

C–F Bond Activation

Double C–F Bond Activation through β -Fluorine Elimination: Nickel-Mediated [3+2] Cycloaddition of 2-Trifluoromethyl-1-alkenes with Alkynes**

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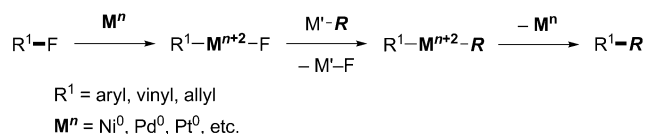
Abstract: The nickel-mediated [3+2] cycloaddition of 2-trifluoromethyl-1-alkenes with alkynes afforded fluorine-containing multi-substituted cyclopentadienes in a regioselective manner. This reaction involves the consecutive two C–F bond cleavage of a trifluoromethyl or a pentafluoroethyl group through β -fluorine elimination.

Transition-metal-mediated C–F bond activation has occupied a significant research area, establishing new synthetic methodologies.^[1–3] In particular, cross-coupling reactions by C–F bond cleavage of aryl, vinyl, and allyl fluorides has been intensively studied in this decade.^[4–6] In most cases, cleavage of a C–F bond was achieved by its oxidative addition to low-valent transition metal complexes (Scheme 1A). However,

oxidative addition of a C–F bond is not necessarily possible because of its high bond energy. In contrast, C–F bond cleavage by β -fluorine elimination has been considered a much more reasonable process compared to oxidative addition because transition-metal-mediated β -heteroatom elimination typically proceeds under milder conditions (Scheme 1B).^[7,8] Furthermore, β -fluorine elimination is sometimes even more preferable than β -hydrogen elimination as an elementary step from complexes with both fluorine and hydrogen atoms on the β -carbon to the metal center.^[7–9] Although β -fluorine elimination is potentially advantageous, the literature contains only a few reports on its practical application to transition-metal-mediated reactions. For example, allylic C–F bond activation of 2-trifluoromethyl-1-alkenes proceeded through sequential imino- or carbometalation and β -fluorine elimination to give 1,1-difluoro-1-alkenes (Scheme 1Ba).^[7f,g] In a similar manner, vinylic C–F bond activation of 1,1-difluoro-1-alkenes by an imino- or carbometalation– β -fluorine elimination process provided monofluorinated alkenes (Scheme 1Bb).^[7c,d]

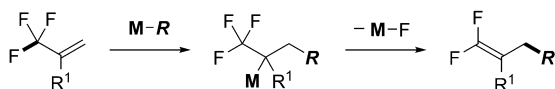
To take complete advantage of these processes, we attempted the double C–F bond activation of 2-trifluoromethyl-1-alkenes through the sequential use of β -fluorine elimination (Scheme 2). Because electron-deficient alkenes

A) Oxidative addition

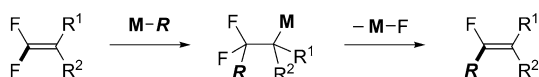


B) β -Fluorine elimination

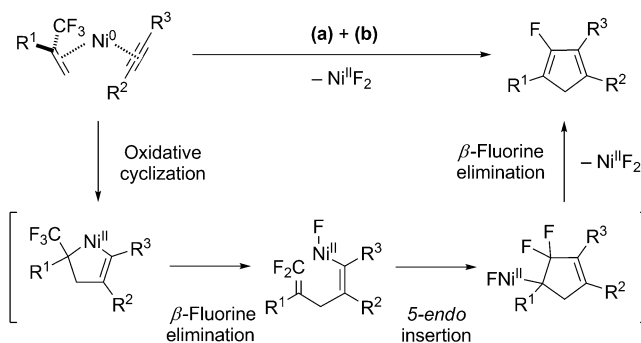
a) Allylic C–F bond activation



b) Vinylic C–F bond activation



Scheme 1. C–F bond activation by A) oxidative addition and B) β -fluorine elimination.



Scheme 2. Double C–F bond activation of a CF_3 group by a) allylic C–F bond activation via nickelacycles and b) intramolecular vinylic C–F bond activation.

