

PGMs IN THE LAB

New, Efficient Tools for Palladium-Catalysed Functionalisation of Heteroaromatics

Johnson Matthey and Alfa Aesar support new platinum group metals research

Here another researcher whose work has benefited from the support of Johnson Matthey and Alfa Aesar, A Johnson Matthey Company, is profiled. Jean-Cyrille Hierso is a Full Professor and Member of the Institut Universitaire de France (IUF) at the University of Burgundy in Dijon, France. He is interested in metal and ligand chemistry, catalysis and nanomaterials.

About the Research

A project has been initiated at the University of Burgundy based on ligand chemistry for catalysis under ultra-low metal loading. For this purpose, novel polyphosphine ligands based on a ferrocene backbone have been developed (see for example **Figure 1**). A library of more than fifty ferrocenyl di-, tri- and tetraphosphines has been obtained, from which some ligands displaying outstanding performance have been identified. Carbon–carbon and carbon–nitrogen bond formation (Suzuki, Heck, Sonogashira and Tsuji-Trost reactions) proceeded with high turnover numbers and catalyst loadings as low as 10^{-4} mol% relative to the substrates.

The mechanistic features of cooperating polydentate ligands are being explored with electrochemistry for measuring kinetics and the identification of intermediary species. Additionally, internationally recognised work has been done in the field of phosphines characterisation through the discovery and investigation of nonbonded ‘through-space’ NMR spin–spin couplings in organophosphorus and organometallic compounds. Recently a patent was deposited, jointly held by the CNRS and the University of Burgundy, on the heterogenisation of a new family of ligands for recycling and heterogeneous catalysis. Low-loading palladium catalysis is now being explored for direct functionalisation of C–H bonds in heteroaromatics and for the formation of C–N, C–O and C–S bonds. C–C coupling for C–H functionalisation has been achieved in cooperation

About the Researcher



Professor Jean-Cyrille Hierso

- * **Name:** Jean-Cyrille Hierso
- * **Position:** Full Professor – Member of the Institut Universitaire de France (IUF)
- * **Department:** Institute of Molecular Chemistry – Mixte CNRS Unit 6302
- * **University:** University of Burgundy
- * **Street:** 9 Avenue Alain Savary – Faculté Mirande
- * **City:** Dijon
- * **Post or Zip Code:** 21000
- * **Country:** France
- * **Email Address:** jean-cyrille.hierso@u-bourgogne.fr
- * **Website:** <http://www.icmub.fr/185-membres?r=185&action=view&id=15>

with Henri Doucet at the University of Rennes, France, and the success of ferrocenyl polyphosphine ligands in low-loading catalysis has led to their commercialisation under the name “HiersoPHOS”.

In addition to the work on screening conditions for palladium-catalysed C–C bond and C–X bond formation (X = S, O, N), iridium and rhodium precursor

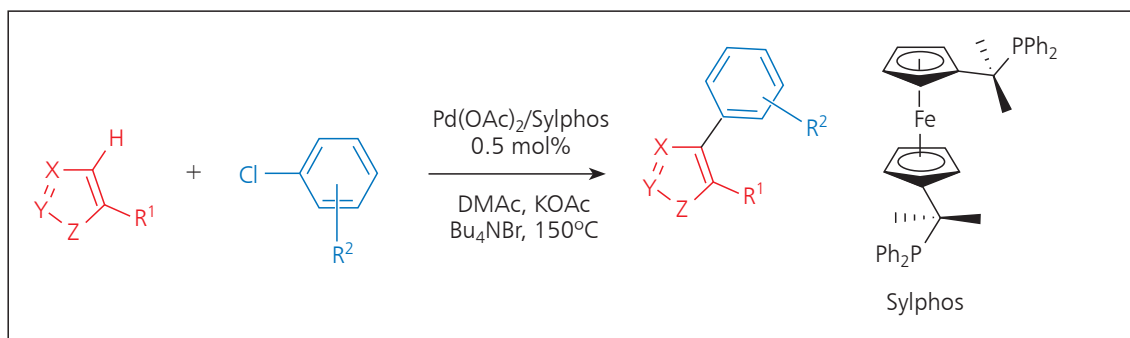


Fig. 1. Direct arylation at C3 or C4 of heteroarenes in the presence of a palladium catalyst with the sterically relieved ferrocenyl diphosphane Sylphos, developed by the Hierso group (Reprinted with permission. Copyright 2012 American Chemical Society)

salts are now also being investigated for direct specific C–H functionalisation.

This fundamental research in synthesis methodology may find many applications in total synthesis or synthesis of fine chemicals, including pharmaceuticals, agrochemicals and molecular materials.

Selected Publications

- J.-C. Hierso, M. Beaupérin and P. Meunier, Centre National de la Recherche Scientifique, 'Supported Ligands Having a High Local Density of Coordinating Atoms', *World Appl.* 2012/001,601
- D. Roy, S. Mom, S. Royer, D. Lucas, H. Cattey, J.-C. Hierso and H. Doucet, *ACS Catal.*, 2012, **2**, (6), 1033
- M. Platon, L. Cui, S. Mom, P. Richard, M. Saeys and J.-C. Hierso, *Adv. Synth. Catal.*, 2011, **353**, (18), 3403
- D. Roy, S. Mom, M. Beaupérin, H. Doucet and J.-C. Hierso, *Angew. Chem. Int. Ed.*, 2010, **49**, (37), 6650
- R. V. Smaliy, M. Beaupérin, H. Cattey, P. Meunier, J.-C. Hierso, J. Roger, H. Doucet and Y. Coppel, *Organometallics*, 2009, **28**, (11), 3152
- D. Evrard, D. Lucas, Y. Mugnier, P. Meunier and J.-C. Hierso, *Organometallics*, 2008, **27**, (11), 2643
- J.-C. Hierso, J. Boudon, M. Picquet and P. Meunier, *Eur. J. Org. Chem.*, 2007, (4), 583
- D. H. Nguyen, M. Urrutigoity, A. Fihri, J.-C. Hierso, P. Meunier and P. Kalck, *Appl. Organomet. Chem.*, 2006, **20**, (12), 845
- J.-C. Hierso, A. Fihri, R. Amardeil, P. Meunier, H. Doucet and M. Santelli, *Tetrahedron*, 2005, **61**, (41), 9759
- J.-C. Hierso, A. Fihri, R. Amardeil, P. Meunier, H. Doucet, M. Santelli and V. V. Ivanov, *Org. Lett.*, 2004, **6**, (20), 3473
- J.-C. Hierso, A. Fihri, R. Amardeil, P. Meunier, H. Doucet, M. Santelli and B. Donnadiu, *Organometallics*, 2003, **22**, (22), 4490