands, such as $(\text{PPh}_3)_2\text{NiCl}_2$ and $(\text{dppp})\text{NiCl}_2$, afforded undecane in 8 and 57 % yield, respectively, in the presence of 1,3-butadiene (entries 10 and 11). Further increase of 1,3-butadiene up to 8 mmol did not lead to significant improvement of the yield (entry 14). It is probably because under high concentration of 1,3-butadiene, Ni^0 reacts with more than 2 molecules of 1,3-butadiene resulting in the low concentration of the bis- π -allyl nickel complex **1** [10]. We could solve this problem by employing tetraene **4** that constructs a bis- π -allyl Ni structure with the Ni^0 species exclusively [11]. When 0.01 molar amount of NiCl_2 and 0.15 molar amount of the tetraene **4** as an additive was employed, undecane was obtained in 93 % yield with complete suppression of formation of octane and octenes (entry 15) [12].

A plausible reaction pathway is shown in Scheme 2 for the case of tetraene **4** as an additive. Bis- π -allylnickel complex **5** is constructed by the oxidative cycloaddition of Ni^0 with two butadiene moieties of tetraene **4**. Grignard reagent attacks **5** to generate nickelate complex **6**, which then reacts with alkyl fluorides to give **7**. Subsequent reductive elimination affords the coupling product along with **5** to complete the catalytic cycle. Selective and efficient formation of **5** from Ni^0 and **4** in comparison to the case of 1,3-butadiene would facilitate the generation of ate complex **6**. Cationic magnesium of the nick-



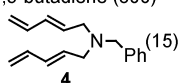
Scheme 2 A plausible reaction pathway for the case of tetraene.

elate complex **6** would activate C–F bonds by the eminent Mg–F interaction in this catalytic system. In order to reveal the thermodynamic properties of this coupling reaction, theoretical calculations were performed using the G2 method of the Gaussian 98 program. Calculated bond energies of X–MgCl are 142, 112, 101 kcal/mol, and those of X–CH₃ are 112, 85, 74 kcal/mol for X = F, Cl, Br, respectively. Energy differences between these two bonds for F, Cl, Br are similar (30, 28, 27 kcal/mol, respectively), indicating that the formation of a strong F–MgCl bond can compensate for destabilization arising from C–F bond cleavage and reaction of fluorides are not thermodynamically unfavorable in comparison to those of chlorides and bromides.

Although *n*-alkyl Grignard reagents afforded the cross-coupling products in high yields, this Ni-catalyzed reaction system cannot be applied to branched alkyl Grignard reagents, such as *s*- and *t*-butyl Grignard reagents. For example, reactions of *n*-OctF with *i*-PrMgBr and *t*-BuMgCl under the identical conditions as Table 1 in entry 6 afforded the corresponding coupling products in 3 and 6 % yield, respectively. It should be noted that cross-coupling reaction of alkyl fluoride with these branched alkyl Grignard reagents proceeds efficiently by the use of Cu as catalysts in the presence of 1,3-butadiene.

Representative results of Cu-catalyzed cross-coupling reaction of *n*-OctF with some Grignard reagents are shown in Table 2. It was found that 1.3 equiv of RMgX and 10 mol % of 1,3-butadiene (based on the halide, 0.07 M in THF) is sufficient to promote the cross-coupling reaction efficiently (entry 1). Isoprene is much less effective under these conditions (entry 2). Undecane was obtained in 20 % yield even in the absence of 1,3-butadiene (entry 3). The coupling reaction of *s*- and *t*-butyl Grignard reagents was also facilitated by 1,3-butadiene (entries 5 and 7); however, phenyl Grignard reagent gave poor yields of the cross-coupling products under the same conditions (entry 9). 1-Phenyl-1-propyne shows by far the highest activity for all of these Grignard reagents under THF reflux conditions (entries 4, 6, 8, 10) [13].

