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Nickel-catalyzed Three-component Coupling Reaction of Tetrafluoroethylene and Aldehydes with Silanes via Oxa-Nickelacycles

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Abstract: The nickel-catalyzed synthesis of a variety of fluorinecontaining silyl ethers from tetrafluoroethylene (TFE) and aldehydes with silanes in a selective manner is disclosed. Stoichiometric reactions revealed that the oxa-nickelacycle, which is generated upon oxidative cyclization of TFE and an aldehyde with Ni(0), is the key intermediate, whose molecular structure was confirmed by singlecrystal X-ray diffraction analysis. In order to demonstrate the synthetic utility of this procedure, one of the reaction products was transformed into trifluorovinyl and organic silicon compounds via deprotonation with a Lewis base.

Introduction

Organofluorine species are widely used in physiologically active compounds (e.g. pharmaceuticals and agrochemicals) and functional materials (e.g. liquid crystals)^[1] on account of the unique features of the fluorine atom.^[2] Therefore, extensive research over the past few decades has been focused on synthetic routes to such compounds. Indeed, fluorination of organic compounds using fluorinating reagents is a wellestablished approach.^[3] However, this approach is unsuitable for the synthesis of highly fluorinated organic compounds due to i) the cost of these fluorination reagents, and ii) the limited availability of suitable substrates. On the other hand, the transformation of industrially available perfluorinated compounds into a variety of highly fluorinated organic compounds is more straightforward.^[4] Among such perfluorinated derivatives, tetrafluoroethylene (TFE) is particularly attractive because it is not only an economical feedstock for the preparation of polytetrafluoroethylene (PTFE) and co-polymers with other alkenes,[5a-c] but also an environmentally friendly compound with negligible global warming potential.^[5d] Thus, the development of methods for the efficient transformation of TFE has been extensively explored.[6]

Our group has been focusing on Ni-catalyzed transformations of TFE in which the oxidative cyclization of TFE and ethylene with Ni(0) is involved as a key reaction step.^[7–9] We have rationalized

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 Supporting information can be found under: ((Please delete this text if not appropriate)) the unique chemo- and regio-selectivity in these catalytic reactions in terms of an ingenious combination between TFE and ethylene,^[7] since oxidative cyclizations between electron-deficient and -rich substrates on Ni(0) are in general kinetically much more favorable than those occurring between other substrate combinations.^[10] In contrast, the development of Ni-catalyzed reactions that involve the oxidative cyclization between TFE and another electron-deficient substrate remain challenging, since such electron-deficient substrates, including TFE itself, can inherently undergo an oxidative cyclization with the homogeneous substrates. For this very reason, we have not achieved the Nicatalyzed selective formation of the cross-Tishchenko reaction products using two different types of electron-deficient aryl aldehydes.^[10a] Moreover, the hitherto reported Ni-catalyzed threecomponent coupling reactions^[11,12] with combinations of alkenes and aldehydes have been limited to cases of intramolecular reactions,^[13] while intermolecular reactions were achieved only for highly reactive alkenes such as norbornenes.^[14] This is due to the substantial differences between alkenes and aldehydes regarding their coordination ability to Ni(0), and hence, their simultaneous coordination to Ni(0) is difficult. The development of the catalytic three-component coupling reactions via an oxa-nickelacycle generated from TFE and aldehydes thus represents an significant extension of the current state-of-the-art in this area.

Results and Discussion

Based on this notion, we started investigating the optimal reaction conditions for a Ni-catalyzed three-component coupling reaction between TFE, benzaldehyde (1a), and Et₃SiH. When a toluene solution of **1a** and Et₃SiH was exposed to TFE (3.5 atm) in the presence of Ni(cod)₂ (10 mol%) and PPh₃ (20 mol%), neither the three-component coupling product, (2,2,3,3tetrafluoro-1-phenylpropoxy)triethylsilane (2a), nor the 1,2addition product, benzoxytriethylsilane (3a), was generated due to the formation of (CF₂)₄Ni(PPh₃)₂ ^[6b] (Table 1, entry 1). Employing PCy₃ instead of PPh₃ yielded 2a and 3a in 2% and 75% yield, respectively (entry 2). In contrast, the use of P^tBu₃ (10 mol%) afforded 2a in 72% yield and dramatically improved the product ratio of 2a/3a (entry 3). The unique role of the P^tBu₃ ligand should be emphasized; unlike PPh3 and PCy3, any TFEcontaining complexes are not generated when TFE is added to a mixture of Ni(cod)₂ and P^tBu₃,^[6b] and the same mixture can catalyze the 1,2-addition of 1a toward Et₃SiH. Further control experiments in the absence of either P^tBu₃ or Ni(cod)₂ revealed that both are essential for this three-component coupling reaction (entries 4 and 5). The reaction was then performed with various

