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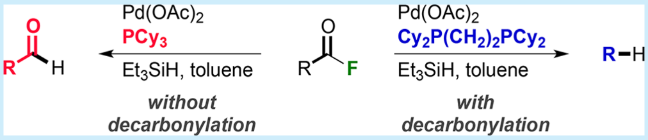
Palladium-Catalyzed Reductive Conversion of Acyl Fluorides via Ligand-Controlled Decarbonylation

Yohei Ogiwara,* Yuka Sakurai, Hiroyuki Hattori, and Norio Sakai*

Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, Noda, Chiba 278-8510, Japan

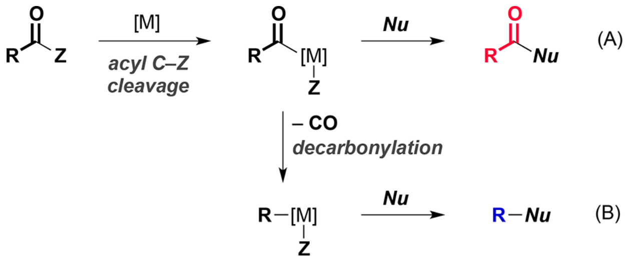
Supporting Information

ABSTRACT: Ligand-controlled non-decarbonylative and decarbonylative conversions of acyl fluorides were developed using a $Pd(OAc)_2/Et_3SiH$ combination. When tricyclohexylphosphine (PCy_3) was used as the ligand, aldehydes were obtained as simple reductive conversion products. The use of 1,2-bis(dicyclohexylphosphino)ethane ($Cy_2P(CH_2)_2PCy_2$, DCPE) as the ligand, however, favored the formation of hydrocarbons, which are decarbonylative reduction products.



Acyl carbon−heteroatom (acyl C−Z) bond cleavage of carboxylic acid derivatives (RCOZ) by transition-metal complexes to form acyl metal species has been widely investigated and utilized as the initiation step in various catalytic molecular transformations.[1] In the presence of a nucleophilic compound under the system, the acyl metal species potentially displays the following two different reaction modes. The first reaction mode is a simple acylation, when the acyl fragment (RCO) of an acyl metal complex can be transferred into nucleophiles from the transition-metal center (Scheme 1A). Another mode includes a decarbonylation process, wherein the carboxylic acid functions as a hydrocarbon (R) source, and in many cases, these involve an arylation (R = Ar) of nucleophiles (Scheme 1B).

Scheme 1. Two Reaction Modes of Carboxylic Acid Derivatives via Acyl C−Z Bond Cleavage by a Transition-Metal Catalyst



Due to the potential utility of carboxylic acid derivatives as a divergent building block in synthetic chemistry, extensive effort has been devoted to developing a novel catalytic transformation of carboxylic acids with or without the decarbonylation process. To control the reaction mode using either a non-decarbonylative (A-type) or a decarbonylative (B-type) reaction, however, an individual fine-tuning of each reaction system is essential.[2−7]

For both types of transformations, acyl fluorides are considered highly attractive and versatile carboxylic acid derivatives. They are readily available from the corresponding carboxylic acids or acyl chlorides,[8] and are easy to handling due to their chemical stability toward nucleophiles such as water. A pioneering work by Rovis showed that acyl fluorides could be applied as acylation reagents in a nickel-catalyzed coupling with organozinc reagents.[9] Our group also reported the A-type coupling of acyl fluorides as carboxylic acid derivatives with organometallic reagents such as organosilicon[10a] and organoboron[10b] compounds by palladium catalysis. In these reactions, acyl fluorides acted as a novel acyl electrophile, and their acyl C−F bonds were converted into the corresponding acyl C−C bonds, which suppressed the loss of the carbonyl moiety and yielded the desired ketones. Quite recently, Schoenebeck reported a palladium-catalyzed decarbonylative coupling of acyl fluorides and Et_3SiCF_3. This reaction is the first example of the B-type transformation of acyl fluorides, which provided trifluoromethyl arenes.[11]