Table 1 Cross-coupling reaction of *n*-OctF with *n*-PrMgBr.^a

entry	catalyst	additive (mol %)	product yield (%) ^b		
			undecane	octane	octenes ^c
1	NiCl ₂	–	0	0	0
2	(PPh ₃) ₂ NiCl ₂	–	0	0	0
3	(dppp)NiCl ₂	–	0	0	0
4	NiCl ₂	1,3-butadiene (10)	9	1	0
5	NiCl ₂	1,3-butadiene (50)	44	2	1
6	NiCl ₂	1,3-butadiene (100)	64	4	2
7	NiCl ₂	isoprene (100)	47	0	0
8	NiCl ₂	2,3-dimethyl-1,3-butadiene (100)	0	0	0
9	NiCl ₂	1,5-cyclooctadiene (100)	0	0	0
10	(PPh ₃) ₂ NiCl ₂	1,3-butadiene (100)	8	3	2
11	(dppp)NiCl ₂	1,3-butadiene (100)	57	3	2
12	NiCl ₂	1,3-butadiene (200)	67	3	1
13	NiCl ₂	1,3-butadiene (400)	64	3	2
14	NiCl ₂	1,3-butadiene (800)	59	5	1
15	NiCl ₂	 (15)	93	0	0

^aConditions: *n*-OctF (2 mmol), 3 mol % of catalyst, additive (mol % based on the substrate), and *n*-PrMgBr (2 equiv, 1 M), in THF, 25 °C, 3 h. ^bDetermined by GC. ^cA mixture of 1-octene and 2-octenes.

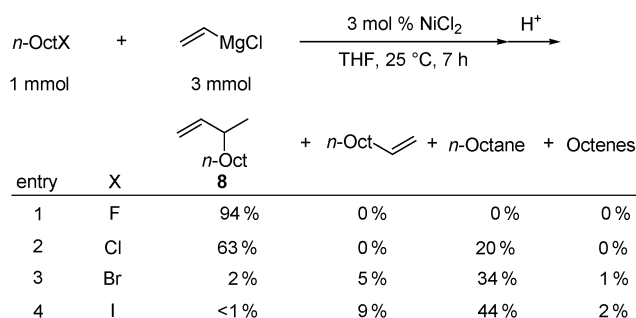
Table 2 Cu-catalyzed cross-coupling reaction of *n*-OctF with Grignard reagents.

entry	<i>n</i> -OctF 2 mmol	+ RMgX 2.6 mmol	CuCl ₂ (3 mol %) additive, THF, 6 h		<i>n</i> -Oct-R
			additive (0.2 mmol)	temp. (°C)	
1	<i>n</i> -PrMgBr		1,3-butadiene	25	94
2			isoprene	25	34
3			none	25	20
4	<i>i</i> -PrMgBr		1-phenyl-1-propyne	67 (reflux)	>98%
5			1,3-butadiene	25	81
6			1-phenyl-1-propyne	67 (reflux)	>98%
7	<i>t</i> -BuMgCl		1,3-butadiene	25	>98%
8			1-phenyl-1-propyne	67 (reflux)	>98%
9	PhMgBr		1,3-butadiene	25	38
10			1-phenyl-1-propyne	67 (reflux)	>98%

NI-CATALYZED ALKYLATIVE DIMERIZATION OF VINYL GRIGNARD REAGENTS USING ALKYL FLUORIDES

When we carried out similar reactions using vinyl Grignard reagents, we found that highly regioselective three-component coupling reactions of 2 molecules of vinyl Grignard reagents with alkyl fluorides can take place by the use of a Ni catalyst [14]. This reaction proceeds efficiently between primary or secondary alkyl fluorides and vinyl Grignard reagents under mild conditions affording a 2-alkyl-3-butenyl Grignard reagent.

