JOC Note

Palladium-Catalyzed 1,2-Addition of Potassium Aryl- and Alkenyltrifluoroborates to Aldehydes using Thioether−Imidazolinium Carbene Ligands

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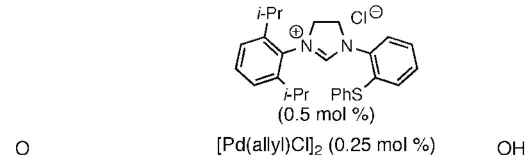

Palladium-catalyzed 1,2-addition of potassium aryl- and alkenyltrifluoroborates to aldehydes using thioether−imidazolinium carbene ligands proceeded readily under aqueous conditions. This process tolerated a diverse range of potassium trifluoroborate salts and aldehydes, giving a variety of carbinol derivatives with good to excellent yields.

Organoboron compounds are known as useful reagents for carbon−carbon bond formation with various electrophiles in the presence of transition metals.[1] Particularly, because of the usefulness of organoboronic acids such as low toxicity and easy manipulation[1] and the importance of the addition products as intermediates for the synthesis of biologically active compounds,[2] transition-metal-catalyzed 1,2-addition reactions of organoboronic acids to aldehydes have been attracting much attention since Miyaura and co-workers reported the rhodium-catalyzed 1,2-addition in 1998.[3] For this kind of reaction, several types of active catalysts have been developed, such as rhodium,[4,5] palladium,[6] nickel,[7] copper,[8] and platinum[9] complexes.

Recently, potassium organotrifluoroborates have been focused as alternatives to organoboronic acids because of their superior features.[10] Boronic acids often dimerize and trimerize to form boronic acids anhydrides and boroxines,[11] which make difficulties in the direct purification and in the determination of the exact stoichiometry for reactions. On the other hand, potassium trifluoroborate salts are quite highly air- and moisture-stable[12] crystalline solids that are more easily prepared, purified, and handled.[10] In spite of the advantages, examples of transition-metal-catalyzed 1,2-addition of potassium organotrifluoroborates to aldehydes are scarce, and only two types of rhodium(I)−phosphine complexes as catalysts for this reaction were reported.[10d,13] Herein, we would like to describe the palladium-catalyzed 1,2-addition of potassium aryl-, heteroaryl-, and alkenyltrifluorobo-

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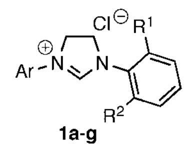
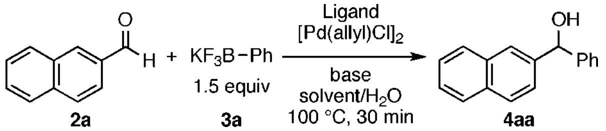


1a-g

1a: Ar= 2,4,6-trimethylphenyl, R^1= H, R^2= SMe
1b: Ar= 2,4,6-trimethylphenyl, R^1= H, R^2= SPh
1c: Ar= 2,4,6-trimethylphenyl, R^1= H, R^2= S*i*-Pr
1d: Ar= 2,6-diisopropylphenyl, R^1= H, R^2= SMe
1e: Ar= 2,6-diisopropylphenyl, R^1= H, R^2= SPh
1f: Ar= 2,6-diisopropylphenyl, R^1= H, R^2= S*i*-Pr
1g: Ar= 2,6-diisopropylphenyl, R^1, R^2= *i*-Pr

FIGURE 1. Precursors of *N*-heterocyclic carbene ligands.

TABLE 1. Palladium-Catalyzed 1,2-Addition of Potassium Phenyltrifluoroborate to 2-Naphthaldehyde Using Thioether−Imidazolinium Carbene Ligands under Various Reaction Conditions[a]



