

# Nickel-Catalyzed Formation of Fluorine-Containing Ketones via the Selective Cross-Trimerization Reaction of Tetrafluoroethylene, Ethylene, and Aldehydes

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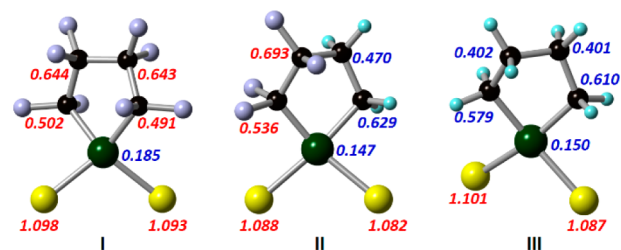
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**S** Supporting Information

**ABSTRACT:** In the presence of a catalytic amount of Ni(cod)<sub>2</sub> and IPr (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), a cross-trimerization reaction of tetrafluoroethylene (TFE), ethylene, and aldehydes proceeded in a selective manner to afford a variety of 4,4,5,5-tetrafluoro-1-pentanone derivatives in good to excellent yields. The present system involves a five-membered nickelacycle key intermediate generated via the oxidative cyclization of TFE and ethylene.

Organofluorine compounds are important components in a variety of commercial products.<sup>1</sup> Therefore, economical organofluorine feedstock is needed in bulk to supply the starting materials for the synthesis of commercial products. Therefore, we pursued the development of a novel strategy that was focused on the effective utilization of tetrafluoroethylene (TFE; CF<sub>2</sub>=CF<sub>2</sub>) as an ideal starting material, since the conventional usage of industrial-grade economical TFE has been mostly limited to the production of poly(tetrafluoroethylene) and copolymers with other alkenes.<sup>2</sup> We reported the first coupling reaction of TFE with arylzinc compounds to yield ( $\alpha,\beta,\beta$ -trifluoro)styrene derivatives.<sup>3a,b</sup> We have successfully applied this Negishi-type reaction to the Suzuki–Miyaura and the Hiyama-type reactions of TFE, which requires no extraneous base.<sup>3c,d</sup> Our next target was to incorporate a TFE molecule into an organic framework as a tetrafluoroethylene unit (–CF<sub>2</sub>CF<sub>2</sub>–) without the loss of fluorine atoms.<sup>3e</sup> Although insertion reactions of TFE into either a N–H or an O–H bond were well-known as preparation methods for partially fluorinated amines and alcohols,<sup>4,5</sup> the corresponding reactions involving a C–C bond formation are quite rare, with the noted exception of radical additions.<sup>6</sup> Only one catalytic reaction involving the oxidative cyclization of TFE as a C–C bond formation step has been reported,<sup>7,8</sup> whereas oxidative cyclization has received much attention because of its efficiency in the construction of C–C bonds between a variety of unsaturated compounds.<sup>9</sup> Very recently, we developed a novel Ni(0)-catalyzed cotrimerization reaction using TFE with ethylene leading to 5,5,6,6-tetrafluoro-1-hexene.<sup>10</sup> In this catalytic reaction, a five-membered nickelacycle generated via the oxidative cyclization of TFE and ethylene with nickel(0) is a key reaction intermediate. We also demonstrated the unique reactivity of (CF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Ni(PPh<sub>3</sub>)<sub>2</sub> (II), the  $\alpha$ -CH<sub>2</sub>

moiety of which selectively participated in a Michael addition reaction toward  $\alpha,\beta$ -unsaturated carbonyl compounds.<sup>10</sup> This can be rationalized via natural bond order (NBO) charge distribution analysis; the  $\alpha$ -carbon in II is the most nucleophilic of the related five-membered nickelacycles (Figure 1).<sup>11</sup>



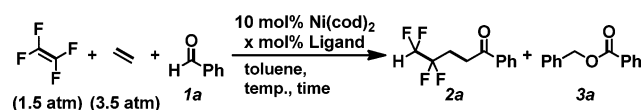
**Figure 1.** Natural population analysis of (CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>)Ni(PPh<sub>3</sub>)<sub>2</sub> (I), (CF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Ni(PPh<sub>3</sub>)<sub>2</sub> (II), and (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)Ni(PPh<sub>3</sub>)<sub>2</sub> (III). Red and blue values represent positive and negative charge, respectively. All phenyl groups on the phosphorus atoms have been omitted for clarity.

