



## From a 175 Year Old Ruthenium to His Empire on Green Catalysis and Sustainable Chemistry

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The Ruthenium element was the last Platinum group metals to be discovered in 1844 by Karl Klaus[1]. The ruthenium salts were later easily transformed into a variety of simple ruthenium(II) complexes which showed efficiency as catalysts for simple reactions such as hydrogenation and it was preferably used as less expensive than the Os, Rh, Ir, Pd or Pt metals.

During the last 2 decades more sophisticated ruthenium complexes were made in attempts to perform reactions of interest for industry, then to contribute to clean processes and Green catalysis. The transformations of renewables by molecular ruthenium catalysts attract innovations for the development of sustainable chemistry.

***The lecture will present examples of successful catalytic reactions discovered in Rennes.***

Specific ruthenium-carbene complexes have been designed to perform alkene metathesis catalysis and these catalysts can now lead to the selective transformation of natural products such as terpene derivatives or renewables such as plant oil derivatives [2].

Ruthenium(II) catalysts associated to a carboxylate partner are able to promote the regioselective  $sp^2$  C-H bond activation of functional arenes and heterocycles to selectively lead to cross-couplings with hetero(aryl) halides [3]. It is possible now to perform such processes in water as renewable solvent without surfactant and with higher catalyst activity [4].

Catalytic  $sp^2$  C-H bond activation/functionalization in water can be directed to produce Hexaheteroarylbenzenes, as potential ligands for photocatalysis [5].

The nature of the ligands linked to the metal is crucial to reach efficiency of the related catalyst. Thus it is a challenge to quickly modify the ligands to reach better catalyst activity. This concept has been applied for the modification of phosphines via their phosphine oxides and ruthenium catalysts are shown to allow the selective alkylation of ortho C-H bonds[6].

Rhodium(I) catalysts by contrast can alkylate the biaryl group C-H bonds of phosphines to produce functional dialkylated phosphines which are now to offer the efficient carboxylation of arylbromides with  $CO_2$  with the help of Pd catalyst and photoredox system. [7]

New perspectives of catalytic C-H bond functionalisation will be pointed out [7,8], including with the contribution of ruthenium photoredox systems.

## References

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