

## Alkyl formates as transfer hydroalkylation reagents – Hydrobenzylation of imines

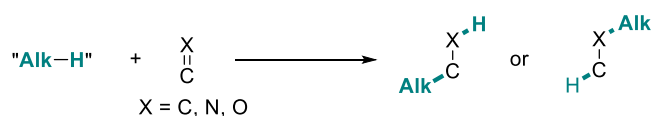
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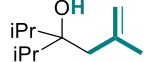
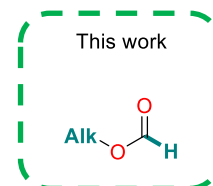
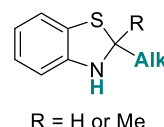
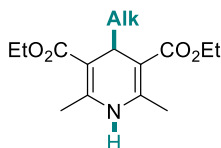
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Hydrofunctionalization of unsaturated bonds, such as carbonyl, imines, alkenes or alkynes, provide a rapid and atom-economic access to functionalized molecules.<sup>1</sup> Among those processes, hydroalkylation, which formally adds a R-H alkane across a C=C, C=O or C=N bond, has been intensively studied. However, in these reactions a sacrificial hydride or hydrogen donor is required, usually a hydrosilane or a hydroborane.<sup>2</sup> Therefore, hydroalkylation by transfer was explored to increase the atom economy. In 2011, Oshima's group proposed a transfer from allenyl or homoallyl alcohols to aldehydes or imines under Cu-catalysis.<sup>3</sup> Then, in 2013, Tang's group designed efficient and versatile hydroalkyl-donors based on Hantzsch esters or benzothiazoles.<sup>4</sup> Yet, these two reactions did not improved the atom economy, although recyclable but under harsh conditions. Following previous work on transfer hydrosilylation,<sup>5</sup> formate appeared as a new potential transfer reagent. We assumed that alkyl formates can perform transfer hydroalkylation reactions through transition-metal catalysis. This process would present a high atom economy and CO<sub>2</sub>, as the only byproduct, can be recycle in formic acid, which can also be biosourced. As a proof of concept, we developed a novel catalytic reaction of transfer hydroalkylation from alkyl formates using benzyl formates and imines as model reagents.

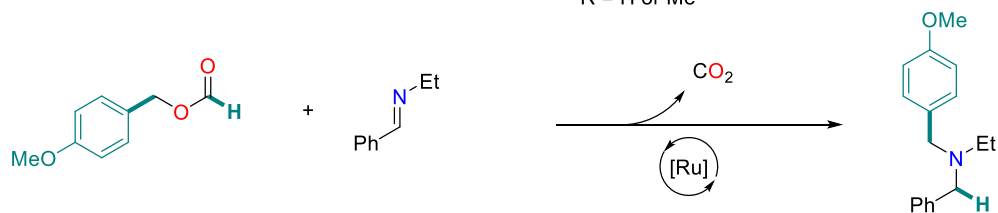
## Hydroalkylation



## Transfer reagents

Oshima *et al.*, 2011Tang *et al.*, 2013

## An example



- (1) *Hydrofunctionalization*; Ananikov, V. P., Tanaka, M., Eds.; Topics in Organometallic Chemistry; Springer Berlin Heidelberg: Berlin, Heidelberg, **2013**; Vol. 43.
- (2) Wang, X.-X.; Lu, X.; Li, Y.; Wang, J.-W.; Fu, Y. *Sci. China Chem.* **2020**, 63 (11), 1586–1600.
- (3) Sai, M.; Yorimitsu, H.; Oshima, K. *Angew. Chem. Int. Ed.* **2011**, 50 (14), 3294–3298.
- (4) Li, G.; Chen, R.; Wu, L.; Fu, Q.; Zhang, X.; Tang, Z. *Angew. Chem. Int. Ed.* **2013**, 52 (32), 8432–8436.
- (5) Chauvier, C.; Godou, T.; Cantat, T. *Chem. Commun.* **2017**, 53 (85), 11697–11700.