Therefore, we explored the reaction of TFE, ethylene, and aldehydes in the presence of a Ni(0) catalyst in anticipation of the occurrence of a nucleophilic addition of the resultant five-membered nickelacycle to the carbonyl group.

When the toluene solution of benzaldehyde (**1a**) was exposed to the mix gas containing TFE (partial pressure = 1.5 atm) and ethylene (partial pressure = 3.5 atm) at 40 °C for 10 h in the presence of Ni(cod)<sub>2</sub> and PCy<sub>3</sub> (10 and 20 mol %, respectively), the cross-trimerization product, 4,4,5,5-tetrafluoro-1-phenylpentan-1-one (**2a**), was formed in 32% yield (Table 1, run 1). In this reaction, the homo-Tishchenko reaction product, benzyl benzoate (**3a**), was also generated in 13% yield.<sup>12</sup> Encouraged by this result, reaction conditions were optimized by employing TFE, ethylene, and **1a** in the presence of 10 mol % of Ni(cod)<sub>2</sub> and various ligands. The use of PPh<sub>3</sub> in place of PCy<sub>3</sub> afforded **2a** and **3a** in 12% and 4% yields, respectively (run 2), whereas P<sup>*t*</sup>Bu<sub>3</sub> hardly gave the desired product (run 3). Neither P(*o*-tol)<sub>3</sub> nor P<sup>*t*</sup>Bu<sub>3</sub> was effective, which was most likely due to their excess bulkiness (runs 4 and 5). The use of bidentate ligands such as DCPB (1,4-bis(dicyclohexylphosphino)butane) and DPPB (1,4-bis-

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**Table 1.** Ni(0)-Catalyzed Cross-Trimerization Reaction of TFE, Ethylene, and Benzaldehyde **1a**<sup>a</sup>

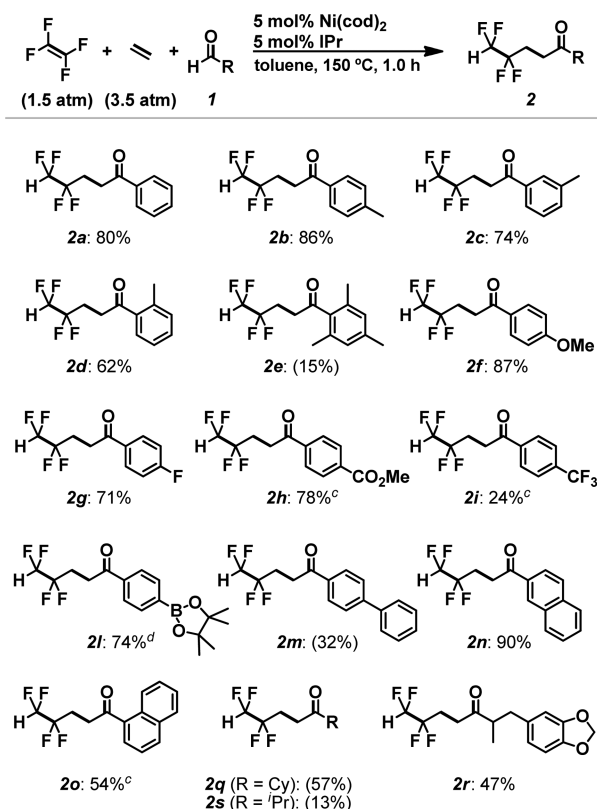
run	ligand (x mol %)	temp (°C)	time (h)	conv (%) <sup>b</sup>	yield (%) <sup>b</sup>	
					2a	3a
1	PCy <sub>3</sub> (20)	40	10	>99	32	13
2	PPh <sub>3</sub> (20)	40	10	20	12	4
3	P <sup>n</sup> Bu <sub>3</sub> (20)	40	10	3	<1	<1
4	P( <i>o</i> -tol) <sub>3</sub> (20)	40	10	2	—	—
5	P <sup>t</sup> Bu <sub>3</sub> (20)	40	10	13	—	<1
6	DCPB (10)	40	10	<1	—	—
7	DPPB (10)	40	10	<1	—	—
8	IPr (10)	40	10	>99	45	28
9	IPrCl (10)	40	10	>99	43	30
10	SIPr (10)	40	10	>99	18	37
11	ICy (10)	40	10	<1	—	—
12	tBu (10)	40	10	8	—	4
13	IPr (10)	80	3	>99	63	12
14	IPr (10)	120	3	>99	89	5
15	IPr (10)	150	0.17	>99	95	4
16	PCy <sub>3</sub> (20)	150	1	>99	48	24
17	PPh <sub>3</sub> (20)	150	1	67	22	2
18 <sup>c</sup>	IPr (5)	150	0.5	>99	98	4
19 <sup>d</sup>	IPr (2)	150	0.5	44	4	<1
20	none	150	0.5	—	—	—
21 <sup>e</sup>	IPr (5)	150	0.5	—	—	—

