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Nickel-Copper-Catalyzed Hydroacylation of Vinylarenes with Acyl Fluorides and Hydrosilanes

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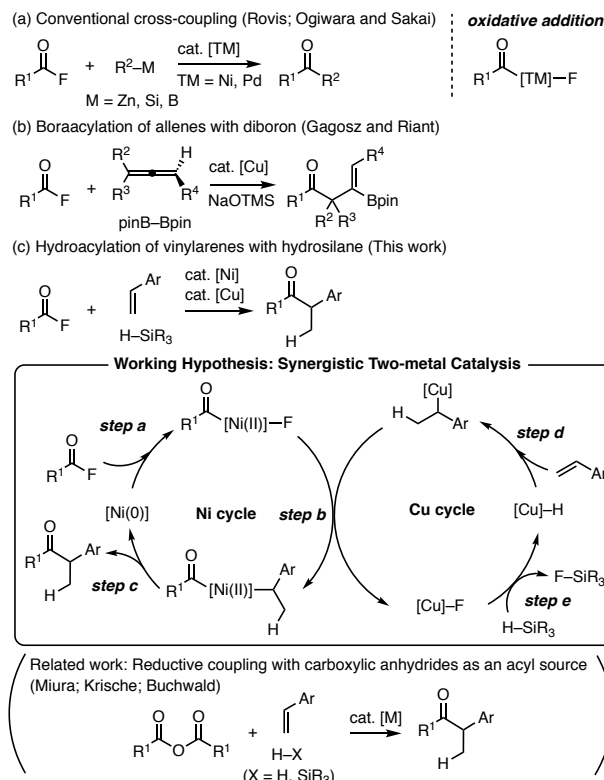
Abstract: The hydroacylation of vinylarenes with acyl fluorides and hydrosilanes by synergistic Ni/Cu two-metal catalysis was developed, giving the corresponding branched ketone products. The reaction occurs under mild conditions at 25–80 °C and tolerates base-sensitive functional groups such as methoxycarbonyl and acetoxy groups.

Acyl fluorides, which are easily prepared from carboxylic acids,^[1] are less common as acylating reagents than the corresponding chlorides and bromides due to their inertness as acylating reagents under conventional conditions. However, the use of acyl fluorides as reagents in organic synthesis through activation of the C–F bond have attracted growing interest in recent years, offering new types of molecular transformations that have not been achieved with acyl chlorides or bromides. Generally, the fluorides show better tolerance toward nucleophilic or basic functional groups than the chlorides and bromides. A pioneering work by Rovis described an efficient ketone synthesis through Ni-catalyzed cross-coupling of acyl fluorides with organozincs (Scheme 1a).^[2] Later, Ogiwara and Sakai reported similar transformations using organosilicons or organoborons by Pd catalysis.^[3] These reactions were initiated by oxidative addition of the acyl C(sp²)–F bonds to low-valent metal complexes, producing acyl metal intermediates.^[4,5]

Catalytic *in situ* generation of nucleophilic organometallic species via insertion of unsaturated C–C bonds to M–X bonds followed by trapping with acyl electrophiles affords attractive synthetic methods, which can avoid the use of stoichiometric amounts of pre-formed organometallic reagents.^[6] Metal-catalyzed reductive coupling of C–C unsaturated compounds with electrophiles is representative.^[7,8] For acylation, carboxylic anhydrides were used as acylating electrophiles in the reaction of vinylarenes in the presence of hydrosilanes or H₂ as H sources.^[6a,7a,b] More recently, Gagosz and Riant used acyl

fluorides as acylating reagents for the Cu-catalyzed boraacylation of allenes with bis(pinacolato)diboron (Scheme 1b).^[9]

Our long-standing interest in synergistic two-metal catalysis prompted us to explore the possibility of enabling the hydroacylation of vinylarenes with acyl fluorides and hydrosilanes by synergistic Ni/Cu two-metal catalysis.^[10–15] As shown in Scheme 1c, an acyl fluoride is activated through oxidative addition to a Ni(0) complex (step a). Concurrently, a vinylarene is converted to a nucleophilic alkylcopper species *via* insertion into a Cu–H species (hydrocupration, step d)^[16] that is generated *in situ* from a Cu–F species with a hydrosilane (step e).^[17] The two catalytic species meet and transmetalation occurs to give the corresponding diorganonickel(II) complex with simultaneous regeneration of the Cu–F species (step b). Finally, reductive elimination of the diorganonickel(II) complex furnishes the hydroacylation product (step c) and the Ni(0) species to complete the two-cycle catalytic reaction pathway.^[18]



Scheme 1. Transition metal catalysis using acyl fluorides as acyl sources.

