Improvement of Molecular Metal-Ligand Catalysts via fast Catalytic C-H bond Functionalization of pyridines and Phosphine Ligands

Pierre H. DIXNEUF, Zhuan ZHANG, Jean François SOULE'

Institut Sciences Chimiques UMR 6226 CNRS-Université de Rennes, 35042 Rennes, France,
Pierre.dixneuf@univ-rennes1.fr, jean-francois.soule@univ-rennes1.fr

Abstract

Catalysis with Metal-Ligand complexes has been shown to decrease the energy of combination of molecules, or the transformation of renewables, to form useful derivatives, without the use of toxic reagents and with atom economy.
Polypyridines are key ligands for photocatalysts such as $\{Ru(bipy)_3]^{2+}\}$[1] and to promote selective catalytic addition of radicals. In parallel Phosphine ligands have been shown to control the activity of molecular metal catalysts for numerous useful catalytic reactions. Fast modifications of these P and N ligands via C-H bond functionalization[2,3] have potential to create quickly new and more efficient catalysts for useful transformations.

The lecture will present several aspects of C-H bond functionalization of pyridines and phosphines.

i),Pyridines
-Ruthenium(II) catalysts in water solvent without surfactant can promote sp^2C-H bond activation and can be directed to produce polyheterocycles and even hexa(hetero)arylbenzenes leading to simple metal complexes.
-Copper catalysts can be applied for the C(sp^3)-H bond functionalization of pyridine alkyl goups using in situ generated radicals to produce functional pyridines or heterocycles[4,5].

ii) Phosphines
-Ruthenium(II)-catalyzed selective sp^2C-H bond alkylations with alkenes of arylphosphine oxides can be controlled to give access to bifunctional phosphines with carboxylic group[6].
-Rhodium(I) catalysts promote the regioselective mono or dialkylation of the biaryl ortho'C-H bonds of phosphines to produce functional dialkylated phosphines even with long chain[7].

-The modified phosphines will be shown to increase tremendously the activity of catalysts for carboxylation with CO_2 of arylhalides with photocatalyst[7]
-New Bulky dialkenyl phosphines with Palladium salt will be shown to efficiently catalyze the amidation of arylchlorides via Cross coupling of C-N bonds. [8]

References

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Biography

Pierre H. Dixneuf created a CNRS-University center of Organometallics and Catalysis in Rennes innovating towards Green and Sustainable Catalysis succesiveny via selective transformations of alkynes, incorporations of CO2 such as in vinylcarbamates and carbonates, ruthenium-vinylidenes and –allenylidenes in catalysis, creation of alkene metathesis catalysts from ruthenium-allenylidenes and catalytic transformations of plant oils. He is now contributing to Green C–H bond activation/functionalization using Ru(II) catalysts operating in water or Rhodium catalysts for the activation of molecules and ligands such as Heterocycles, Pyridine and Phosphine ligands to improve Catalyst activity. He has co-authored 470 publications and reviews, co-edited 7 books with a Hindex = 70. His work has led to various prizes : A. v Humboldt prize for Research 1990, French Le Bel SFC award and Grignard-Wittig Prize (GDCh) in 2000, Institut universitaire de France member since 2000, academie des sciences IFP prize, Sacconi medal (Italy) in 2006, Spanish and Chinese Society of Chemistry award in 2014, member of the European Academy Sciences and arts in 2014, of Portugal academy of sciences in 2017 and of National Academy of Sciences, India in 2020. He is currently a Research and Emeritus Professor at the University of Rennes.

Email: Pierre.dixneuf@univ-rennes1.fr