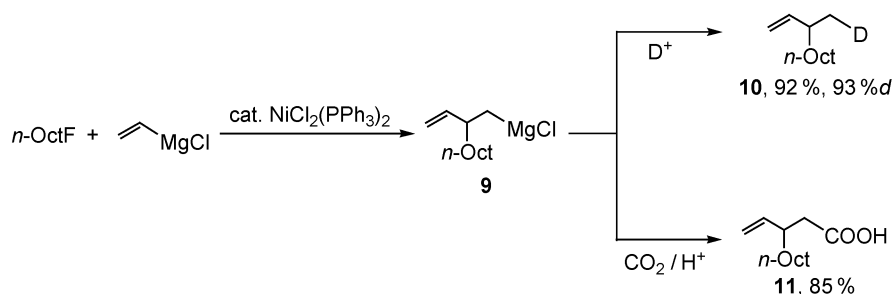
When a reaction of octyl fluoride (1 mmol) with vinylmagnesium chloride (3 mmol) was conducted in the presence of NiCl₂ (0.03 mmol) in THF at 25 °C for 7 h, 3-methyl-1-undecene (**8**) was obtained after protonolysis in 94 % yield as the sole product (Scheme 3). An interesting feature of this reaction is that alkyl fluorides react as the most suitable alkylating reagent in comparison with the corresponding chlorides, bromides, and iodides which undergo reduction, elimination, or cross-cou-



Scheme 3 Ni-catalyzed coupling reaction of alkyl halides with vinyl Grignard reagents.

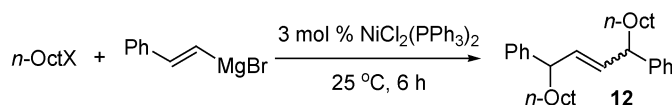
pling with the vinyl Grignard reagent concomitantly or predominantly. This reaction is a rare example of a catalytic reaction that demonstrates the superiority of alkyl fluorides as alkylating reagents over bromides and iodides as well as chlorides.

The deuterated product **10** and carboxylic acid **11** were obtained in good yields when the reaction mixtures were treated with D_2O and CO_2 , respectively (Scheme 4). These results imply that the butenyl Grignard reagent **9** is formed in the present reaction medium.



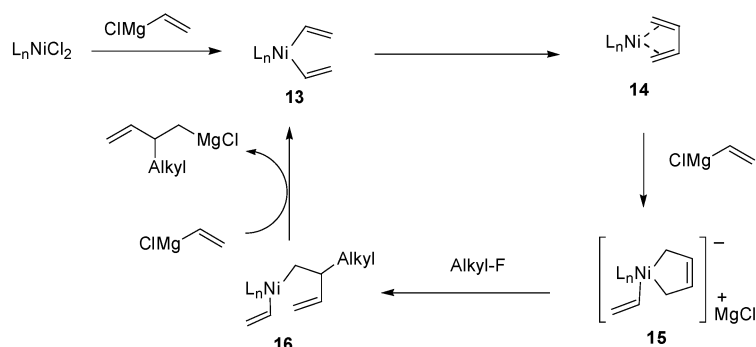
Scheme 4 Formation of 3-butenyl Grignard reagent **9**.

No reaction took place with either MeCH=CHMgBr or $\text{CH}_2=\text{CMeMgBr}$ under identical conditions of Scheme 3 and alkyl fluorides were recovered. It should be noted that PhCH=CHMgBr gave double alkylative vinyl coupling product **12** in 69 % yield as the sole product ($E/Z = 62/38$) (Scheme 5). In comparison to alkyl fluorides, reactions using alkyl chloride (40 %) and bromide (18 %) were both less efficient.



Scheme 5 Ni-catalyzed coupling reaction of alkyl halides with PhCH=CHMgBr .

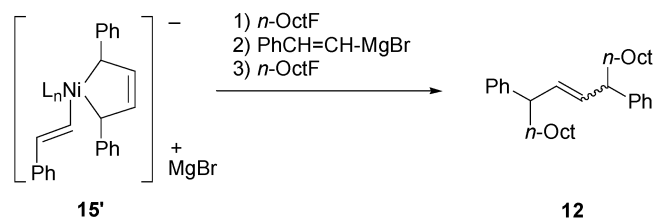
A plausible reaction pathway for the present reaction is outlined in Scheme 6. Nickel dichlorides react with 2 molar amounts of vinyl Grignard reagents to generate the divinylnickel complex **13**, which readily forms the nickel-butadiene complex **14** via reductive coupling [15]. **14** reacts again with the vinyl Grignard reagent to afford the nickelate complex **15** [16]. Cationic magnesium of this nickelate complex **15** would also act as a Lewis acid and promote C–F bond cleavage. Direct reaction of alkyl