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To this end, the conditions were optimized for the reaction between benzoyl fluoride (**1a**) and styrene (**2a**). The results are summarized in Table 1, with the optimal conditions given in entry 1. Namely, a THF solution of a Ni catalyst was prepared from [Ni(cod)₂] (5 mol%) and DCYPBz (5 mol%), featuring high electron-donating and rigid chelating properties, at room temperature.^[19] Meanwhile, a Cu catalyst was prepared from CuF₂ (10 mol%) and DPPBz (10 mol%) in THF at room temperature. To the Cu catalyst solution, HSiMe(OMe)₂ (2 eq) and styrene (**2a**, 2.5 eq), benzoyl fluoride (**1a**, 0.15 mmol), and the Ni catalyst solution were successively added in this order. The resulting mixture was stirred at 25 °C for 20 h to give the branched

hydroacylation product **3a** as a single constitutional isomer in 71% yield (¹H NMR analysis) along with its carbonyl reduction product **4a** (6%).^[20] No decarbonylative coupling product (1,1-diphenylethylene) was observed in the crude product.^[5] Silica gel column chromatography and preparative TLC purification gave analytically pure **3a** in 52% yield. Control experiments using a single metal component confirmed that both Ni and Cu were indispensable for the hydroacylation to occur (entries 2 and 3). With the synergistic Ni/Cu catalysis, the use of benzoyl chloride instead of the fluoride **1a** induced no hydroacylation (entry 4),^[21] indicating the utility of acyl fluorides as acylating reagents.

Table 1. Conditions for the reaction of benzoyl fluoride (**1a**) and styrene (**2a**) with hydrosilane^[a]

Entry	Ni catalyst		Cu catalyst		Hydrosilane	NMR Yield [%]	
	Metal	Ligand	Metal	Ligand		3a	4a
1	[Ni(cod) ₂]	DCYPBz	CuF ₂	DPPBz	HSiMe(OMe) ₂	71 (52) ^[b]	6
2	none	none	CuF ₂	DPPBz	HSiMe(OMe) ₂	0	0
3	[Ni(cod) ₂]	DCYPBz	none	none	HSiMe(OMe) ₂	0	0
4 ^[c]	[Ni(cod) ₂]	DCYPBz	CuF ₂	DPPBz	HSiMe(OMe) ₂	0	0
5	[Ni(cod) ₂]	DPPBz	CuF ₂	DCYPBz	HSiMe(OMe) ₂	65	7
6	[Ni(cod) ₂]	DCYPBz	CuF ₂	DCYPBz	HSiMe(OMe) ₂	66	9
7	[Ni(cod) ₂]	DPPBz	CuF ₂	DPPBz	HSiMe(OMe) ₂	0	0
8	[Ni(cod) ₂]	DCYPE	CuF ₂	DPPBz	HSiMe(OMe) ₂	29	0
9	[Ni(cod) ₂]	PCy ₃ (10 mol%)	CuF ₂	DPPBz	HSiMe(OMe) ₂	0	0
10	[Ni(cod) ₂]	IPr (10 mol%)	CuF ₂	DPPBz	HSiMe(OMe) ₂	0	0
11	Ni(OAc) ₂	DCYPBz	CuF ₂	DPPBz	HSiMe(OMe) ₂	55	8
12	NiCl ₂	DCYPBz	CuF ₂	DPPBz	HSiMe(OMe) ₂	8	0
13	[Pd(dba) ₂]	DCYPBz	CuF ₂	DPPBz	HSiMe(OMe) ₂	40	8
14	[Ni(cod) ₂]	DCYPBz	CuF ₂	SciOPP	HSiMe(OMe) ₂	65	4
15	[Ni(cod) ₂]	DCYPBz	CuF ₂	PS-DPPBz	HSiMe(OMe) ₂	5	0
16	[Ni(cod) ₂]	DCYPBz	CuF ₂	PCy ₃ (20 mol%)	HSiMe(OMe) ₂	20	0
17	[Ni(cod) ₂]	DCYPBz	CuF ₂	IPr (20 mol%)	HSiMe(OMe) ₂	0	0
18	[Ni(cod) ₂]	DCYPBz	CuCl/NaOtBu	DPPBz	HSiMe(OMe) ₂	0	0
19	[Ni(cod) ₂]	DCYPBz	Cu(OAc) ₂	DPPBz	HSiMe(OMe) ₂	20	9
20	[Ni(cod) ₂]	DCYPBz	CuF ₂	DPPBz	PMHS	70	20
21	[Ni(cod) ₂]	DCYPBz	CuF ₂	DPPBz	HSi(OEt) ₃	59	12
22	[Ni(cod) ₂]	DCYPBz	CuF ₂	DPPBz	H ₃ SiPh	0	0