<sup>a</sup>General conditions: **1a** (0.10 mmol), toluene (0.6 mL). The molar quantities of both material gases, estimated by the equation of state of ideal gas, were higher than that of **1a**. <sup>b</sup>The conversion of **1a** and each yield, based on **1a**, of the products **2a** and **3** were determined by GC analysis using C<sub>14</sub>H<sub>30</sub> as an internal standard. <sup>c</sup>Run using 5 mol % of Ni(cod)<sub>2</sub>. <sup>d</sup>Run using 2 mol % of Ni(cod)<sub>2</sub>. <sup>e</sup>Run in the absence of Ni(cod)<sub>2</sub>.

(diphenylphosphino)butane) did not produce the desired reaction, and **1a** was fully recovered after the reaction (runs 6 and 7). Employing NHC (*N*-heterocyclic carbene) ligands such as IPr and IPrCl allowed the reaction to give **2a** in 45% and 43% yields, respectively, while considerable formation of the undesired dimerization product **3a** was also detected (runs 8 and 9). A significant decrease in the yield of **2a**, however, was observed with the use of SIPr (run 10). In addition, **2a** was not generated at all in the presence of *N*-alkyl substituted NHC ligands (runs 11 and 12). The effects of the solvent and temperature on this reaction were further investigated using IPr as a ligand. As for the solvent, THF was comparable to toluene, while hexane, acetonitrile, and DMF were less effective in both yields.<sup>13</sup> The temperature was critical to this reaction. Both the yield of **2a** and the product ratio of **2a/3a** were drastically improved as the reaction temperature was raised (runs 13–15). Furthermore, a shorter reaction time was required with a higher reaction temperature, and elevating the reaction temperature to 150 °C furnished the desired product **2a** in 95% yield within 10 min (run 15). Although 5,5,6,6-tetrafluoro-1-hexene is a potential side product,<sup>10</sup> it was not detected in this crude reaction mixture. Using PCy<sub>3</sub> under the same reaction conditions also accelerated the catalytic reaction; however, the product selectivity was inferior to that of IPr (run 16). In addition, the use of PPh<sub>3</sub> at 150 °C gave a small amount of **2a**

(22%) with a concomitant formation of 5,5,6,6-tetrafluoro-1-hexene (9%) (run 17). An initial reduction in catalyst loading (5 mol % of Ni(0)/IPr) did not affect the yield or the selectivity of **2a** (run 18), whereas a 2 mol % catalyst loading resulted in a retardation of the reaction (run 19). The product **2a** was not generated in the absence of either IPr or Ni(cod)<sub>2</sub> (runs 20 and 21). Thus, the optimal reaction conditions were determined as follows: 5 mol % of Ni(cod)<sub>2</sub> and IPr in toluene at 150 °C.