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readily undergo oxidative cyclization,^[10–12] we envisioned that oxidative cyclization of a 2-trifluoromethyl-1-alkene and an alkyne on a Ni^0 complex would generate a nickelacyclopentene bearing a trifluoromethyl group. β -Fluorine elimination of this type of nickelacycle would generate organonickel complexes having both a vinylic C–Ni bond and a difluoroalkene moiety. Subsequently, intramolecular vinylic C–F

bond activation of the intermediary difluoroalkene might occur through normally disfavored 5-*endo* insertion^[7c,d] to afford 2-fluoro-1,3-cyclopentadienes. Herein we demonstrate the nickel-mediated [3+2] cycloaddition of 2-trifluoromethyl-1-alkenes with alkynes by double C–F bond activation of a trifluoromethyl group by sequential β -fluorine elimination, which allowed the efficient synthesis of highly substituted 2-fluoro-1,3-cyclopentadienes.

We selected 2-(4'-acetyl)phenyl-3,3,3-trifluoropropene (**1a**) and 4-octyne (**2a**) as model substrates for optimization of the reaction conditions (Table 1). Upon treatment of **1a** with **2a** in the presence of an equimolar amount of [Ni(cod)₂]

Table 1: Optimization of reaction conditions in Ni-mediated [3+2] cycloaddition of 2-trifluoromethyl-1-alkene **1a** with alkyne **2a**.^[a]

1a 2a 3aa Ar = C₆H₄(p-Ac) (1.1 equiv)			
Entry	Ligand	Solvent	Yield [%] ^[b]
1	PPh ₃	toluene	0
2	1,10-phen	toluene	0
3	IMes·HCl ^[c]	toluene	26
4	PCy ₃	toluene	66 ^[d]
5	PCy ₃	THF	48
6	PCy ₃	DME	56
7	PCy ₃	1,4-dioxane	74 ^[d]

[a] Reaction conditions: [Ni(cod)₂] (0.20 mmol), ligand (0.20 mmol), **1a** (0.20 mmol), **2a** (0.22 mmol), solvent (2.0 mL) at room temperature for 3 h. [b] ¹⁹F NMR yield using PhCF₃ as an internal standard. [c] tBuOK (1.0 equiv) was used as a base. [d] Yield of isolated product.

(cod = 1,5-cyclooctadiene) and PPh₃ or 1,10-phenanthroline, no cyclization product was obtained (Table 1, entries 1 and 2). However, when IMes possessing a strong σ -donating ability was employed as a ligand, the expected [3+2] cycloaddition proceeded to afford 2-fluoro-1,3-cyclopentadiene **3aa** in 26 % yield by cleavage of two C–F bonds in the trifluoromethyl group and formation of two C–C bonds (Table 1, entry 3). In the case where PCy₃ was used, the yield of **3aa** was improved to 66 % (entry 4). These results suggest that highly electron-rich Ni⁰ species derived from strong σ -donating ligands promoted oxidative cyclization between **1a** and **2a** in the initial step. Next we screened reaction solvents. Both THF and DME (1,2-dimethoxyethane) gave the product, albeit in low yields (entries 5 and 6). The best result (74 % yield of **3aa**) was obtained using 1,4-dioxane (entry 7).

The scope of the [3+2] cycloaddition was examined using a wide variety of 2-trifluoromethyl-1-alkenes **1a–g** and alkynes **2a–e** under the previously described optimal reaction conditions (Figure 1 and Table 2). Unsymmetrical 4-methyl-2-pentyne (**2b**), 1-phenyl-1-propyne (**2c**), and 1-(4'-methoxyphenyl)-1-pentyne (**2e**) also participated in this reaction to afford the corresponding 2-fluoro-1,3-cyclopentadienes **3ab**, **3ac**, and **3ae** in 77 %, 48 %, and 64 % yields, respectively, with complete regioselectivity (Table 2, entries 2, 3, and 5, respec-

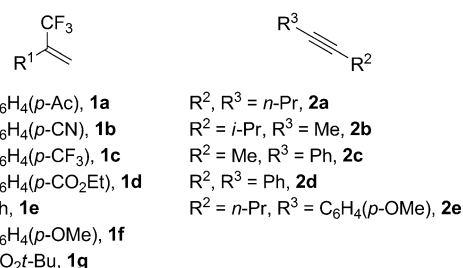


Figure 1. List of substrates.