[a] **1a** (0.15 mmol), **2a** (0.375 mmol), [Ni] (5 mol%, M/L 1:1), [Cu] (10 mol%, M/L 1:1), hydrosilane (0.30 mmol), THF (0.3 mL), 25 °C, 20 h. [b] Isolated yield. [c] Using benzoyl chloride instead of **1a**.

When the metal-ligand combinations were interchanged (Ni-DPPBz and Cu-DCYPBz) or DCYPBz was employed for both the Ni and Cu systems, the yield of the hydroacylation product (**3a**) was only marginally decreased (65 and 66% yields, respectively, Table 1, entries 5 and 6). In sharp contrast, the use of DPPBz for both the Ni and Cu systems resulted in no hydroacylation, while reduction of **1a** occurred to give benzyl alcohol (entry 7). These results suggest the critical importance of the existence of the Ni-DCYPBz species and the occurrence of partial ligand exchange between the Ni and Cu systems to form the active Ni-DCYPBz species when the metals and the ligands were premixed in the wrong order as in entry 5.^[22]

The effects of other ligands premixed with [Ni(cod)₂] are shown in Table 1, entries 8–10. DCYPE, having a flexible ethylene linker between the two Cy₂P groups, decreased the yield (29%, entry 8). Monodentate ligands such as PCy₃ and IPr were ineffective (entries 9 and 10). An air-stable Ni(II) complex Ni(OAc)₂ was applicable, but less effective than [Ni(cod)₂] (55%, entry 11). NiCl₂ was not suitable (8%, entry 12). A Pd catalyst prepared from [Pd(dba)₂] and DCYPBz also induced the hydroacylation, but did not improve the yield over that obtained with the Ni catalyst (40%, entry 13).

Table 1 also includes effects of other parameters with respect to the Cu catalyst system (entries 14–22). The sterically demanding DPPBz-type ligand SciOPP showed a ligand effect similar to DPPBz (65%, entry 14). The polystyrene-cross-linking DPPBz-type ligand, PS-DPPBz, the utility of which was previously demonstrated in our studies on Cu catalysis,^[23] was much less effective than the parent soluble ligand DPPBz (5%, entry 15). Monodentate ligands such as PCy₃ and IPr did not give an efficient catalyst (entries 16 and 17). The use of other copper sources such as CuCl/NaOtBu and Cu(OAc)₂, instead of CuF₂, caused a decrease in the yields (0% and 20%, entries 18 and 19), indicating that the fluoride ligand on Cu was important for the reaction with the hydrosilane to produce the Cu–H species (Scheme 1c, step e). Changing HSiMe(OMe)₂ to other alkoxy-substituted hydrosilanes such as PMHS and HSi(OEt)₃ was possible while maintaining similar reaction efficacies (70% and 59%, entries 20 and 21), but a monoorgano-substituted silane, H₃SiPh, was not effective (entry 22).

With the combination of the [Ni(cod)₂]/DCYPBz and CuF₂/DPPBz system in the presence of HSiMe(OMe)₂, various branched hydroacylation products **3** were obtained from **1** and **2** (Table 2). The 4-substituted styrenes **2b–2f** underwent hydroacylation with **1a**, giving **3b–3f** in 30–68% yields (entries 1–5). Notably, base-sensitive functional groups such as methoxycarbonyl (**3e**) and acetoxyl (**3f**) groups on the benzene ring were tolerated. The reaction of 4-vinylpyridine (**2g**) with **1a** proceeded cleanly to give **3g** in 70% yield (entry 6). When benzoyl chloride was used instead of **1a** in this reaction, no hydroacylation product was obtained due to immediate occurrence of *N*-acylation of **2g** to give the corresponding pyridinium salt. 2-Vinylpyridine (**2h**) was also a suitable substrate for the protocol with acyl fluoride **1a** (**3h**, entry 7).