entry	ligand	base	solvent/H_2O	yield[b] (%)
1	**1a**	Cs_2CO_3	dioxane/H_2O (6/1)	74
2	**1b**	Cs_2CO_3	dioxane/H_2O (6/1)	56
3	**1c**	Cs_2CO_3	dioxane/H_2O (6/1)	73
4	**1d**	Cs_2CO_3	dioxane/H_2O (6/1)	85
5	**1e**	Cs_2CO_3	dioxane/H_2O (6/1)	89
6	**1f**	Cs_2CO_3	dioxane/H_2O (6/1)	86
7	**1g**	Cs_2CO_3	dioxane/H_2O (6/1)	0
8	PhSMe	Cs_2CO_3	dioxane/H_2O (6/1)	0
9	none	Cs_2CO_3	dioxane/H_2O (6/1)	0
10	**1e**	Cs_2CO_3	dioxane/H_2O (3/1)	75
11	**1e**	Cs_2CO_3	dioxane/H_2O (12/1)	69
12	**1e**	Cs_2CO_3	toluene/H_2O (6/1)	95
13	**1e**	Cs_2CO_3	DMA/H_2O (6/1)	0
14	**1e**	Cs_2CO_3	DMSO/H_2O (6/1)	0
15	**1e**	K_2CO_3	toluene/H_2O (6/1)	92
16	**1e**	Na_2CO_3	toluene/H_2O (6/1)	52
17	**1e**	K_3PO_4	toluene/H_2O (6/1)	32
18	**1e**	CsF	toluene/H_2O (6/1)	91

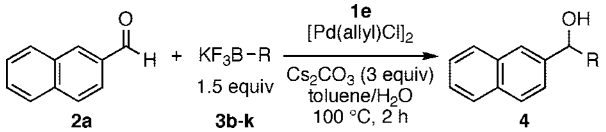
[a] Reaction conditions: 2-naphthaldehyde **2a** (0.6 mmol), potassium phenyltrifluoroborate **3a** (0.9 mmol), ligand (1 mol %), [Pd(allyl)Cl]$_2$ (0.5 mol %), base (1.8 mmol), solvent (1.5 mL), H_2O (0.125−0.5 mL), 100 °C, 30 min. [b] Isolated yield.

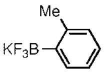
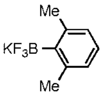
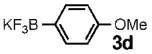
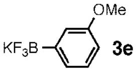
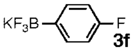
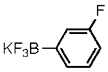
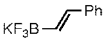
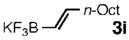
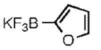
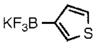
rates to aromatic, heteroaromatic, and aliphatic aldehydes using thioether−imidazolinium carbene ligands.

Initially, optimization of reaction conditions was conducted using potassium phenyltrifluoroborate **3a** and 2-naphthaldehyde **2a**. We examined the 1,2-addition with 1.0 mol % of catalysts (Pd/L = 1/1) generated in situ from thioether−imidazolinium chlorides **1a**−**f**[14] (Figure 1) and [Pd(allyl)Cl]$_2$ in the presence of cesium carbonate in dioxane/H_2O (6/1) at 100 °C for 30 min and found thioether−imidazolinium chloride **1e** was a superior heterobidentate carbene ligand[15] precursor (Table 1, entries 1−6). The monodentate carbene ligand precursor **1g** (SIPr·HCl) showed no reaction (entry 7). The control experiment using thioanisole or no imidazolinium chloride gave no conversion (entries 8 and 9).

The influence of solvents and the amount of water was examined. The rate of the reaction was dependent on the amount of water, and the reactions in dioxane/H_2O (3/1) and (12/1) led to lower yields (entries 5, 10, and 11). While the reaction in toluene/H_2O (6/1) afforded 95% yield (entry 12), highly polar solvents such as DMA and DMSO gave no conversion (entries 13 and 14). The examination of bases proved that cesium carbonate was the reagent of choice (entries 12 and 15−18).

TABLE 2. Palladium-Catalyzed 1,2-Addition of Potassium Aryl-, Heteroaryl-, and Alkenyltrifluoroborates to 2-Naphthaldehyde Using Thioether-Imidazolinium Carbene Ligand[a]



entry	KF_3B-R	product	yield (%)[b]
1	 **3b**	**4ab**	83
2	 **3c**	**4ac**	38
3	 **3d**	**4ad**	90
4	 **3e**	**4ae**	88
5	 **3f**	**4af**	83
6	 **3g**	**4ag**	87
7	 **3h**	**4ah**	92
8	 **3i**	**4ai**	65
9	 **3j**	**4aj**	30
10	 **3k**	**4ak**	82

[a] Reaction conditions: 2-naphthaldehyde **2a** (0.6 mmol), potassium aryl-, heteroaryl-, and alkenyltrifluoroborates **3b**-**k** (0.9 mmol), **1e** (0.5 mol %), [Pd(allyl)Cl]$_2$ (0.25 mol %), Cs_2CO_3 (1.8 mmol), toluene (1.5 mL), H_2O (0.25 mL), 100 °C, 2 h. [b] Isolated yield.