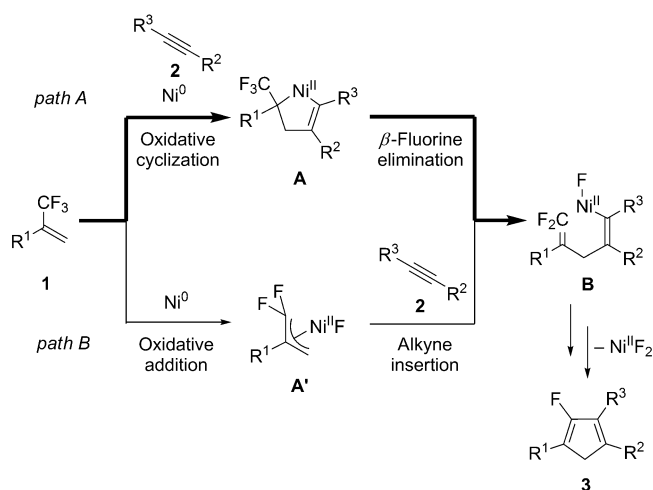
Table 2: Synthesis of 2-fluoro-1,3-cyclopentadienes **3** by Ni-mediated [3+2] cycloaddition of 2-trifluoromethyl-1-alkenes **1** with alkynes **2**.^[a]

1 + 2 (1.1 equiv) → 3					
Entry	1	2	Solvent	Conditions	Yield [%]
1	1a	2a	1,4-dioxane	RT, 3 h	3aa 74 %
2	1a	2b	1,4-dioxane	RT, 10.5 h	3ab 77 %
3	1a	2c	1,4-dioxane	60 °C, 19 h	3ac 48 %
4	1a	2d	1,4-dioxane	100 °C, 3 h	3ad 86 %
5	1a	2e	toluene	100 °C, 3 h	3ae 64 %
6	1b	2a	toluene	RT, 1.5 h then 80 °C, 1.5 h	3ba 82 %
7	1c	2a	toluene	RT, 9 h	3ca 86 %
8	1d	2a	toluene	50 °C, 1 h	3da 78 %
9	1e	2b	1,4-dioxane	60 °C, 6 h	3eb 57 %
10	1f	2d	toluene	100 °C, 3 h	3fd 42 %
11	1g	2a	1,4-dioxane	RT, 3 h	3ga 88 %
12	1g	2b	toluene	RT, 2 h	3gb 93 %

[a] Reaction conditions: [Ni(cod)₂] (0.30 mmol), ligand (0.30 mmol), **1** (0.30 mmol), **2** (0.33 mmol), solvent (3.0 mL).

tively).^[13] The use of diphenylacetylene (**2d**) resulted in the formation of the corresponding cycloaddition product **3ad** in 86 % yield (entry 4). α -Trifluoromethylstyrenes **1b–d** bearing electron-withdrawing cyano, trifluoromethyl, and ethoxycarbonyl groups further provided cyclopentadienes **3ba–da** in good to high yields (entries 6–8). Non-substituted α -trifluoromethylstyrene (**1e**) and α -trifluoromethylstyrene **1f** bearing an electron-donating methoxy group successfully underwent cycloaddition with **2b** or **2d** (entries 9 and 10). The reaction of *tert*-butyl α -trifluoromethylacrylate (**1g**) with alkynes **2a** and **2b** readily proceeded to give 2-fluoro-1,3-cyclopentadiene-1-carboxylates **3ga** and **3gb** in 88 % and 93 % yields, respectively (entries 11 and 12).

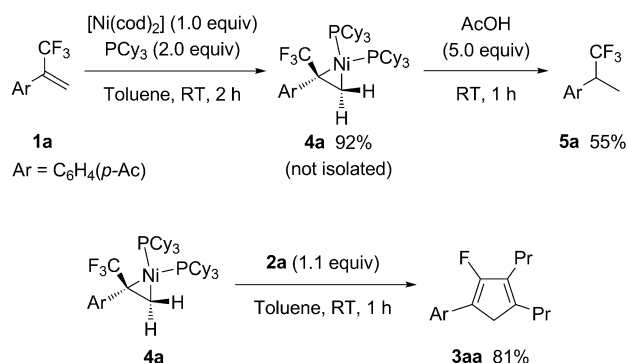
Two plausible mechanisms for this reaction are shown in Scheme 3. Nickelacyclopentene **A** bearing a trifluoromethyl group was probably formed by oxidative cyclization of 2-trifluoromethyl-1-alkene **1** and alkyne **2** with Ni⁰ (Scheme 3, path A). Ring-opening of nickelacycle **A** readily proceeded by β -fluorine elimination to generate alkenylnickel species **B**. Subsequent 5-*endo* insertion and the second β -fluorine elimination afforded 2-fluoro-1,3-cyclopentadiene **3** along with NiF₂ species.^[14] An alternative mechanism could be the oxidative addition pathway (Scheme 3, path B), in which 2-



Scheme 3. Plausible reaction mechanisms.

trifluoromethyl-1-alkene **1** initially reacted with Ni^0 to generate π -allylnickel intermediate **A'** by oxidative addition of a C–F bond to Ni^0 .^[6] Alkyne insertion into the C–Ni bond of **A'** led to **B**, followed by subsequent 5-*endo* insertion and β -fluorine elimination to give the same product **3**.