Scheme 6 A plausible reaction pathway for Ni-catalyzed coupling of vinyl Grignard reagents with alkyl fluorides.

fluorides with **15** at a γ -vinylic carbon leading to **16** followed by transmetalation with the vinyl Grignard reagent regenerates **13**. Although alkyl bromides and iodides as well as chlorides may react with **14**, in either concerted oxidative addition or electron-transfer mechanism, leading to the formation of reduction or cross-coupling products, the corresponding alkyl fluorides are inert for such a mechanism and this is a key to accomplishing this clean reaction.

When $\text{PhCH}=\text{CHMgBr}$ is used, the reaction follows a similar pathway via metalacyclopentene intermediates **15'**, which react directly, or after cleavage of benzyl C–Ni bond, with 2 equiv of alkyl fluorides at both benzylic positions to form **12** (Scheme 7).

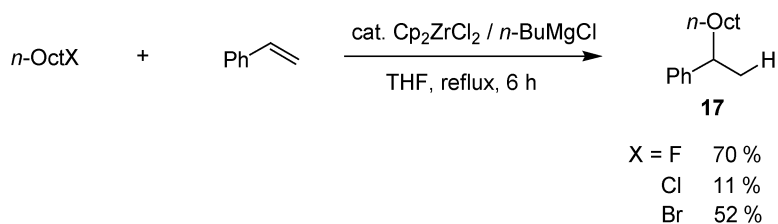


Scheme 7 Intermediary of metalacyclopentene.

Zr-CATALYZED HYDROALKYLATION OF STYLENES USING ALKYL FLUORIDES

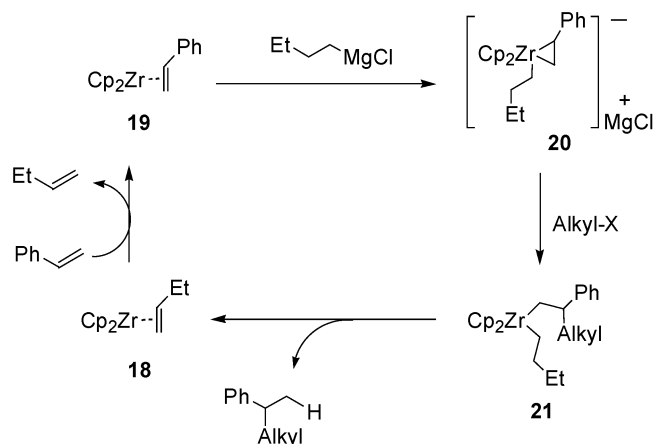
We reported that alkenes underwent silylation by reaction with chlorosilanes employing the $\text{Cp}_2\text{ZrCl}_2/n\text{-BuMgCl}$ system to give alkenyl and/or allylsilanes [17]. This reaction proceeds via zirconocene-olefin ate complexes with the olefinic carbon acting as a nucleophilic center toward chlorosilanes. When alkyl halides are used as electrophiles instead of chlorosilanes, regioselective hydroalkylation of styrenes took place [18].

For example, octyl fluoride (2 mmol) reacted with styrene (3 mmol) in the presence of a catalytic amount of zirconocene dichloride (0.05 molar amount) under THF reflux conditions to give 2-decylbenzene (**17**) in 70 % yield (Scheme 8). Interestingly, reactions using alkyl chloride (11 %) and bromide (52 %) were less efficient.



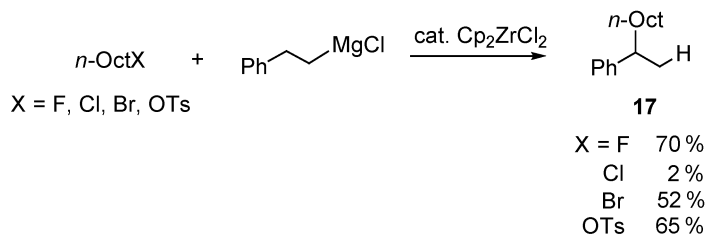
Scheme 8 Zr-catalyzed hydroalkylation of styrenes using alkyl halides.

