EuChemS
European Chemical Society

UNIVERSITÄT BERN

SCS
Swiss Chemical Society

EuCOMC 2025

XXVI European Conference on Organometallic Chemistry
July 6-10, 2025, University of Bern, Switzerland

Plenary Speakers



Prof. Ana Carmen Albeniz, University of Valladolid, Spain



Prof. Gilles Gasser, PSL University, France



Prof. Bill Morandi, ETH Zurich, Switzerland



Prof. Rab Mulvey, University of Strathclyde, UK



Prof. Laurel Schafer, University of British Columbia, Canada

Young Plenary Speakers



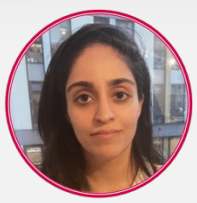
Prof. Danny Broere, Utrecht University, Netherlands



Prof. Alicia Casitas, Philipps University Marburg, Germany



Prof. Graham de Ruiter, Technion, Israel



Prof. Meera Mehta, University of Oxford, UK



Prof. Ainara Nova, University of Oslo, Norway

www.EuCOMC2025.scg.ch

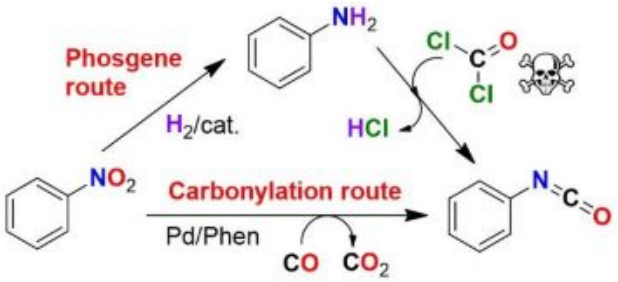
Carbonylation of nitrobenzene to phenyl isocyanate: new life in an old field

F. Ragaini[1], D. R. Ramadan[1,2]*, M. A. Fouad[1,2]*, F. Ferretti[1]*, A. Brotons Rufes[3]*, C. Costabile[3]*, P. Macchi[4]*

[1]Dipartimento di Chimica, Università di Milano, V. C. Golgi 19, Milano, [2]Chemistry Department, Faculty of Science, Alexandria University, P.O. Box 426, Alexandria 21321, Egypt., [3]Dipartimento di Chimica e Biologia "A. Zambelli", Università di Salerno, V. Giovanni Paolo II, Fisciano (SA), [4]Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, V. Mancinelli 7, Milano

Organic isocyanates are fundamental intermediates in the synthesis of many products, including polyurethanes, pesticides and many others. Aromatic isocyanates, accounting for more than 80% of the market, are actually produced by reduction of nitroarenes to anilines, followed by reactions of the latter with phosgene. However, phosgene is a very toxic substance and avoiding its use is highly desirable.

The most direct way to get isocyanates from nitroarenes is their reaction with CO, which only affords CO_2 as a stoichiometric byproduct. However, the direct catalytic carbonylation reaction of nitroarenes to isocyanates is a difficult reaction, which only proceeds with high catalyst loadings and often affords only moderate yields. Consequently, during the last three decades, most efforts have concentrated on an indirect route in which nitroarenes are carbonylated in the presence of methanol to give the corresponding carbamate, which can be later cracked to isocyanate and methanol in a subsequent step. However, a single-step synthesis would be more appealing if its efficiency can be improved.



We took advantage of our experience in the synthesis of carbamates[1-3] to reconsider one of the best catalytic systems for the direct synthesis of isocyanates from nitroarenes, based on the use of a palladium catalyst with phenanthroline as a ligand.[4] In this communication we will describe the results we obtained, which allowed us to increase the substrate/catalyst ratio by an order of magnitude, while maintaining high selectivities. Furthermore, both experimental and computational studies provided deeper insights into the reaction mechanism.

This work was supported by MUR and Next Generation EU (PRIN2022ZJSCW3)

[1] F. Ragaini, C. Cognolato, M. Gasperini, S. Cenini, Angewandte Chemie, International Edition 2003, 42, 2886-2889.

[2] F. Ragaini, M. Gasperini, S. Cenini, L. Arnera, A. Caselli, P. Macchi, N. Casati, Chemistry - European Journal 2009, 15, 8064-8077.

[3] F. Ferretti, F. Ragaini, R. Lariccia, E. Gallo, S. Cenini, Organometallics 2010, 29, 1465-1471.

[4] S. Cenini, F. Ragaini, M. Pizzotti, F. Porta, G. Mestroni, E. Alessio, Journal of Molecular Catalysis 1991, 64, 179-190.