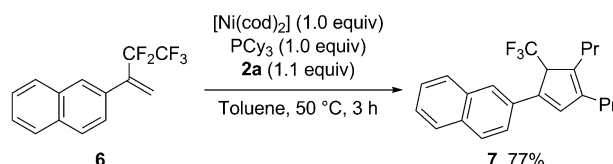
To elucidate the mechanism, the stoichiometric reaction of 2-trifluoromethyl-1-alkene **1** with a Ni^0 complex was conducted in the absence of alkynes (Scheme 4). If the reaction started with oxidative addition of the C–F bond to Ni^0 , the corresponding π -allylnickel complex would be observed. Treatment of **1a** with stoichiometric $[\text{Ni}(\text{cod})_2]$



Scheme 4. Generation and reactions of nickelacyclopentane **4a**.

and PCy_3 in toluene at room temperature, however, afforded nickelacyclopentane **4a** as the sole product in 92% yield; this was confirmed by ^{19}F and ^{31}P NMR spectroscopy.^[5f,11c] In this reaction, no π -allylnickel complexes were observed in the NMR spectra. The formation of **4a** was further supported by the conversion of **4a** to hydrogenated product **5a** in 55% yield upon treatment with an excess of acetic acid.^[15] In addition, **4a** readily reacted with 4-octyne to afford 2-fluoro-1,3-cyclopentadiene **3aa** in 81% yield. Therefore, the cyclopentadiene formation probably proceeded through an oxidative cyclization– β -fluorine elimination sequence (path A).

Furthermore, the sequential double C–F bond activation was successfully applied to pentafluoroethyl compounds under the same reaction conditions to give 5-trifluoromethyl-1,3-cyclopentadienes (Scheme 5). 2-Pentafluoroethyl-1-alkene **6** readily reacted with 4-octyne (**2a**) in the presence of the nickel complex to afford, by isomerization, 5-trifluoromethyl-1,3-cyclopentadiene **7** in 77% yield. Thus, we also achieved the direct synthesis of a ring trifluoromethylated cyclopentadiene.



Scheme 5. Synthesis of 5-trifluoromethyl-1,3-cyclopentadiene **7** by Ni-mediated [3+2] cycloaddition of 2-pentafluoroethyl-1-alkene **6** with alkyne **2a**.

In summary, we have developed a new methodology for allylic and vinylic C–F bond activation based on β -fluorine elimination from nickelacycles generated by oxidative cyclization of 2-trifluoromethyl-1-alkenes with alkynes. The nickel-mediated [3+2] cycloaddition reaction involves the consecutive and regioselective cleavage of two C–F bonds of a trifluoromethyl and a pentafluoroethyl group. This methodology simultaneously enables the direct construction of a multisubstituted cyclopentadiene ring and the introduction of a fluorine substituent or a trifluoromethyl group in a regioselective manner.^[16] Fluorine-containing, multisubstituted cyclopentadienes would be useful compounds as ligands of metallocene-type complexes^[17] and as building blocks for further chemical transformations such as Diels–Alder reactions.^[18,19]

Experimental Section

General procedure for nickel-mediated [3+2] cycloaddition of 2-trifluoromethyl-1-alkenes with alkynes: To a solution of $[\text{Ni}(\text{cod})_2]$ (86 mg, 0.31 mmol) and PCy_3 (88 mg, 0.31 mmol) in 1,4-dioxane (3.2 mL) were added 2-trifluoromethyl-1-alkene **1g** (61 mg, 0.31 mmol) and alkyne **2a** (38 mg, 0.34 mmol) at room temperature. After stirring for 3 h at the same temperature, the reaction mixture was filtered through a pad of silica gel (EtOAc). The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to give 2-fluorocyclopentadiene **3ga** (74 mg, 88%).

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