A plausible catalytic cycle is shown in Scheme 9. Zirconocene dichloride reacts with 2 molar amounts of *n*-BuMgCl to generate dibutylzirconocene, which readily decomposes to the Cp₂Zr(butene) complex **18** [19]. The subsequent alkene exchange reaction between 1-butene and styrene gives the zirconocene-styrene complex **19**. The zirconate complex **20**, formed by the reaction of **19** with *n*-BuMgCl [20], reacts with alkyl electrophiles at the benzylic carbon leading to the dialkyl zirconocene complex **21**. The successive β-hydrogen abstraction proceeds at butyl group to give the corresponding products along with the regeneration of **18** [21].



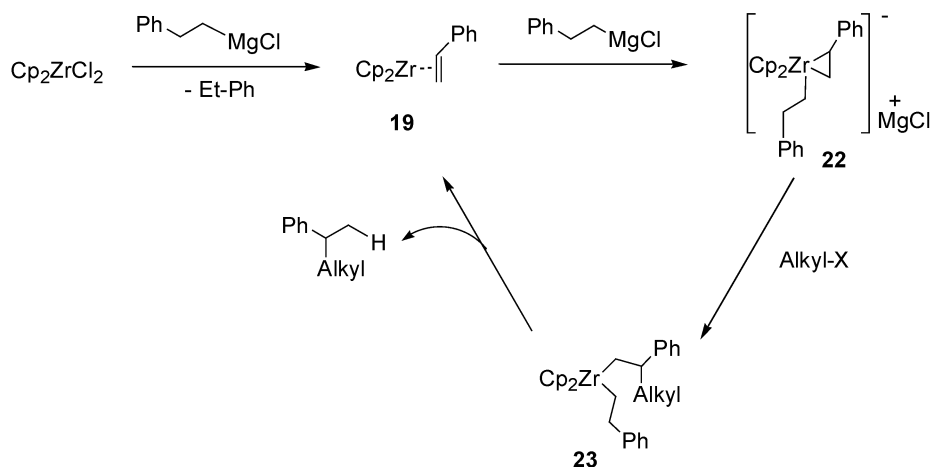
Scheme 9 A plausible reaction pathway of Zr-catalyzed alkylation of styrenes.

According to this reaction mechanism, when the β-phenethyl Grignard reagent is used instead of *n*-BuMgCl, styrene should be formed in situ. As expected, the same products were obtained from β-phenethyl Grignard reagents and alkyl halides by the use of the zirconocene catalyst [22]. The present reaction also proceeds more efficiently with alkyl fluorides as alkylating reagents than with the corresponding chlorides, bromides, or tosylates (Scheme 10).



Scheme 10 Zr-catalyzed coupling reaction of alkyl halides with β-phenethyl Grignard reagent.

A plausible reaction pathway is shown in Scheme 11. The reaction of Cp_2ZrCl_2 with 3 equiv of β -phenethyl Grignard reagent affords a zirconate complex **22** via bis(β -phenethyl)zirconocene complex and styrene-zirconocene complex **19**. The intermediates **19** react with alkylating reagents at the benzylic position, giving rise to dialkylzirconocene complex **23**. The successive intramolecular β -hydrogen shift at the less-hindered benzylic position regenerates **19**.

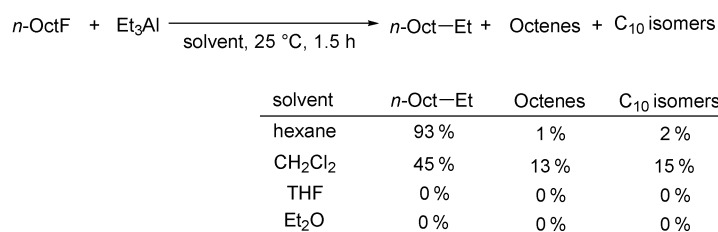


Scheme 11 A plausible reaction pathway of Zr-catalyzed coupling reaction of β -phenethyl Grignard reagents with alkyl halides.