Investigation of potassium aryl-, heteroaryl-, and alkenyltrifluoroborates in the 1,2-addition reactions with 0.5 mol % of the catalyst using 2-naphthaldehyde **2a** was conducted (Table 2). While the potassium aryltrifluoroborate substituted at the 2-position (**3b**) was converted efficiently to give the adduct **4ab** with 83% yield (entry 1), the highly sterically hindered potassium 2,6-dimethylphenyltrifluoroborate **3c** reacted to afford 38% yield (entry 2). Both the electron-rich and -poor potassium aryltrifluoroborates **3d**−**g** gave the adducts **4ad**−**ag** with high yields (entries 3−6). The potassium alkenyltrifluoroborates **3h** and **3i** were still good partners, leading to 92% and 65% yields, respectively (entries 7 and 8). Potassium 2-furantrifluoroborate **3j** was less reactive to afford 30% yield (entry 9), whereas the reaction with potassium 3-thiophenetrifluoroborate **3k** proceeded smoothly with 82% yield (entry 10).

The influence of varying aromatic, heteroaromatic, and aliphatic aldehydes in the 1,2-addition with 0.5 mol % of the catalyst using potassium phenyltrifluoroborate **3a** was also investigated (Table 3). The electron-rich aromatic aldehyde **2b** reacted to give the adduct **4ba** with 85% yield (entry 1). The

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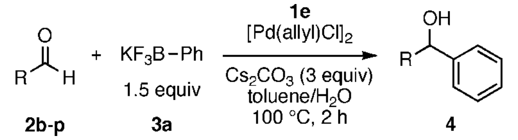
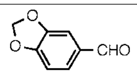
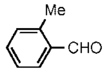
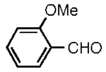
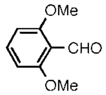
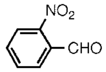
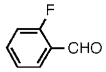
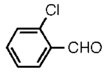
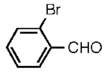
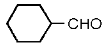
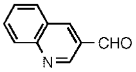
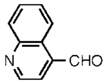
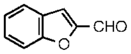
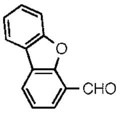
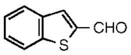
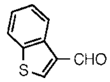
(15) Hemilabile behavior of thioether-functionalized NHC was investigated: Huynh, H. V.; Yeo, C. H.; Tan, G. K. *Chem. Commun.* **2006**, 3833–3835.

TABLE 3. Palladium-Catalyzed 1,2-Addition of Potassium Phenyltrifluoroborate to Aromatic, Heteroaromatic, and Aliphatic Aldehydes Using Thioether−Imidazolinium Carbene Ligand[a]



entry	RCHO	product	yield (%)[b]
1	 **2b**	**4ba**	85
2	 **2c**	**4ca**	89
3	 **2d**	**4da**	94
4	 **2e**	**4ea**	51
5	 **2f**	**4fa**	99
6	 **2g**	**4ga**	99
7	 **2h**	**4ha**	98
8	 **2i**	**4ia**	88
9	 **2j**	**4ja**	58
10	 **2k**	**4ka**	97
11	 **2l**	**4la**	93
12	 **2m**	**4ma**	98
13	 **2n**	**4na**	99
14	 **2o**	**4oa**	96
15	 **2p**	**4pa**	88

[a] Reaction conditions: aldehydes **2b-p** (0.6 mmol), potassium phenyltrifluoroborate **3a** (0.9 mmol), **1e** (0.5 mol %), [Pd(allyl)Cl]$_2$ (0.25 mol %), Cs$_2$CO$_3$ (1.8 mmol), toluene (1.5 mL), H$_2$O (0.25 mL), 100 °C, 2 h. [b] Isolated yield.

1,2-addition to the benzaldehydes substituted at the 2-position by electron-donating groups (**2c** and **2d**) proceeded readily with high yields (entries 2 and 3), and the electron-rich and sterically hindered 2,6-dimethoxybenzaldehyde **2e** led to the moderate yield (entry 4). The electron-poor aromatic aldehydes **2f−i** were converted easily affording excellent results (entries 5−8). Importantly, the halogen substituents on aromatic aldehydes were tolerated under the reaction condition, and undesired products such as the Suzuki coupling and reductive dehalogenation products were not detected. The 1,2-addition to the aliphatic aldehyde **2j** led to the acceptable yield (entry 9). Then, heteroaromatic aldehydes containing nitrogen, oxygen, and sulfur atoms were examined. The aldehydes **2k−p** were also good acceptors, giving the adducts **4ka−pa** with excellent yields (entries 10−15).