With the optimal reaction conditions used in run 18 (Table 1), the scope and limitations of this Ni(0)/IPr-catalyzed cross-trimerization reaction with respect to various aldehydes were examined (Scheme 1).<sup>14</sup> The reaction of the mixed gas

**Scheme 1.** Ni(0)-Catalyzed Selective Cross-Trimerization Reaction of TFE, Ethylene, and Aldehydes<sup>a,b</sup>

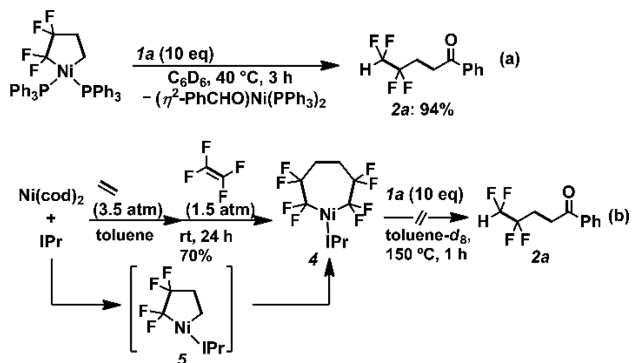
<sup>a</sup>General conditions: IPr, Ni(cod)<sub>2</sub> (0.05 mmol each), aldehyde (**1**; 1.0 mmol), ethylene (3.5 atm), TFE (1.5 atm), toluene (6.0 mL). <sup>b</sup>Isolated yield. The values in parentheses are estimated from <sup>19</sup>F NMR analysis. <sup>c</sup>Run for 24 h by using 10 mol % Ni(cod)<sub>2</sub>/IPr. <sup>d</sup>Run for 3 h by using 10 mol % Ni(cod)<sub>2</sub>/IPr.

containing TFE and ethylene with **1a** afforded **2a** in 80% isolated yield. The use of *p*-tolualdehyde (**1b**) and *m*-tolualdehyde (**1c**) gave the corresponding products (**2b** and **2c**) in 86% and 74% yields, respectively, while *o*-tolualdehyde (**1d**) slightly diminished the yield (62%) due to the formation of the undesired ester (**3d**). Employing mesitylaldehyde (**1e**) retarded the reaction probably due to its excess bulkiness. The reactions with *p*-anisaldehyde (**1f**), *p*-fluorobenzaldehyde (**1g**), and methyl 4-formylbenzoate (**1h**) also afforded the corresponding products (**2f–h**) in excellent yields. On the other hand, *p*-trifluoromethylbenzaldehyde (**1i**) resulted in the formation of the desired trimerization product in 24% isolated yield along with a residual of the aldehyde and considerable generation of the undesired ester (**3i**) in the crude product. In