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 Table 1. Optimization of the Reaction Conditions for the Ni-catalyzed Threecomponent Coupling Reaction of TFE, Benzaldehyde (1a), and Silanes^a

F F	- Н Ц _{Рh} +	R ₃ SiH 10 mo	Ni(cod)₂ N% ligand nt, rt, 3 h	F F OSiR ₃ F F	OSiR ₃ H H H Ph H
(3.5 atm)	1a	1.0 eq		2	3
Entry	Ligand	R₃SiH	Solvent	Yield	(%) ^e
1 ^{<i>b</i>}	PPh ₃	Et ₃ SiH	Toluene	0	0
2 ^b	PCy ₃	Et ₃ SiH	Toluene	2	75
3	P ^t Bu ₃	Et ₃ SiH	Toluene	72	3
4	none	Et ₃ SiH	Toluene	0	0
5 ^c	P ^t Bu ₃	Et ₃ SiH	Toluene	0	0
6	P ^t Bu ₃	Et ₃ SiH	C ₆ D ₆	90	4
7	P ^t Bu ₃	Ph ₃ SiH	C ₆ D ₆	89	10
8	P ^t Bu ₃	(EtO)₃SiH	C ₆ D ₆	2	21
9	P ^t Bu ₃	Et ₃ SiH	THF	48	4
10	P ^t Bu ₃	Et ₃ SiH	Hexane	88	2
11 ^{<i>d</i>}	P ^t Bu₃	Et ₃ SiH	Hexane	88	<1

^a General conditions: **1a** (0.10 mmol), silane (0.10 mmol), solvent (0.6 mL). Based on the ideal gas equation, the molar quantity of TFE was added in excess relative to **1a**. ^b 20 mol% of phosphine ligand. ^c Without Ni(cod)₂. ^d Run for 1 h. ^e Determined by GC using C₁₂H₂₆ as the internal standard, except for Entries 6–8, which were determined by NMR spectroscopy using α , α , α -trifluorotoluene as the internal standard.

silanes in the presence of Ni(cod)₂ and P^rBu₃. Employing Et₃SiH and Ph₃SiH in C₆D₆ afforded the corresponding target products in 90% and 89% yield, respectively, while the use of (EtO)₃SiH yielded merely trace amounts of the desired product (entries 6–8). The effect of the solvents was studied. The yield with hexane was comparable to that with C₆D₆, whereas THF was less effective for the reaction (entries 9 and 10). Under the optimal reaction conditions (entry 11), the catalytic reaction was completed in 1 h producing **2a** in 88% yield,^[15] although the dimerization product of **1a**, i.e., benzyl benzoate, was generated as a by-product in 4% yield.^[10]

Subsequently, we investigated the scope of the Ni-catalyzed three-component coupling reaction with respect to aldehydes under optimal reaction conditions (Scheme 1).^[16] Some of the reactions had to be conducted in a mixture of hexane/benzene due to the low solubility of the aldehdyes. Using the Ni(0)/P^tBu₃ system, the reaction of TFE, 1a, and Et₃SiH gave 2a in 71% isolated yield. p-Tolualdehyde (1b) furnished 2b in 92% yield, while m-tolualdehyde (1c), o-tolualdehyde (1d), and mesitylaldehyde (1e) produced the corresponding products (2c-e) in moderate yield, whereby longer times were required to complete the reactions. The use of *p*-fluorobenzaldehyde (1f) afforded the corresponding product (2f) in 75% yield, while the use of p-chlorobenzaldehyde (1g) generated a much lower yield (39%) of 2g, whereby unreacted starting material was observed. The low conversion is probably due to a deactivation of the catalyst on account of the undesired oxidative addition of Ni(0) to a C-CI bonds. Thus, p-bromobenzaldehyde (1h) could not be used as a substrate in this reaction (cf. SI). p-Anisaldehyde (1i) furnished 2i in 55% yield. When the electron-deficient aromatic aldehydes such as methyl 4-formylbenzoate (1j), p-trifluoromethylbenzaldehyde (1k), and 4-biphenylaldehyde (1l) were used, the reaction effectively afforded 2j-I. 1-Naphthaldehyde (1m) and 2naphthaldehyde (1n) generated 2m and 2n in 59% and 52% yield, respectively. The p-boronate substituted silyl ether (20), which

