

# **CHEMISTRY** A European Journal



## Accepted Article

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

Authors: Yusuke Ueda, Tomohiro Iwai, and Masaya Sawamura

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Chem. Eur. J. 10.1002/chem.201900822

Link to VoR: http://dx.doi.org/10.1002/chem.201900822

Supported by ACES



## COMMUNICATION

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

Yusuke Ueda, Tomohiro Iwai,\* and Masaya Sawamura\*

**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,<sup>[1]</sup> 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).<sup>[2]</sup> Later, Ogiwara and Sakai reported similar transformations using organosilicons or organoborons by Pd catalysis.<sup>[3]</sup> These reactions were initiated by oxidative addition of the acyl C(sp<sup>2</sup>)-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.<sup>[6]</sup> Metal-catalyzed reductive coupling of C–C unsaturated compounds with electrophiles is representative.<sup>[7,8]</sup> For acylation, carboxylic anhydrides were used as acylating electrophiles in the reaction of vinylarenes in the presence of hydrosilanes or H<sub>2</sub> as H sources.<sup>[6a,7a,b]</sup> More recently, Gagosz and Riant used acyl

 [\*] Prof. Dr. M. Sawamura Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University Kita 21, Nishi 10, Kita-ku, Sapporo 001-0021 (Japan) E-mail: <u>sawamura@sci.hokudai.ac.jp</u>
 Y. Ueda, Dr. T. Iwai, Prof. Dr. M. Sawamura Department of Chemistry, Faculty of Science, Hokkaido University Sapporo 060-0810 (Japan)

E-mail: <u>iwai-t@sci.hokudai.ac.jp</u> sawamura@sci.hokudai.ac.jp Homepage: <u>http://wwwchem.sci.hokudai.ac.jp/~orgmet/</u>

Supporting information for this article is given via a link at the end of the document.

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

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.<sup>[10-15]</sup> 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)<sup>[16]</sup> that is generated *in situ* from a Cu–F species with a hydrosilane (step e).<sup>[17]</sup> 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.<sup>[18]</sup>



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

#### COMMUNICATION

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)<sub>2</sub>] (5 mol%) and DCYPBz (5 mol%), featuring high electron-donating and rigid chelating properties, at room temperature.<sup>[19]</sup> Meanwhile, a Cu catalyst was prepared from CuF<sub>2</sub> (10 mol%) and DPPBz (10 mol%) in THF at room temperature. To the Cu catalyst solution, HSiMe(OMe)<sub>2</sub> (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 (<sup>1</sup>H NMR analysis) along with its carbonyl reduction product **4a** (6%).<sup>[20]</sup> No decarbonylative coupling product (1,1-diphenylethylene) was observed in the crude product.<sup>[5]</sup> 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),<sup>[21]</sup> indicating the utility of acyl fluorides as acylating reagents.

 Table 1. Conditions for the reaction of benzoyl fluoride (1a) and styrene (2a) with hydrosilane<sup>[a]</sup>



[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**.

## COMMUNICATION

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.<sup>[22]</sup>

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 Cy<sub>2</sub>P groups, decreased the yield (29%, entry 8). Monodentate ligands such as PCy<sub>3</sub> and IPr were ineffective (entries 9 and 10). An air-stable Ni(II) complex Ni(OAc)<sub>2</sub> was applicable, but less effective than  $[Ni(cod)_2]$  (55%, entry 11). NiCl<sub>2</sub> 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)<sub>2</sub>, instead of CuF<sub>2</sub>, 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)<sub>2</sub> to other alkoxysubstituted hydrosilanes such as PMHS and HSi(OEt)<sub>3</sub> was possible while maintaining similar reaction efficacies (70% and 59%, entries 20 and 21), but a monoorgano-substituted silane, H<sub>3</sub>SiPh, was not effective (entry 22).

With the combination of the [Ni(cod)<sub>2</sub>]/DCYPBz and CuF<sub>2</sub>/DPPBz system in the presence of HSiMe(OMe)<sub>2</sub>, 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 acetoxy (**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).