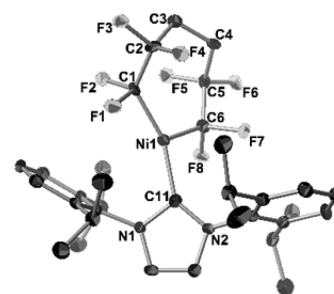
addition, neither *p*-chlorobenzaldehyde (**1j**) nor *p*-bromobenzaldehyde (**1k**) gave the desired products, which might have been due to the occurrence of an undesired oxidative addition of either a C–Cl or C–Br bond. The *p*-boronate substituted benzaldehyde (**1l**) was used to prepare the corresponding ketone (**2l**) in 74% yield, in which the boronate moiety was applied to a further cross-coupling reaction to synthesize highly functionalized derivatives. The use of biphenylaldehyde (**1m**), however, retarded the reaction, and a small amount of the product (**2m**) was detected by  $^{19}\text{F}$  NMR analysis (32%) of the crude reaction mixture. In the reaction with naphthaldehydes, 2-naphthaldehydes (**1n**) gave the corresponding ketone (**2n**) in 90% yield. In contrast, the use of 1-naphthaldehydes (**1o**) underwent the undesired Tishchenko reaction to some extent, and the yield of the product (**2o**) was diminished to 54%. The reaction using aldehydes with a heteroaromatic ring, such as 2-pyridyl aldehyde (**1p**), did not afford the corresponding product. Among the reactions of aliphatic aldehydes, either cyclohexyl carboxaldehyde (**1q**) or 3-(benzodioxol-5-yl)-2-methylpropanal (**1r**) gave **2q** or **2r** in 57% and 47% yields, respectively, whereas the former product could not be isolated due to a relatively high degree of volatility. Other aldehydes, such as 2-butanal (**1s**), 1-butanal (**1t**), 1-hexanal (**1u**), and pivalaldehyde (**1v**), can participate in the reaction, but the efficiency was not as high.<sup>15</sup>

To gain deeper insights into the reaction mechanism in this selective cross-trimerization reaction, stoichiometric reactions were conducted. The treatment of **II** with an excess amount of benzaldehyde in  $\text{C}_6\text{D}_6$  at 40 °C led to the formation of **2a** in 94% yield (Scheme 2a). The resultant Ni(0) was trapped by

### Scheme 2. Stoichiometric Reactions



PhCHO and led to the quantitative formation of  $(\eta^2\text{-PhCHO})\text{Ni}(\text{PPh}_3)_2$ . However, attempts to isolate the assumed nickelacycle intermediates bearing IPr as an auxiliary ligand were not so fruitful. The reaction of TFE and ethylene in the presence of an equimolar mixture of  $\text{Ni}(\text{cod})_2$  and IPr resulted in the isolation of a seven-membered nickelacycle,  $(\text{CF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2)_2\text{Ni}(\text{IPr})$  (**4**), which was composed of the molecules of two TFE and one of ethylene (Scheme 2b). The expected five-membered nickelacycle (**5**) was too transient to be observed even under strictly controlled conditions with respect to the TFE/ethylene ratio. The molecular structure of **4** was unambiguously confirmed by X-ray diffraction studies (Figure 2). Neither **2a** nor **3a** was obtained when **4** was treated with **1a** (10 equiv) under the catalytic reaction conditions (in toluene- $d_8$ , 150 °C, 1 h), which indicated that **4** was not involved in the catalytic cycle.<sup>16</sup> The lower efficiency of generating **4** in the presence of aldehydes was confirmed on the

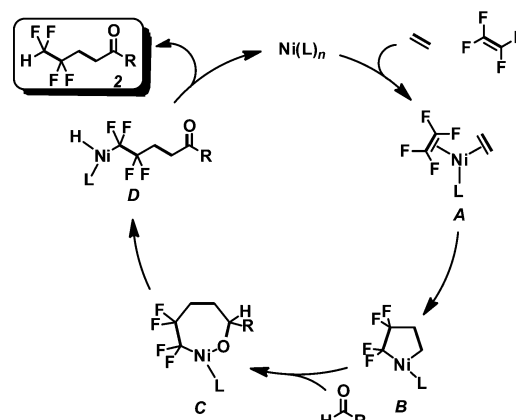


**Figure 2.** Molecular structure of **4** with thermal ellipsoids at the 30% probability level. One of the crystallographically independent molecules in the unit cell has been depicted. H atoms have been omitted for clarity.

basis of the fact that it was not contained in the crude products from reactions at 40 and 150 °C (Table 1, runs 8 and 15).