Since the reductive transformation of carboxylic acid derivatives is an important synthetic strategy in organic chemistry, various catalytic procedures have been developed utilizing a hydrosilane,[2−6] which is a mild reducing reagent with highly functional group tolerance and chemoselectivity. Selecting acyl fluorides as a novel electrophile in the reaction with a hydrosilane, therefore, provides an alternative synthetic route. Despite the synthetic potential, however, there has been no report of the successful reductive conversion of acyl fluorides.[12]

We describe, herein, a palladium-catalyzed reductive transformation of acyl fluorides using a hydrosilane. In an attempt to use a hydrosilane in the reductive transformation of acyl fluorides, we found that C−H bond formation occurred via acyl C−F bond cleavage, wherein the decarbonylation event of

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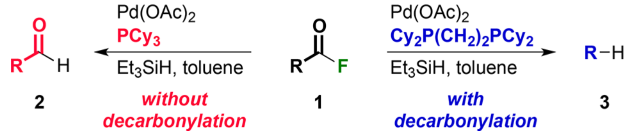
acyl fluorides can be controlled by a simple switching of the phosphorus ligand. By employing monodentate PCy_3 as a ligand, acyl fluorides **1** were converted to the corresponding aldehydes **2** without decarbonylation. On the other hand, the decarbonylation switch was turned "ON" by changing the ligand from PCy_3 to bidentate DCPE $[Cy_2P(CH_2)_2PCy_2]$, which formed hydrocarbons **3** (Scheme 2).[13]

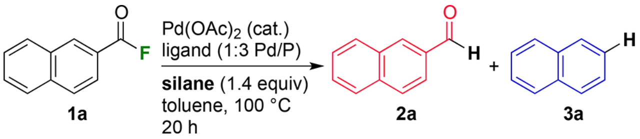
Scheme 2. This Work: Ligand-Controlled Divergent Transformation of Acyl Fluorides in a Palladium-Catalyzed Reduction Using a Hydrosilane



To achieve the selective conversion of acyl fluoride **1a** to either the corresponding aldehyde **2a** or the decarbonylative reduction product **3a**, ligand screening was initially conducted using a catalytic amount of $Pd(OAc)_2$ and 1.4 equiv of Et_3SiH in toluene at 100 °C for 20 h (Table 1). When the reaction was performed using PPh_3 as a ligand, only trace amounts of the desired products **2a** and **3a** were detected by GC analysis (entry 1). Although $P(4\text{-}CF_3C_6H_4)_3$ gave similar results, the use of $P(4\text{-}MeOC_6H_4)_3$ increased the yield of **2a** to 53% (with 85:15 selectivity of **2a**/**3a**) (entries 2 and 3). Dialkylbiarylphosphines, such as JohnPhos and CyJohnPhos, and a trialkylphosphine, P^tBu_3, were less effective for the reaction in terms of both reactivity and selectivity (entries 4−6). The best result for the selective formation of aldehyde **2a** was obtained using PCy_3 as a ligand (entry 7), and a decrease in the catalyst loading (5 mol % to 2.5 mol % of [Pd]) slightly improved the yield of **2a** to 92% (with 99:1 selectivity of **2a**/**3a**) (entry 8). Next, we performed reactions using a series of bidentate phosphine ligands: DPPBz, DPPE, DCPE, DPPP, DPPF, and Xantphos. These ligands induced the decarbonylation step, which provided naphthalene **3a** (entries 9−15). In particular, when DCPE was used as a ligand, a significant improvement was observed in the formation of **3a** (82% yield of **3a** with 4:96 selectivity of **2a**/**3a**) (entry 11). With a lower catalyst loading (5 mol % to 2.5 mol % of [Pd]), the reaction also proceeded to form **3a** in an 84% yield (with 8:92 selectivity of **2a**/**3a**) (entry 12). In the absence of a palladium catalyst, however, the reductive conversions did not proceed (entries 16 and 17).

