



Oral Presentations

OP35.

Phenyl Formate: an Excellent CO Source for the Synthesis of Heterocycles from Nitroarenes

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Many different *N*-heterocycles can be prepared in high yields from suitably substituted nitroarenes in the presence of CO as a reductant [1], but the need for high-pressure CO lines have prevented a widespread use of these reactions. Here we report a general protocol for the preparation of *N*-heterocycles using phenyl formate as a practical CO surrogate. Indoles were mostly investigated, but the methodology was successfully extended to other heterocycles (carbazoles, quinolones, and oxazines). The desired compounds were obtained in yields often higher than those previously reported using gaseous CO. A cheap glass pressure tube can be employed as the reaction vessel. Mechanistic and kinetic analyses were successfully employed for clarifying both the decarbonylation reaction of phenyl formate and the cyclization mechanism.

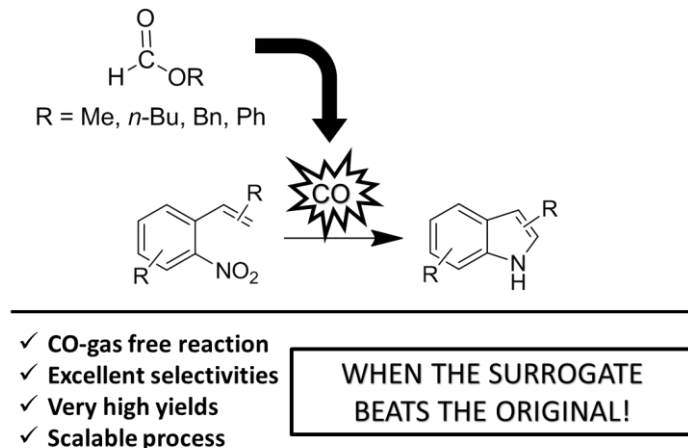


Figure 1

[1] (a) Ragaini, F.; Cenini, S.; Gallo, E.; Caselli, A.; Fantauzzi, S. *Curr. Org. Chem.* 10, (2006), 1479-1510. (b) Ferretti, F.; Formenti, D.; Ragaini, F. *Rend. Fis. Acc. Lincei* (2017), dx.doi.org/10.1007/s12210-12017-10601-12217.

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OP36.

Auxiliary catalysis: β -arylation of alcohols by dual relay of cooperative transition-metal catalysts

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The combination of multiple catalysts in one process opens great possibilities to afford new transformations and to produce complex molecules in a single vessel. [1,2]

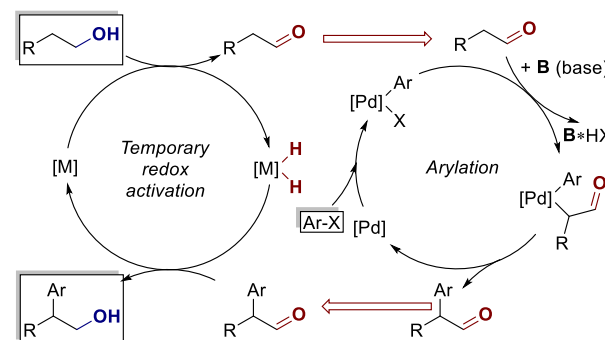


Figure 1 Dual relay catalytic system for direct β -arylation of alcohols.

Here, we report a new mode of operation for multi-relay systems by introducing a concept of an 'auxiliary' catalyst that indirectly enables a new reaction. The 'auxiliary' catalyst undergoes a reversible reaction of a substrate, which temporarily modulates its reactivity. Specifically, a direct β -arylation of alcohols is established (Figure 1). In the relay, the alcohol is first oxidized by an 'auxiliary' hydrogen-borrowing catalyst. Next, the aldehyde undergoes arylation by a Pd-catalyst. Finally, the aryl aldehyde is reduced to the product, recovering the alcohol function and the 'auxiliary' catalyst.

We foresee that the approach is general and can be extended to other reactions.

[1] Lohr, T. L., Marks, T. J. *Nat. Chem.* 7 (2015) 477.

[2] Wende, R. C., Schreiner, P.R. *Green Chem.*, 14, (2012), 182.

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