Based on our recent report involving the Ni(0)-catalyzed cotrimerization reaction of TFE and ethylene,<sup>10</sup> the Ni(0)/IPr-catalyzed cross-trimerization reaction of TFE, ethylene, and aldehydes might proceed via the mechanism depicted in Scheme 3. The oxidative cyclization of TFE and ethylene with

### Scheme 3. A Plausible Mechanism



Ni(0) would occur to generate a 2,2,3,3-tetrafluoronickelacyclopentane species (**B**) via an  $(\eta^2\text{-TFE})(\eta^2\text{-ethylene})\text{Ni}(0)(\text{IPr})$  intermediate (**A**). Then, a nucleophilic addition of the Ni- $\text{CH}_2$  moiety to the carbonyl group in an aldehyde would proceed to give a seven-membered oxa-nickelacycle intermediate (**C**). A nickel hydride intermediate (**D**) would be generated via  $\beta$ -hydride elimination, and then it would undergo reductive elimination to afford the 4,4,5,5-tetrafluoro-1-pentanone derivative **2** along with a regeneration of the Ni(0) species. The higher reaction temperature is essential for not only accelerating the catalytic reaction but also improving the ratio between the desired/undesired products (**2/3**). Another possible mechanism where the oxidative cyclization of an ethylene and an aldehyde occurs prior to that of TFE and ethylene was unlikely to have occurred based on the fact that the generation of  $(\eta^2\text{-CH}_2=\text{CH}_2)_2\text{Ni}(\text{IPr})$  was indicated by NMR analysis when the catalytic reaction was monitored prior to the pressurization of TFE.<sup>17</sup>

In summary, we have demonstrated a selective cross-trimerization reaction of tetrafluoroethylene, ethylene, and aldehydes to give a variety of fluorine-containing ketone derivatives. Other than the use of a radical mechanism, this is

the first example of the net insertion reaction of a TFE molecule into a C–H bond leading to a tetrafluoroethylene unit (–CF<sub>2</sub>CF<sub>2</sub>–). The key reaction intermediate was the partially fluorinated five-membered nickelacycle generated via the oxidative cyclization of TFE and ethylene with nickel(0).

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Detailed experimental procedures, analytical and spectral data for all new compounds, and CIF data for **4**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b03587.

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### ■ Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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- (11) Two of them, **I** and **II**, were isolated and structurally defined by X-ray diffraction study, whereas the rest has not been isolated. See also refs 3b and 12. Computational details are found in the Supporting Information.
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- (13) See the Supporting Information for optimization of the catalytic reaction conditions.
- (14) Attempts to employ 1-substituted terminal alkenes, such as styrene and 1-hexene, gave no desired cross-trimerization products.
- (15) See Supporting Information for details. Although employing ketones in place of aldehydes would be anticipated to form tetrafluorotetrahydro-2H-pyran derivatives, such attempts except for using PhC(O)CF<sub>3</sub> yielded no desired products. Unexpectedly, PhC(O)CF<sub>3</sub> gave 1,1,1-trifluoro-2-phenyl-5-hexen-2-ol.
- (16) In the presence or absence of **1a**, **4** underwent thermolysis at 150 °C to yield unidentified products. In addition, treating **4** with **1a** in C<sub>6</sub>D<sub>6</sub> at 40 °C for 3 h led to the generation of a complicated mixture in which **2a** was not contained.
- (17) For a related bis-η<sup>2</sup>-styrene complex, see: Iglesias, M. J.; Blandez, J. F.; Fructos, M. R.; Prieto, A.; Alarez, E.; Blederrain, T. R.; Nicasio, M. C. *Organometallics* **2012**, *31*, 6312–6316. When the catalytic reaction was monitored prior to pressurizing both ethylene and TFE, the formation of (η<sup>2</sup>-aldehyde)<sub>2</sub>Ni(IPr) was observed. See also ref 12.