#### WILEY-VCH

Table 2. Scope of acyl fluorides (1) and vinylarenes (2)				
	O Ar [Ni(cod) <sub>2</sub> ]/DCYPBz (5 mol%) O CYPBz (10 mol%) Ar			
	$R^1 \wedge F^+ \parallel$	HSiMe(OMe)	2 (2.0 eq) R <sup>1</sup> Ar	
	ι <b>ε</b> (ε.υ	eq) THF (0.5 M),	25 °C, 20 h 3 Me	
Entry	Acyl Fluorides	Vinylarenes	Product (3)	Yield [%]
		rBu	Q ℓ <sup>tBu</sup>	
1	1a	2b	Ph	44
			Me 3b	
2	10	$\bigwedge^{F}$	Î	47
2	Ta	20	Ph A	47
		CN		
3	1a			68
-		2d	Pn Y Su Me	
		CO <sub>2</sub> Me	0 CO <sub>2</sub> Me	
4	1a	2e	Ph 3e	30
			Me	
_		OAc	O OAc	
5	1a	2f	Ph 3f	63
		" 	Me	
6	1a			70
		2g	Me <b>3g</b>	
		N	o N	
7	1a	25	Ph 3h	40
	0	2	Me	
<b>Q</b> [b,c]	, T <sub>F</sub>	22	, i l	35
	Me 1b	20	Me 3i	55
9 <sup>[b]</sup>	1b	2α		69
-		-3	Me 3j	
	Q		o 🦳	
10 <sup>[c]</sup>	F	2a		49
	MeO 1c		MeO Me 3k	
			o n	
11	1c	2g		48
			MeO Me 3I	
	0			
12 <sup>[c]</sup>	F	2g		43
	CI 1d		CI Me 3m	
	ہ ا			
13 <sup>[b,c]</sup>		'⊦ 2g	Me 3n	50
	MeO <sub>2</sub> C 💛		MeO <sub>2</sub> C <sup>2</sup> ····································	
	چ بار	_		
14 <sup>[D,d]</sup>	N. F	2g		47

[a] 1 (0.15 mmol), 2 (0.375 mmol), [Ni(cod)<sub>2</sub>]/DCYPBz (5 mol%), CuF<sub>2</sub>/DPPBz (10 mol%), HSiMe(OMe)<sub>2</sub> (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.

## COMMUNICATION

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).<sup>[24]</sup> In some cases, the use of SciOPP instead of DPPBz on Cu increased the yields. Notably, the C(sp<sup>2</sup>)–Cl bond on the benzene ring, which can undergo oxidative addition to Ni(0) species, was tolerated.<sup>[25]</sup> *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)<sub>2</sub> at 25 °C, affording **3p** as a 1:1 diastereomeric mixture in 48% yield without reduction of the cyclopentanone moiety.<sup>[26]</sup>

#### 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.

#### Acknowledgements

This work was supported by JSPS KAKENHI Grant Number JP 17H04877 in Young Scientists (A) to T.I., and by JSPS KAKENHI Grant Number JP15H05801 in Precisely Designed Catalysts with Customized Scaffolding to M.S.

**Keywords:** nickel • copper • cooperative catalysis • acyl fluorides • hydroacylation

- For selected papers, see: a) G. A. Olah, S. J. Kuhn, J. Org. Chem. 1961, 26, 225–227; b) L. A. Carpino, D. Sadat-Aalaee, H. G. Chao, R. J. DeSelms, J. Am. Chem. Soc. 1990, 112, 9652–9654; c) T. Scattolin, K. Deckers, F. Schoenebeck, Org. Lett. 2017, 19, 5740–5743.
- [2] Y. Zhang, T. Rovis, J. Am. Chem. Soc. 2004, 126, 15964–15965.
- a) Y. Ogiwara, Y. Maegawa, D. Sakino, N. Sakai, *Chem. Lett.* 2016, 45, 790–792; b) Y. Ogiwara, D. Sakino, Y. Sakurai, N. Sakai, *Eur. J. Org. Chem.* 2017, 2017, 4324–4327.
- [4] a) D. R. Fahey, J. E. Mahan, J. Am. Chem. Soc. 1977, 99, 2501–2508.
  For isolation of the oxidative addition product [Ni(PhCO)F(PEt<sub>3</sub>)<sub>2</sub>], see:
  b) C. A. Malapit, J. R. Bour, C. E. Brigham, M. S. Sanford, *Nature* 2018, 563, 100–104.
- [5] For decarbonylative transformations of acyl fluorides with transition metal catalysts, see: Y. Ogiwara, Y. Sakurai, H. Hattori, N. Sakai, Org. Lett.

**2018**, 20, 4204–4208; b) S. T. Keaveney, F. Schoenebeck, *Angew. Chem.* **2018**, 130, 4137–4141; *Angew. Chem. Int. Ed.* **2018**, 57, 4073–4077; c) Okuda, J. Xu, T. Ishida, C. Wang, Y. Nishihara, *ACS Omega* **2018**, 3, 13129–13140; d) Z. Wang, X. Wang, Y. Nishihara, *Chem. Commun.* **2018**, *54*, 13969–13972; e) S. Sakurai, T. Yoshida, M. Tobisu, *Chem. Lett.* **2019**, *48*, 94–97. See also ref 4b.