With employment of PCy_3 as the ligand under the conditions of entry 8 in Table 1, the scope and limitations for the selective formation of aldehydes **2** from various acyl fluorides **1** were examined (Scheme 3). A wide range of benzoic acid fluorides was applicable to the selective transformation that formed the corresponding benzaldehyde derivatives. Benzoic acid fluoride **1b** and its derivatives bearing an alkyl or phenyl substituent at the benzene ring, **1c**−**g**, were successfully converted into aldehydes **2b**−**g** with excellent

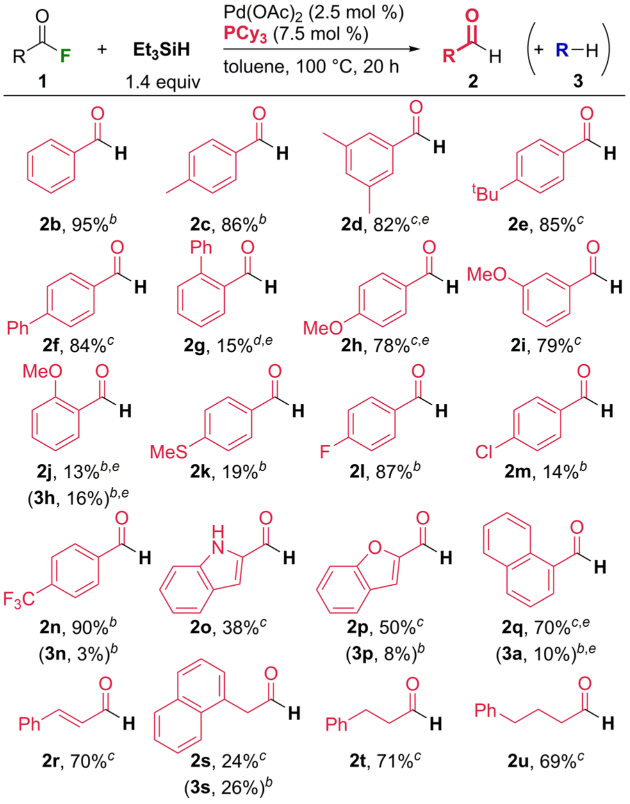
Table 1. Ligand Screening for the Divergent Conversion of Acyl Fluoride 1a[a]



			GC results (%)		
entry	ligand	conversion	**2a**	**3a**	selectivity (**2a**/**3a**)
1	PPh_3	21	2	<1	
2	$P(4\text{-}CF_3C_6H_4)_3$	12	<1	<1	
3	$P(4\text{-}MeOC_6H_4)_3$	83	53	9	85:15
4	JohnPhos	77	17	1	94:6
5	CyJohnPhos	63	10	11	48:52
6	P^tBu_3	31	<1	<1	
7	PCy_3	>99	77	2	97:3
8[b]	PCy_3	>99	92 (90)[c]	<1	99:1
9	DPPBz	>99	7	46	13:87
10	DPPE	>99	37	34	52:48
11	DCPE	>99	3	82	4:96
12[b]	DCPE	>99	7	84 (84)[c]	8:92
13	DPPP	>99	43	38	53:47
14	DPPF	>99	45	21	68:32
15	Xantphos	74	17	17	50:50
16[d]	PCy_3	10	0	0	
17[d]	DCPE	36	4	0	

[a] Reaction conditions: **1a** (0.2 mmol), Et_3SiH (0.28 mmol), $Pd(OAc)_2$ (5 mol %), and ligand (15 mol % of P) in toluene (0.2 mL) at 100 °C for 20 h. [b] **1a** (1 mmol), $Pd(OAc)_2$ (2.5 mol %), and ligand (7.5 mol % of P) in toluene (1 mL). [c] Isolated yield. [d] Without a palladium catalyst.

Scheme 3. Substrate Scope for the Production of Aldehydes 2[a]



[a] Reaction conditions: **1** (1.0 mmol), Et_3SiH (1.4 mmol), $Pd(OAc)_2$ (0.025 mmol), and PCy_3 (0.075 mmol) in toluene (1 mL) at 100 °C for 20 h. [b] GC yield. [c] Isolated yield. [d] ^1H NMR yield. [e] $Pd(OAc)_2$ (5 mol %, 0.05 mmol) and PCy_3 (15 mol %, 0.15 mmol).

