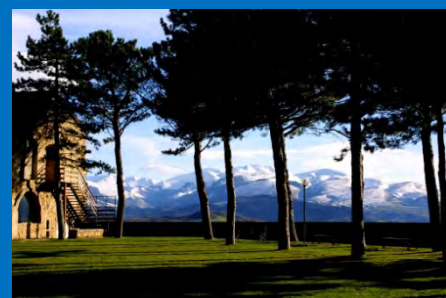


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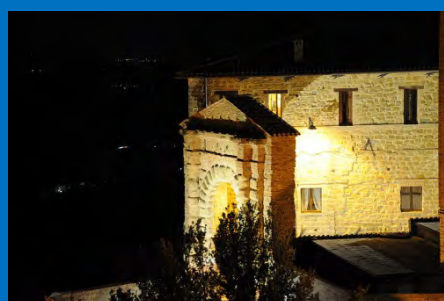
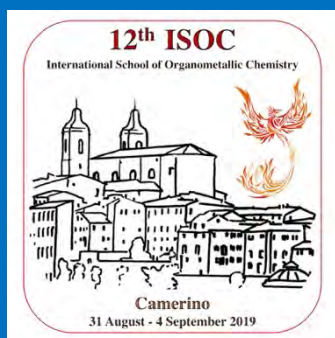
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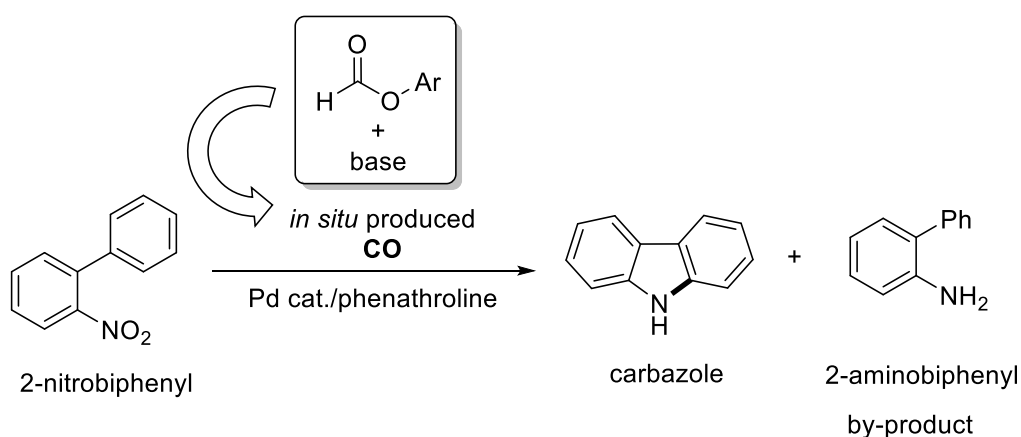
Palladium Catalyzed Reductive Cyclization of Nitrobiphenyls Using Formate Esters as CO Surrogates

Poster 36

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Palladium complexes with phenanthroline ligands are so far the most effective catalysts for the reductive cyclization of nitroarenes by carbon monoxide to yield a variety of heterocyclic compounds.^[1] Despite the high efficiency and the high atom-economical character of many of these reactions, they have not become of widespread use. This is mainly attributed to the need for pressurized CO and pressure equipment (requiring CO safety measures). In the aim of turning this kind of reaction into a “general tool” for the synthetic chemist, we developed a procedure based on the use of phenyl formate as an *in situ* source of CO. The reaction can be performed in a glass pressure tube, a cheap equipment accessible to every laboratory. Our previous work was mainly focused on the synthesis of indoles by reductive cyclization of *o*-nitrostyrenes^[2] and oxazines by the hetero Diels-Alder condensation of a conjugated diene with a nitrosoarene formed in situ by the reduction of the starting nitroarene.^[3] However, the application of the previously developed method to the reductive cyclization of 2-nitrobiphenyls to carbazoles (Scheme 1) afforded only moderate yields even under harsher conditions and higher catalyst loadings. The result is not totally unexpected since this reductive cyclization is known to be more difficult than the other previously studied. Here we report the results of our investigations on this reaction aimed at both improving the catalytic performance and better understanding the reaction mechanism.



Scheme 1. Reductive cyclization of 2-nitrobiphenyls to carbazoles using formates as CO source.

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[2] D. Formenti, F. Ferretti, F. Ragaini, *ChemCatChem* **2018**, 10, 148-152.

[3] M. A. EL-Atawy, D. Formenti, F. Ferretti, F. Ragaini, *ChemCatChem* **2018**, 10, 4707-4717.