In summary, the palladium-catalyzed 1,2-additon reactions of potassium aryl- and alkenyltrifluoroborates to aldehydes using the thioether−imidazolinium carbene ligand were achieved in good to excellent yields. They were carried out rapidly using 0.5 mol % of catalyst loading with good substrate tolerance, giving a variety of carbinol derivatives. Mechanistic studies and the development of asymmetric versions are currently in progress in our research group.

Experimental Section

Typical Procedure of Palladium-Catalyzed 1,2-Addition Reaction Using Thioether−Imidazolinium Carbene Ligand. Under argon atmosphere, a reaction tube was charged with [Pd(allyl)Cl]$_2$ (0.55 mg, 1.5 μmol), thioether−imidazolinium chloride **1e** (1.35 mg, 3.0 μmol), and cesium carbonate (587 mg, 1.8 mmol), and then toluene (1.5 mL) was added. The mixture was stirred for 15 min at 80 °C and cooled to room temperature. Then, water (0.25 mL), 2-naphthaldehyde **2a** (94 mg, 0.6 mmol), and potassium 2,6-dimethylphenyltrifluoroborate **3c** (191 mg, 0.9 mmol) were added, and the reaction mixture was stirred at 100 °C for 2 h. The mixture was cooled to room temperature, water and satd NH$_4$Cl were added, and then the mixture was extracted with CH$_2$Cl$_2$. The combined organic layers were washed with brine and then dried over MgSO$_4$. Concentration and purification through silica gel column chromatography gave the product **4ac**.

2,6-Dimethylphenyl(2-naphthyl)methanol (4ac) (Table 2, Entry 2). Silica gel column chromatography (hexane/AcOEt = 10/1) gave 60 mg (0.23 mmol, 38% yield) of the product as a colorless solid. Mp: 90−91 °C. ^{1}H NMR (CDCl$_3$) δ: 2.28 (1H, d, J = 3.5 Hz), 2.31 (6H, s), 6.52 (1H, d, J = 3.5 Hz), 7.06 (2H, d, J = 7.5 Hz), 7.16 (1H, t, J = 7.5 Hz), 7.35 (1H, dd, J = 1.5, 8.5 Hz), 7.43−7.47 (2H, m), 7.76−7.82 (4H, m). ^{13}C NMR (CDCl$_3$) δ: 20.7, 71.3, 123.9, 124.1, 125.6, 125.9, 127.5, 127.9, 128.0, 129.4, 132.3, 133.2, 137.2, 139.1, 140.3. IR (KBr) ν: 3560 cm^{-1}. HRMS (EI): calcd for C$_{19}$H$_{18}$O (M$^+$) 262.1358, found 262.1358.

3-Methoxyphenyl(2-naphthyl)methanol (4ae) (Table 2, Entry 4). Silica gel column chromatography (hexane/AcOEt = 5/1) gave 139 mg (0.53 mmol, 88% yield) of the product as colorless oil. ^{1}H NMR (CDCl$_3$) δ: 2.31 (1H, d, J = 3.5 Hz), 3.78 (3H, s), 5.98 (1H, d, J = 3.5 Hz), 6.81−6.83 (1H, m), 6.99−7.00 (2H, m), 7.24−7.27 (1H, m), 7.43−7.50 (3H, m), 7.79−7.85 (3H, m), 7.89 (1H, s). ^{13}C NMR (CDCl$_3$) δ: 55.2, 76.2, 112.2, 113.0, 119.0, 124.7, 125.0, 125.9, 126.1, 127.6, 128.1, 128.3, 129.5, 132.9, 133.2, 141.0, 145.3, 159.8. IR (neat) ν: 1260, 3410 cm^{-1}. HRMS (EI): calcd for C$_{18}$H$_{16}$O$_2$ (M$^+$) 264.1150, found 264.1149.