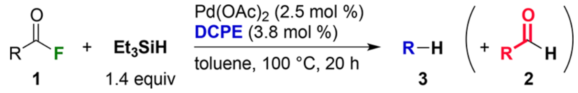
selectivity. Reactions of methoxy-substituted versions at the 4- and 3-positions, **1h** and **1i**, afforded the corresponding aldehydes **2h** and **2i** in high yields with good selectivity. When 2-methoxy **1j** was used as a starting substrate, however, the yield and selectivity of **2j** were decreased. Functional groups, including a sulfur and a halogen atom, **1k**−**n**, were also tolerant of the present non-decarbonylative conditions, giving **2k**−**n**. Several acyl fluorides containing heterocycles, such as an indole or a benzofuran moiety, and a 1-naphthyl one **1o**−**1q**, were available to provide **2o**−**q** with high selectivity. Vinylic carboxylic acid fluoride **1r**, which is derived from cinnamic acid, was also converted into aldehyde **2r**. The use of aliphatic acid derivative **1s** bearing a fluorocarbonyl group at its benzylic carbon failed to yield the desired selectivity of **2s**/**3s**, but the selective reaction of the starting acyl fluorides with longer linear alkyl chains, such as **1t** and **1u**, proceeded to form the corresponding aldehydes **2t** and **2u**, respectively.

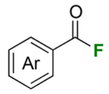
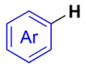
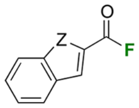
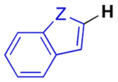
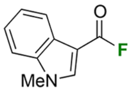
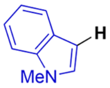
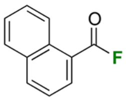
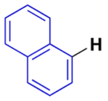
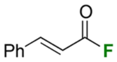
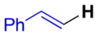
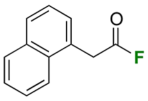
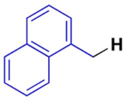
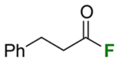
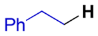
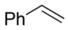
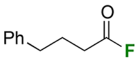
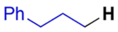
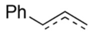
Next, we explored a decarbonylative reaction of acyl fluorides **1** utilizing DCPE as the ligand, as shown by entry 12 in Table 1. In a manner similar to that for the reaction of PCy_3 in the preparation of aldehydes, the complementary decarbonylative reaction was also applicable to various types of acyl fluorides **1**, leading to the corresponding hydrocarbons **3** with high yields and selectivities (Table 2). Benzoic acid fluoride analogues **1b** and **1d**−**n** undertook a decarbonylative reaction to produce arenes **3b** and **3d**−**n** in efficient yields and selectivities with good functional group tolerance (entries 1−12). Heteroaromatics and a fused aromatic substrate **1o**, **1p**, **1v**, and **1q**, were also available to form the corresponding aromatic compounds **3o**, **3p**, **3v**, and **3a**, respectively (entries 13−16). Although starting substrates bearing a fluorocarbonyl group at the vinylic carbon **1r** or benzylic carbon **1s** were available for decarbonylative conversion to form **3r** and **3s** (entries 17 and 18), aliphatic carboxylic acid fluorides with a β-hydrogen, **1t** and **1u**, did not provide the expected decarbonylative reduction products **3t** and **3u**. Then, the formation of aldehydes **2t** and **2u** was observed along with olefins **3r** and **3u′** via decarbonylation and β-hydrogen elimination (entries 19 and 20).

Plausible pathways of the divergent transformations of acyl fluoride **1** to aldehyde **2** or hydrocarbon **3** are shown in Figure 1. In both cases, for the production of **2** using PCy_3, or **3** using DCPE, each mechanism is possible beginning with the oxidative addition of an acyl C−F bond of **1** to palladium(0), which would form an acylpalladium fluoride species (RCO-[Pd]F). For the generation of **2** in the presence of PCy_3, transmetalation then occurs between the Pd−F and the Si−H of a hydrosilane, and the subsequent reductive elimination of the acyl C−H bond would provide aldehyde **2** (Figure 1A). On the other hand, when DCPE is used as a ligand, decarbonylation would proceed prior to the acyl C−H bond formation of aldehyde **2**, and then, the pathways involving transmetalation and C−H reductive elimination would result in the production of hydrocarbon **3** (Figure 1B).[14]