- [6] For selected examples using Cu catalysts, see: a) J. S. Bandar, E. Ascic, S. L. Buchwald, J. Am. Chem. Soc. 2016, 138, 5821–5824; b) Y. Zhou, J. S. Bandar, S. L. Buchwald, J. Am. Chem. Soc. 2017, 139, 8126–8129; c) Y. Huang, K. B. Smith, M. K. Brown, Angew. Chem. 2017, 129, 13499–13503; Angew. Chem. Int. Ed. 2017, 56, 13314–13318; d) T. Fujihara, A. Sawada, T. Yamaguchi, Y. Tani, J. Terao, Y. Tsuji, Angew. Chem. 2017, 129, 1561–1565; Angew. Chem. Int. Ed. 2017, 56, 1539–1543.
- [7] For selected papers on metal-catalyzed reductive coupling, see: a) K. Kokubo, M. Miura, M. Nomura, *Organometallics* 1995, *14*, 4521–4524;
  b) Y.-T. Hong, A. Barchuk, M. J. Krische, *Angew. Chem.* 2006, *118*, 7039–7042; *Angew. Chem. Int. Ed.* 2006, *45*, 6885–6888; c) H. Xiao, G. Wang, M. J. Krische, *Angew. Chem.* 2016, *128*, 16353–16356; *Angew. Chem. Int. Ed.* 2016, *55*, 16119–16122. See also ref 6a.
- [8] For selected reviews on metal-catalyzed reductive coupling, see: a) K. D. Nguyen, B. Y. Park, T. Luong, H. Sato, V. J. Garza, M. J. Krische, *Science* 2016, 354, aah5133; b) M. Holmes, L. A. Schwartz, M. J. Krische, *Chem. Rev.* 2018, 118, 6026–6052.
- [9] A. Boreux, K. Indukuri, F. Gagosz, O. Riant, ACS Catal. 2017, 7, 8200– 8204.
- [10] For our work on synergistic cooperative enantioselective Rh/Pd twometal catalysis, see: M. Sawamura, M. Sudoh, Y. Ito, *J. Am. Chem. Soc.* **1996**, *118*, 3309–3310.
- [11] For a review on synergistic catalysis, see: A. E. Allen, D. W. C. MacMillan, Chem. Sci. 2012, 3, 633–658.
- [12] For selected reviews on cooperative two-metal catalysis, see: a) J. M.
   Lee, Y. Na, H. Han, S. Chang, *Chem. Soc. Rev.* 2004, 33, 302–312; b)
   D. R. Pye, N. P. Mankad, *Chem. Sci.* 2017, *8*, 1705–1718; c) K. Semba,
   Y. Nakao, *Tetrahedron* 2019, 75, 709–719.
- [13] For selected papers on cooperative two-metal catalysis in cross-coupling, see: for Pd/Cu catalysis, a) K. Sonogashira, Y. Tohda, N. Hagihara, Tetrahedron Lett. 1975, 16, 4467–4470; b) F. Nahra, Y. Macé, D. Lambin, O. Riant, Angew. Chem. 2013, 125, 3290-3294; Angew. Chem. Int. Ed. 2013. 52. 3208-3212; c) K. Semba, Y. Nakao, J. Am. Chem. Soc. 2014. 136, 7567-7570; d) K. B. Smith, K. M. Logan, W. You, M. K. Brown, Chem. Eur. J. 2014. 20. 12032–12036; e) K. M. Logan, K. B. Smith, M. K. Brown, Angew. Chem. 2015, 127, 5317-5320; Angew. Chem. Int. Ed. 2015, 54, 5228-5231; f) T. Jia, P. Cao, B. Wang, Y. Lou, X. Yin, M. Wang, J. Liao, J. Am. Chem. Soc. 2015, 137, 13760-13763; g) K. Semba, K. Ariyama, H. Zheng, R. Kameyama, S. Sakaki, Y. Nakao, Angew. Chem. 2016, 128, 6383-6387; Angew. Chem. Int. Ed. 2016, 55, 6275-6279; h) S. D. Friis, M. T. Pirnot, S. L. Buchwald, J. Am. Chem. Soc. 2016, 138, 8372-8375; i) S. D. Friis, M. T. Pirnot, L. N. Dupuis, S. L. Buchwald, Angew. Chem. 2017, 129, 7348–7352; Angew. Chem. Int. Ed. 2017, 56, 7242-7246; for Ni/Cu catalysis, j) I. P. Beletskaya, G. V. Latyshev, A. V. Tsvetkov, N. V. Lukashev, Tetrahedron Lett. 2003, 44, 5011-5013; k) O. Vechorkin, D. Barmaz, V. Proust, X. Hu, J. Am. Chem. Soc. 2009, 131, 12078–12079; I) O. Vechorkin, V. Proust, X. Hu, Angew. Chem. 2010, 122, 3125-3128; Angew. Chem. Int. Ed. 2010, 49, 3061-3064; m) J. Yi, X. Lu, Y.-Y. Sun, B. Xiao, L. Liu, Angew. Chem. 2013, 125, 12635-12639; Angew. Chem. Int. Ed. 2013, 52, 12409-12413; n) Y. Wang, S.-B. Wu, W.-J. Shi, Z.-J. Shi, Org. Lett. 2016, 18, 2548-2551; o) K. Semba, Y. Ohtagaki, Y. Nakao, Org. Lett. 2016, 18, 3956-3959; for Ni/Pd catalysis, p) L. K. G. Ackerman, M. M. Lovell, D. J. Weix, Nature 2015, 524, 454-457; for Ni/Co catalysis, q) S. A. Green, J. L. Matos, A. Yagi, R. A. Shenvi, J. Am. Chem. Soc. 2016, 138, 12779-12782.
- [14] For selected reviews on hydroacylation, see: a) M. C. Willis, *Chem. Rev.* 2010, 110, 725–748; b) J. C. Leung, M. J. Krische, *Chem. Sci.* 2012, 3, 2202–2209; c) R. Guo, G. Zhang, *Synlett* 2018, 29, 1801–1806.
- [15] Hydroacylation of allenes with acyl chlorides and hydrosilanes as acylating and hydride sources, respectively, in the presence of Pd