 $\label{eq:Scheme 1. Aldehyde Substrate Scope of the Ni-catalyzed Three-component Coupling Reaction of TFE, Aldehyde (1), and Et_3SiH {}^{a,b}$



^a General conditions: Ni(cod)₂ (0.10 mmol), P^tBu₃ (0.10 mmol), TFE (3.5 atm), **1** (1.0 mmol), Et₃SiH (1.0 mmol), hexane (6.0 mL). ^b Isolated yield. ^cRun for 3 h. ^d Solvent: hexane:benzene = 2:1 (v/v)

may potentially be used in the subsequent cross-coupling reactions, was obtained in 83% yield from the reaction with a *p*-boronate substituted aldehyde (**1o**). Employing cyclohexane carboaldehyde (**1p**) afforded the corresponding product (**2p**) in 48% yield. In contrast, the use of pivalaldehyde (**1q**) reduced the yield of **2q** to 14% yield due to undesired 1,2-addition and dimerization reactions.^[15]

Next, we carried out stoichiometric reactions in order to gain deeper insight into the reaction mechanism. Treatment of an equimolar mixture of Ni(cod)₂ and P^tBu₃ with **1a** under an atmosphere of TFE, followed by recrystallization from THF and pentane, produced an oxa-nickelacycle dimer complex (syn-4) in 90% isolated yield (Scheme 2, Figure 1a).^[17,18] In the ¹⁹F and ³¹P NMR spectra of the reaction mixture in toluene-d₈, broadened resonances were observed even at low temperature, which suggests a dimerization equilibrium of the oxa-nickelacycle units accompanied by a P^tBu₃ coordination/dissociation process. When this stoichiometric reaction was conducted without P^tBu₃ in a THF solution, syn-4 was not obtained. Therefore, the presence of the P^tBu₃ ligand is crucial for the oxidative cyclization. Subsequently, treating of syn-4 with P^tBu₃ and BF₃·Et₂O afforded the monomeric oxa-nickelacycle complex (5) in 99% yield.^[17] The X-ray crystallography of 5 revealed a distorted T-shaped configuration (Figure 1b).^[18] The dissociation of P^tBu₃ from **5** does not occur in C_6D_6 as the coupling between the α -CF₂ fluorine atom and the P^tBu₃ phosphorus atom is evident in both the ¹⁹F and ³¹P NMR spectra. These results demonstrate again that the oxanickelacycle dimer dissociates into the corresponding monomer in the presence of the P^tBu_3 . Indeed, the reaction of **syn-4** with PCy₃, instead of P^tBu₃, produced a PCy₃-ligated oxa-nickelacycle dimer complex (syn-6) in 98% yield. As in the case of solid-state

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Scheme 2. Isolation of Oxa-nickelacycles.



Figure 1. ORTEP drawings of (a) **syn-4**, (b) **5**, and (c) **syn-6** with thermal ellipsoids at 30% probability (except for the organic substituents of the phosphine ligands in **syn-6**). Selected hydrogen atoms have been omitted for clarity.



syn-4, the nickel center in *syn-6* also adopts a distorted squareplanar geometry (Figure 1c).^[17,18]

The reaction of **syn-4** with Et₃SiH did not proceed at room temperature in the absence of P^IBu₃ (Scheme 3, entry 1). On the other hand, the desired product **2a** was formed in 67% yield when P^IBu₃ was used for the reaction as an additional ligand (entry 2). Based on these results, it seems most likely that the catalytic reaction proceeds via an oxa-nickelacycle monomer generated from TFE and aldehydes, while both the oxa-nickelacycle monomer and dimer could be key intermediates. Moreover, the reaction of **5** with Et₃SiH at room temperature for 1 h afforded **2a** in merely 4% yield, whereby unreacted complex **5** was observed (entry 3). When the reaction time was extended to 24 h, the yield of **2a** was slightly improved (entry 4). The low reactivity of **5** toward Et₃SiH results from the O atom coordination to BF₃. Therefore, 1,4-diazabicyclo[2.2.2]octane (DABCO) was added in order to dissociate BF₃ from the O atom of **5**, which resulted in the

Scheme 3. Stoichiometric Reactions of Oxa-nickelacycles with Et₃SiH.