For both transformations of acyl fluoride **1l** into aldehyde **2l** by PCy_3, and into arene **3l** by DCPE, the rates of the reactions were affected by the initial ratios of the Pd/ligand. Monitoring of the reaction of **1l** and Et_3SiH with three different ratios of Pd/PCy_3 (1:2, 1:3, and 1:4) by ^{19}F NMR spectroscopy revealed that 1:3 and 1:4 Pd/PCy_3 ratios provided aldehyde **2l** at similar rates. However, the reaction rate was suppressed by a Pd/PCy_3 catalysis in a 1:2 ratio (Figure 2A). The effect of the ratio of Pd/DCPE was also significant in the conversion of **1l**

Table 2. Substrate Scope for the Production of Hydrocarbons 3[a]



entry	acyl fluoride **1**	product(s), yield(s) (%)[b]
		
1	**1b** (Ar = Ph)	**3b**, 74
2	**1d** (Ar = 3,5-$Me_2C_6H_3$)	**3d**, 65
3	**1e** (Ar = 4-$^tBuC_6H_4$)	**3e**, 76 (**2e**, 5)
4	**1f** (Ar = 4-PhC_6H_4)	**3f**, 70[c]
5	**1g** (Ar = 2-PhC_6H_4)	**3f**, 74[c]
6	**1h** (Ar = 4-$MeOC_6H_4$)	**3h**, 62 (**2h**, 19)
7	**1i** (Ar = 3-$MeOC_6H_4$)	**3h**, 78 (**2i**, 11)
8	**1j** (Ar = 2-$MeOC_6H_4$)	**3h**, 92
9	**1k** (Ar = 4-$MeSC_6H_4$)	**3k**, 45 (**2k**, 1)
10	**1l** (Ar = 4-FC_6H_4)	**3l**, 86 (**2l**, 7)
11	**1m** (Ar = 4-ClC_6H_4)	**3m**, 83 (**2m**, <5)
12	**1n** (Ar = 4-$CF_3C_6H_4$)	**3n**, 76 (**2n**, 5)
		
13	**1o** (Z = NH)	**3o**, 81
14	**1p** (Z = O)	**3p**, 89
15	 **1v**	 **3v**, 76[c]
16	 **1q**	 **3a**, 91[c]
17	 **1r**	 **3r**, 87
18	 **1s**	 **3s**, 15
19	 **1t**	 **3t**, trace (**2t**, 24)  **3r**, 33
20	 **1u**	 **3u**, 6 (**2u**, 25)  **3u'**, 20

[a]Reaction conditions: **1** (1.0 mmol), Et_3SiH (1.4 mmol), $Pd(OAc)_2$ (0.025 mmol), and DCPE (0.038 mmol) in toluene (1 mL) at 100 °C for 20 h. [b]GC yield. [c]Isolated yield.

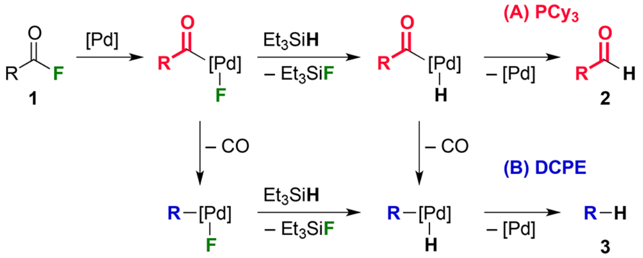


Figure 1. Plausible pathways for the production of (A) aldehyde **2** and (B) hydrocarbon **3**.