Table 2. Scope of acyl fluorides (**1**) and vinylarenes (**2**)

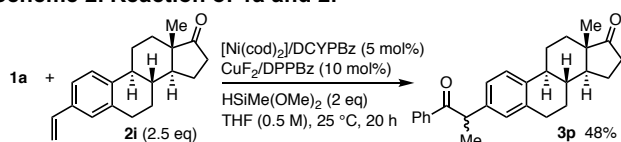
$ \begin{array}{c} \text{R}^1-\text{C}(=\text{O})-\text{F} \\ \mathbf{1} \end{array} + \begin{array}{c} \text{Ar} \\ \\ \text{CH}=\text{CH}_2 \\ \mathbf{2} \text{ (2.5 eq)} \end{array} \xrightarrow[\text{THF (0.5 M), 25 }^\circ\text{C, 20 h}]{\begin{array}{l} \text{[Ni(cod)}_2\text{]/DCYPBz (5 mol\%)} \\ \text{CuF}_2\text{/DPPBz (10 mol\%)} \\ \text{HSiMe(OMe)}_2 \text{ (2.0 eq)} \end{array}} \begin{array}{c} \text{R}^1-\text{C}(=\text{O})-\text{CH}(\text{Ar})-\text{CH}_3 \\ \mathbf{3} \end{array} $				
Entry	Acyl Fluorides	Vinylarenes	Product (3)	Yield [%]
1	1a	2b	3b	44
2	1a	2c	3c	47
3	1a	2d	3d	68
4	1a	2e	3e	30
5	1a	2f	3f	63
6	1a	2g	3g	70
7	1a	2h	3h	40
8 ^[b,c]	1b	2a	3i	35
9 ^[b]	1b	2g	3j	69
10 ^[c]	1c	2a	3k	49
11	1c	2g	3l	48
12 ^[c]	1d	2g	3m	43
13 ^[b,c]	1e	2g	3n	50
14 ^[b,d]	1f	2g	3o	47

[a] **1** (0.15 mmol), **2** (0.375 mmol), [Ni(cod)₂]/DCYPBz (5 mol%), CuF₂/DPPBz (10 mol%), HSiMe(OMe)₂ (0.30 mmol), THF (0.3 mL), 25 °C, 20 h. Isolated yields. [b] SciOPP was used as a ligand on Cu instead of DPPBz. [c] 60 °C. [d] 80 °C.

In addition to an electronically non-biased acid fluoride (**1b**), electron-rich and -poor acid fluorides **1c–1e** participated in the hydroacylation of vinylarenes **2a** or **2g** at 25–60 °C (Table 2, entries 8–13).^[24] In some cases, the use of SciOPP instead of DPPBz on Cu increased the yields. Notably, the C(sp²)–Cl bond on the benzene ring, which can undergo oxidative addition to Ni(0) species, was tolerated.^[25] *N*-Methyl-2-indolyl carbonyl fluoride reacted with **2g** at 80 °C, giving **3o** in 47% yield (entry 14). Neither aliphatic acid fluorides nor aliphatic alkenes provided the hydroacylation products **3**.

Finally, the synergistic Ni/Cu two-metal catalyst was applied to the derivatization of a complex molecule. Vinylestrone **2i** underwent hydroacylation with **1a** and HSiMe(OMe)₂ at 25 °C, affording **3p** as a 1:1 diastereomeric mixture in 48% yield without reduction of the cyclopentanone moiety.^[26]

Scheme 2. Reaction of 1a and 2i



In summary, the hydroacylation of vinylarenes with acyl fluorides and hydrosilanes by synergistic Ni/Cu two-metal catalysis was developed. The use of DCYPBz as a ligand with its electron-donating, sterically demanding, and rigid properties was effective for producing the catalytically active Ni species. The stability of the acyl fluorides and the mildness of the reaction conditions are attractive features of this alkene hydroacylation protocol. Further studies on synergistic two-metal catalysis for efficient C–F transformations are ongoing in our laboratory.

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- [26] For Ru-catalyzed hydroacylation of **2i** with benzaldehyde to form **3p**, see: J. Kim, C. S. Yi, *ACS Catal.* **2016**, 6, 3336–3339.

Synergistic Ni/Cu Two-Metal Catalysis

The hydroacylation of vinylarenes with acyl fluorides and hydrosilanes by synergistic Ni/Cu two-metal catalysis was developed, giving the corresponding branched ketone products. The reaction occurs under mild conditions at 25–80 °C and tolerates base-sensitive functional groups such as methoxycarbonyl and acetoxy groups.

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**Nickel-Copper-Catalyzed
Hydroacylation of Vinylarenes with
Acyl Fluorides and Hydrosilanes**