	$-\frac{Ph}{x e}$	eq Et ₃ SiH eq additive		F OSiEt ₃
F		D ₆ , rt, time	- 11	F F
-				28
Entry	Ni complex	Additive (x eq)	Time (h)	Yield (%)
1	syn-4	none	9	0
2	syn-4	P ^t Bu ₃ (2.0)	9	67
3	5	none	1	4
4	5	none	24	16
5	5	DABCO (1.0)	1	21
	-		•	•

Scheme 4. Plausible Mechanism for the Ni-catalyzed Three-component Coupling Reaction of TFE, Aldehyde, and Silane.



formation of **2a** in 21% yield (entry 5). ^[6b] In this reaction, the conversion of **5** reached in fact 100%, whereby the relatively low yield of **2a** should be due to decomposition. These results indicate that the Si atom of Et₃SiH approaches the O atom of the oxanickelacycle monomer, which facilitates the transmetallation with Et₃SiH. It should be noted that the target compound was not generated from the reaction of **5** with (EtO)₃SiH, which is an ineffective silane in the catalytic reaction, in the presence of DABCO. These results suggest that the transmetallation of the oxanickelacycle with such silane should be a difficult. Since the reaction of **syn-6** with Et₃SiH did not afford **2a**, we concluded that the steric hindrance of the phosphine ligand may be important for the dissociation of the dimer into monomer (entry 6).^[19]

Based on these results and those of previous studies on the mechanism of Ni-catalyzed three-component coupling reactions, ^[19,20] this catalytic reaction likely proceeds as shown in Scheme 4. A simultaneous coordination of TFE and aldehydes to Ni(0) results in the formation of $\eta^2:\eta^2$ nickel complex **A**. Then, an oxidative cyclization of the two different components with Ni(0) generates five-membered oxa-nickelacycle **B** as the key intermediate. Subsequently, the Si atom of the silane approaches the O atom of **B** to form **C**. Finally, transmetallation affords the Ni(II) hydride species **D**, followed by a reductive elimination to yield the desired product under concomitant regeneration of the Ni(0) species.

The reactivity and utility of the reaction products obtained from the catalytic reaction are exemplified for 2b (See also Schemes S13 and S14 in the SI). As outlined in previous studies, ^[21] the addition of lithium diisopropyl amide (LDA) deprotonates 2b to give 2,2,3-trifluoroallyl alcohol 8b in 90% yield under concomitant generation of LiF. Such trifluoroallyl alcohols are desirable comonomers to tune the solubility of PTFE and other co-polymers by using the hydroxyl group obtained from desilylation and the substituents on the aromatic ring. Moreover, the transient fluoroalkyl lithium species formed upon deprotonation of 2b by LDA can be trapped with Me₃SiCl to produce Me₃SiCF₂CF₂CH-(OSiEt₃)(p-C₆H₄CH₃) (9b) in 90% yield.^[3e,22] Although tetrafluoroethylene-containing alcohols are expected to be physiologically active, studies on the subject remain scarce due to the lack of efficient synthetic methods.^[23] These applications demonstrate the synthetic utility of the present catalytic reaction.

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Conclusions

In conclusion, we have developed a Ni(0)/P'Bu₃-catalyzed threecomponent coupling reaction of TFE, aldehydes, and silanes that affords fluorine-containing silyl ethers. Stoichiometric reactions identified the oxidative cyclization of TFE and aldehydes with Ni(0) as the key step in this catalytic reaction. The obtained products can be deprotonated by a Lewis base and transformed into 2,2,3-trifluoroallyl alcohols or organosilicon compounds, which may be further used for the preparation of fluorinecontaining polymers and physiologically active compounds. The present Ni-catalyzed system, which is based on the oxidative cyclization between two different types of electron-deficient substrates, may open new avenues for the preparation of a variety of organofluorine compounds.

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Conflict of interest

The authors declare no competing financial interests.

Keywords: tetrafluoroethylene • nickel • three-component coupling reaction • oxidative cyclization

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- [16] See the SI for details about substrate coverage including other aldehydes, ketones, imines, enones and fluorinated olefins.

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- [17] See the SI for details about stoichiometric reactions, X-ray crystallography, and catalytic reactions with oxa-nickelacycles.
- [18] CCDCs 1875740 (*syn-4*), 1875741 (5), 1875742 (*syn-6*), and 1875743
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Nickle-catalyzed three-component coupling reactions of tetrafluoroethylene, aldehydes, and silanes are reported. Mechanistic studies revealed that the oxanickelacycles generated via the oxidative cyclziation of TFE and aldehydes were key intermediates for the catalytic reactions. The obtained products can be effectively transformed into the valuable trifluorovinyl compounds and organo silyl compounds.

Tetrafluoroethylene, Oxa-Nickelacycle

Hiroshi Shirataki, Masato Ohashi,* and Sensuke Ogoshi*

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Nickel-catalyzed Three-component Coupling Reaction of Tetrafluoroethylene and Aldehydes with Silanes via Oxa-Nickelacycles