## COMMUNICATION

catalyst was reported. T. Fujihara, K. Tatsumi, Y. Tsuji, *Org. Lett.* **2013**, 15, 2286–2289.

- [16] For selected examples of Cu catalysis via Markovnikov hydrocupration of vinylarenes, see: D. Noh, H. Chea, J. Ju, J. Yun, Angew. Chem. 2009, 121, 6178–6180; Angew. Chem. Int. Ed. 2009, 48, 6062–6064; b) R. D. Grigg, R. V. Hoveln, J. M. Schomaker, J. Am. Chem. Soc. 2012, 134, 16131–16134; c) S. Zhu, N. Niljianskul, S. L. Buchwald, J. Am. Chem. Soc. 2013, 135, 15746–15749. See also refs 6a,b. Isolation of benzylic organocopper complexes was reported. d) D. S. Laitar, E. Y. Tsui, J. P. Sadighi, Organometallics 2006, 25, 2405–2408. e) Y. Xi, J. F. Hartwig, J. Am. Chem. Soc. 2017, 139, 12758–12772.
- [17] T. Vergote, F. Nahra, D. Peeters, O. Riant, T. Leyssens, J. Organomet. Chem. 2013, 730, 95–103
- [18] Similar Markovnikov-type alkene hydrocupration followed by trapping of an alkylcopper(I) intermediate with an acyl electrophile has been proposed in the Cu-catalyzed reductive coupling of vinylarenes with carboxylic anhydrides using HSiMe(OMe)<sub>2</sub> as a reducing agent, while the reaction pathway has not been experimentally proved (ref 6a).

- [19] For our work on the use of Ni-DCYPBz catalyst system for amination of aryl fluorides, see: T. Harada, Y. Ueda, T. Iwai, M. Sawamura, *Chem. Commun.* 2018, 54, 1718–1721.
- [20] 4a was generated via reduction of 3a during the reaction. Similar C=O reduction by Cu–H catalysis was described in ref 6a.
- [21] The acylative cleavage of THF occurred to give 4-chlorobutylbenzoate. For an early paper, see; J. B. Cloke, F. J. Pilgrim, *J. Am. Chem. Soc.* 1939, *61*, 2667–2669.
- [22] Similar phenomena of ligand exchange between two metals were observed in our previous work on the synergistic Rh/Pd two-metal catalysis. See ref. 10.
- [23] T. Iwai, T. Harada, H. Shimada, K. Asano, Sawamura, M. ACS Catal. 2017, 7, 1681–1692.
- [24] The hydroacylation efficacy of **2g** seems to be higher than that of **2a**.
- [25] S. Bajo, G. Laidlaw, A. R. Kennedy, S. Sproules, D. J. Nelson, Organometallics 2017, 36, 1662–1672.
- [26] For Ru-catalyzed hydroacylation of 2i with benzaldehyde to form 3p, see: J. Kim, C. S. Yi, ACS Catal. 2016, 6, 3336–3339.

## COMMUNICATION

### COMMUNICATION

#### Synergistic Ni/Cu Two-Metal Catalysis

 $Ar^{1} = \int_{cu}^{cu} Ar^{2} + HSi(OMe)_{2}Me \xrightarrow{(N)}_{cu} Ar^{1} \xrightarrow{(N)}_{cu} Ar^{2}$ 

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.

Yusuke Ueda, Tomohiro Iwai,\* and Masaya Sawamura\*

Page No. – Page No.

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