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BOOK OF ABSTRACTS

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IL-43 Palladium/Phenanthrolines Catalyzed Carbonylation of Nitroarenes; the Key Role of the Nitrogen Ligand

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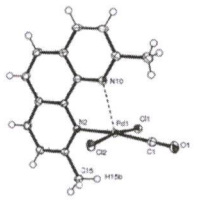
Abstract

Nitroarene carbonylation is the most direct alternative to the currently employed phosgene-based strategy for the industrial production of aryl isocyanates such as toluendiisocyanate (TDI) and 4,4'-methylendiphenyildiisocyanate (MDI). Despite the high toxicity of phosgene, several million tons of this product are still produced each year. Catalytic systems based on the palladium/phenanthroline combinations are by far the most promising for an industrial application of the carbonylation strategy.[1] Phenantrolines are unique in their ability to stabilize the catalyst under the forcing conditions and, unlike phosphines, are not oxidized by nitroarenes.In recent years, we have much improved the efficiency of the catalytic system by employing phosphorus acids as promoters.[2] An in-depth mechanistic study of this reaction allowed us to unveil several features of the metal-ligand-acidic promoter interplay that makes this combination so active.[3] Most of these can be relevant even to other catalytic systems with similar ligands or promoters. Key features include:1) The ligand easily detaches from the metal during the reaction. 2) During the reaction a CO adduct is formed with a partial detachment of just one of the two nitrogen atoms of the ligand, to give an adduct having a geometry ranging between distorted square planar and bipyramidal depending on the other ligands. This finding has allowed a further optimization of the catalytic system based on the use of unprecedented non-symmetrical phenanthrolines.[4] 3) The acidic promoter acts as a bifunctional promoter, favoring the transfer of a proton from one position to another of the molecule in the r.d.s. of the reaction. The latter is the carbonylation of aniline, intermediately formed during the reaction. A strategy for the recovery of the catalyst based on a thermomorphic ligand will also be described.[5]During the lecture, these and other effects will be analyzed, with a focus on those aspects that have a more general impact on different catalytic reactions.



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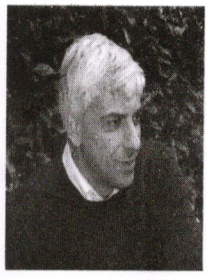
Personal Profile

Professor Fabio Ragaini obtained his Ph.D. in chemistry at the University of Milan, where he later became Assistant, Associate and finally Full Professor in 2011. In 1993 he was also visiting scientist at The Pennsylvania State University. Since 2016, he is the Coordinator of the Interdivisional Organometallic Chemistry Group of the Italian chemical Society. Author of 115 papers on scientific journals, a monograph entitled "Catalytic Reductive Carbonylation of Organic Nitro Compounds" (Kluwer Academic Publishers, 1997), 2 book chapters, and 3 patents. He has over 2900 citations and an h-index of 33.Scientific interests are in the field of organometallic chemistry and homogeneous catalysis.



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