3-Fluorophenyl(2-naphthyl)methanol (4ag) (Table 2, Entry 6). Silica gel column chromatography (hexane/AcOEt = 10/1) gave 131 mg (0.52 mmol, 87% yield) of the product as a colorless solid. Mp: 63−64 °C. ^{1}H NMR (CDCl$_3$) δ: 2.34 (1H, d, J = 3.5 Hz), 6.00 (1H, d, J = 3.5 Hz), 6.94−6.98 (1H, m), 7.16−7.20 (2H, m), 7.28−7.32 (1H, m), 7.42 (1H, dd, J = 1.5, 8.5 Hz), 7.46−7.51 (2H, m), 7.80−7.86 (3H, m), 7.87 (1H, s). ^{13}C NMR (CDCl$_3$) δ: 75.8, (d, J = 1.5 Hz), 113.5 (d, J = 21.9 Hz), 114.4 (d, J = 20.9 Hz), 122.2 (d, J = 2.6 Hz), 124.5, 125.2, 126.2, 126.3, 127.7, 128.1, 128.6, 130.0 (d, J = 8.1), 133.0, 133.2, 140.6, 146.1 (d, J = 6.8 Hz), 162.9 (d, J = 244.6 Hz). IR (KBr) ν: 1240, 3350 cm^{-1}. EIMS *m/z*: 252 (M$^+$). Anal. Calcd for C$_{17}$H$_{13}$OF: C, 80.93; H, 5.19. Found: C, 80.81; H, 5.16.

(*E*)-1-Decenyl(2-naphthyl)methanol (4ai) (Table 2, Entry 8). Silica gel column chromatography (hexane/AcOEt = 20/1) gave

115 mg (0.39 mmol, 65% yield) of the product as colorless oil. ^{1}H NMR ($CDCl_3$) δ: 0.87 (3H, t, $J = 7.5$ Hz), 1.25−1.32 (10H, m), 1.37−1.42 (2H, m), 1.95 (1H, d, $J = 3.5$ Hz), 2.07 (2H, q, $J = 7.0$ Hz), 5.34 (1H, dd, $J = 3.0, 6.5$ Hz), 5.73 (1H, dd, $J = 6.5, 15.0$ Hz), 5.82 (1H, dt, $J = 6.5, 15.0$ Hz), 7.44−7.49 (3H, m), 7.81−7.84 (4H, m). ^{13}C NMR ($CDCl_3$) δ: 14.1, 22.7, 29.0, 29.2, 29.3, 29.4, 31.9, 32.2, 75.3, 124.5, 125.8, 126.1, 127.6, 128.0, 128.2, 132.1, 132.9, 133.2, 133.3, 140.8. IR (neat) ν: 3350 cm^{-1}. HRMS (EI): calcd for $C_{21}H_{28}O$ (M^+) 296.2140, found 296.2140.

4-Dibenzofuranyl(phenyl)methanol (4na) (Table 3, Entry 13). Silica gel column chromatography (hexane/AcOEt = 10/1) gave 163 mg (0.59 mmol, 99% yield) of the product as colorless oil. ^{1}H NMR ($CDCl_3$) δ: 2.64 (1H, d, $J = 4.0$ Hz), 6.48 (1H, d, $J = 4.0$ Hz), 7.27 (1H, t, $J = 7.5$ Hz), 7.34 (4H, t, $J = 7.5$ Hz), 7.46 (1H, t, $J = 7.5$ Hz), 7.50 (1H, d, $J = 7.5$ Hz), 7.53 (2H, d, $J = 7.5$ Hz), 7.58 (1H, d, $J = 7.5$ Hz), 7.88 (1H, d, $J = 7.5$ Hz), 7.95 (1H, d, $J = 7.5$ Hz). ^{13}C NMR ($CDCl_3$) δ: 71.4, 111.7, 119.8, 120.6, 122.7, 122.9, 124.0, 124.2, 124.5, 126.5, 127.1, 127.5, 127.9, 128.3, 142.7, 153.1, 156.0. IR (neat) ν: 3380 cm^{-1}. HRMS (EI): calcd for $C_{19}H_{14}O_2$ (M^+) 274.0994, found 274.0994.

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Supporting Information Available: General procedure of palladium-catalyzed 1,2-addition of potassium organotrifluoroborates to aldehydes using thioether−imidazolinium carbene ligands, spectral data of products, and copies of ^{1}H and ^{13}C NMR spectra of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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