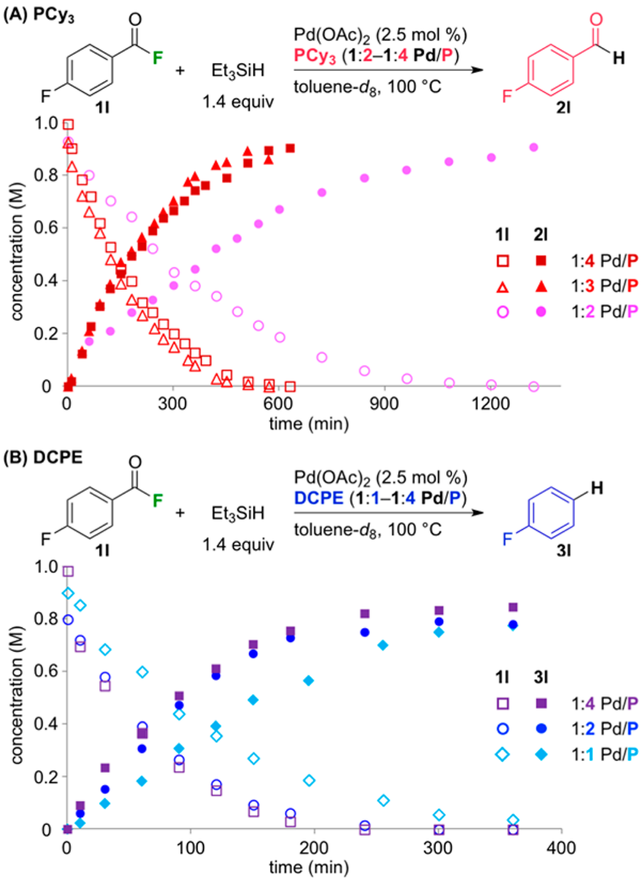


Figure 2. Time−concentration plots of the conversion of **1l**. Reaction conditions: **1l** (0.6 mmol), Et$_3$SiH (0.84 mmol), and Pd(OAc)$_2$ (0.015 mmol) in toluene-d_8 (0.6 mL) at 100 °C. (A) Formation of **2l** using PCy$_3$ (0.03−0.06 mmol). (B) Formation of **3l** using DCPE (0.0075−0.03 mmol). Concentrations of substrates were calculated by ^{19}F NMR analysis using CF$_3$C$_6$H$_5$ as an internal standard.

into arene **3l** (Figure 2B). The reaction of **1l** and Et$_3$SiH with 1:2 and 1:4 of Pd/P (1:1 and 1:2 of Pd/$\widehat{PP}$) proceeded to form **3l** in a similar manner, but the reaction became slower by a 1:1 ratio of Pd/P (1:0.5 of Pd/$\widehat{PP}$).

These kinetic profiles suggested that an essentially effective Pd/P ratio for non-decarbonylative reaction is 1:3 for Pd/PCy$_3$ and that for decarbonylative one is 1:2 for Pd/P (1:1 of Pd/DCPE). One of the possible explanations of the results is that the acylpalladium complex bearing three monodentate phosphines (1:3 Pd/P), which is coordinatively saturated, provides aldehydes prior to the decarbonylation (Figure 3A). In the case of the acylpalladium with one bidentate phosphine (1:2 Pd/P, 1:1 Pd/$\widehat{PP}$), on the other hand, the decarbonylation is more favorable due to the presence of an open coordination site at the palladium center (Figure 3B). However, the detailed mechanism of the ligand effects for the selectivity is unclear at this stage.[15]

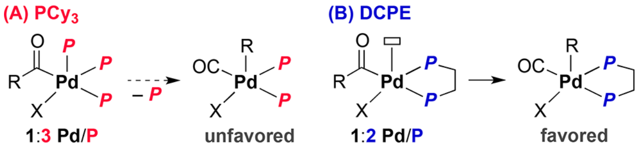


Figure 3. Possible intermediates (X = H or F) for the production of (A) aldehyde **2** and (B) hydrocarbon **3**.

In summary, we have developed the first palladium-catalyzed selective transformation of acyl fluorides using a hydrosilane. The decarbonylation process can be completely controlled with only a change of ligands, which affords different products in high selectivity: aldehydes by PCy$_3$ or hydrocarbons by DCPE. These applications, the detailed mechanistic investigations, and computational studies on the effect of the ligands are now underway by this research group.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b01582.

Experimental procedures and characterization data for all compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: yoheiogiwara@rs.tus.ac.jp.
*E-mail: sakachem@rs.noda.tus.ac.jp.

ORCID

Yohei Ogiwara: 0000-0003-1438-0916
Norio Sakai: 0000-0003-0722-4800

Notes

The authors declare no competing financial interest.

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