C–C BOND FORMATION OF PRIMARY ALKYL FLUORIDES WITH $\text{R}_2\text{Al-R}'$

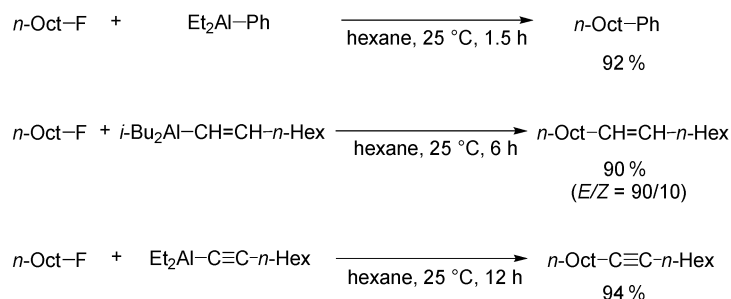
It is known that $(\text{sp}^3)\text{C-F}$ bonds can be cleaved by organoaluminum reagents or aluminum salts in polar solvent, but the substrates employed are limited to tertiary alkyl fluorides or activated ones [23]. The use of primary alkyl fluorides usually gives unsatisfactory results due mainly to proton elimination, hydride shift, and skeleton rearrangement [24] from *primary*-alkyl cation intermediates in the $\text{S}_{\text{N}}1$ mechanism. Recently, construction of the $(\text{sp}^3)\text{C}-(\text{sp}^3)\text{C}$ linkage with cleavage of non-activated $(\text{sp}^3)\text{C-F}$ bonds has been achieved by the use of tertiary alkyl and allyl fluorides along with organoaluminums [25] or $\text{BF}_3 \cdot \text{OEt}_2$ [26] as mediators or catalysts. In these reactions, C–F bond cleavage proceeds in $\text{S}_{\text{N}}1$ fashion, and primary and secondary alkyl fluorides and corresponding chlorides showed lower reactivity. During the course of our study on the synthetic application of alkyl fluorides, we found that C–F bonds of non-activated alkyl fluorides can be converted efficiently into C–C bond by using organoaluminum reagents ($\text{R}_2\text{Al-R}'$) in hexane under mild conditions [27].

For example, when a reaction of *n*-octyl fluoride (1.0 mmol) with triethylaluminum (1.2 equiv, 1 M in hexane) was performed at 25 °C for 1.5 h, *n*-decane was obtained in 93 % yield. In this reaction, only a trace amount of octenes (1 %) and C_{10} isomers (2 %) were formed as the by-products probably via proton elimination and 1,2-hydride shift of the 1-octyl carbenium cation (Scheme 12). When dichloromethane was used as solvent instead of hexane, a mixture of *n*-decane, octanes, and C_{10} isomers was obtained in 45, 13, and 15 % yields, respectively, under similar conditions, but no reaction took place in THF or diethyl ether.



Scheme 12 Reaction of alkyl fluoride with Et₃Al.

When diethyl(phenyl)aluminum was treated similarly in hexane, the corresponding octylbenzene was obtained in 92 % yield. Reaction of *n*-octyl fluoride with alkenyl(diisopropyl)aluminum, prepared in situ from *i*-Bu₂AlH and 1-octyne, in hexane at 25 °C for 6 h afforded the corresponding coupling product in 90 % yield with an *E/Z* ratio of 90/10. When diethyl(1-octynyl)aluminum was used, 7-hexadecyne was obtained in 94 % yield. These results indicate the selective transfer of the alkenyl or alkynyl group on the aluminum center over alkyl groups (Scheme 13).



Scheme 13 Reaction of alkyl fluoride with R₂Al-R'.

In conclusion, novel catalytic systems for C–C bond formation using alkyl fluorides have been developed by the combined use of transition metals (Ni, Cu, or Zr) and Grignard reagents. The present study provides unique examples that demonstrate superiority of alkyl fluorides as carbon sources over the corresponding bromides and iodides as well as chlorides. These reactions proceed under mild conditions via transition-metal ate complex intermediates and provide prototypes for the use of alkyl fluorides in transition-metal-catalyzed reactions. We have also found that organoaluminum reagents react with primary alkyl fluorides in hexane under mild conditions.

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