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ICOMC 2018

Florence Italy

BOOK OF ABSTRACT

28th International Conference
on Organometallic Chemistry

FLORENCE, ITALY

Congress & Exhibition Centre

15 – 20 JULY 2018

www.icomc2018.com



Effect of Iron Cocatalysts on the Palladium-Catalyzed Oxidative Carbonylation of Aniline

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Isocyanates are key intermediates for the chemical industry, but their production is actually based on the use of toxic phosgene (path A in Figure 1). Among suitable alternatives, the reductive carbonylation of nitroarenes (Path B) and the oxidative carbonylation of amines (Path C) are the most investigated.

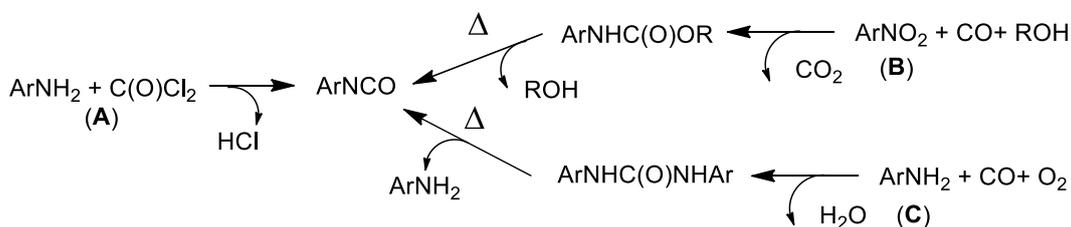


Figure 1. Alternative synthetic procedures for aromatic isocyanates

Research in our group mostly focused on the reductive carbonylation of nitroarenes, but the connections we could identify between this reaction and the oxidative carbonylation of amines¹ recently pushed us to investigate the latter reaction. The most active catalytic system reported to date is based on palladium catalysts with iodide as promoter.² We decided to investigate this system in more detail and found some surprising results. The most important new findings are:

- 1) When the reaction is performed directly in a steel autoclave, the reported data are fully reproducible. However, if the reaction is performed in a glass liner or a Teflon lined autoclave, the activity of the catalytic system drops to about 1/3 of the original one or lesser.
- 2) One essential role of iodide is to etch some iron from the autoclave walls. The high activity can be restored even in a Teflon coated autoclave if small amounts of iron salts are added.
- 3) Iodide and iron have complex interactions and can even deactivate each other when their molar ratio falls within a certain range.
- 4) If iron is present, iodide is no longer necessary, but a halide (chloride) is anyway required.
- 5) The solvent is not completely innocent in the reaction.

These and other trends will be discussed.

References

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2. (a) Fukuoka, S.; Chono, M.; Kohno, M. *J. Chem. Soc., Chem. Commun.* **1984**, 399. (b) Gabriele, B.; Salerno, G.; Mancuso, R.; Costa, M. *J. Org. Chem.* **2004**, 69, 4741.