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Eco-sustainability and chemistry of olefins: development of "green" organometallic compounds for homogeneous catalysis

The increasingly advanced materials used in modern technological applications imply a parallel increasing demand for dozens of different chemical elements, among which rare and precious ones.^[1] Unfortunately, most of these elements are finite resources on Earth, which makes us very far from the concept of elemental sustainability, i.e. *the use of an element by the current generation should not impair or restrict its use by future generations*.^[2] In Fig. 1 we report the remaining years until depletion of known reserves of the elements across the Periodic Table, showing that the danger of losing various strategic elements within few decades is a concrete and actual issue. So, concerns of

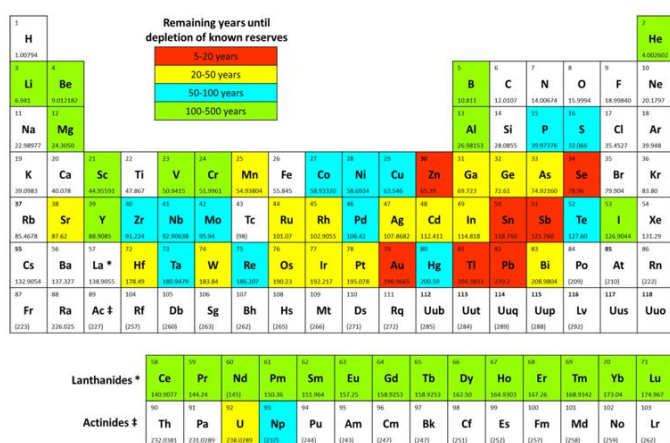


Figure 1. Remaining years until known reserves of the elements are depleted (based on current rate of use).^[1,2]

industries and governments about critical-element supply arose from both the availability issues and the increase of demand of finite raw materials. In addition, mining processes to extract metal ores (or elements) are particularly energy-intensive, aggravating the environmental sustainability problem.^[1] Therefore, current challenges are to minimize the losses and maximize the recycling to reuse such finite raw materials, but at the same time to look for valid alternatives to these “critical elements”.

In this frame, the use of precious metals for homogeneous catalysis is an especially important issue to be faced and solved. Indeed, the reactions underlying the production of many fine chemicals and commodities often rely on precious and rare metal catalysts. Examples include hydroformylation (Rh), hydrosilylation (Pt), Wacker-oxidation (Pd), acetic acid production (Rh, Ir), cross-coupling (Pd) and asymmetric hydrogenation (Ru, Rh, Ir, etc.).^[3] The volatility of the market prices of such metals, together with their limited availability, high toxicity, and serious environmental implications, are leading to evaluate first-row transition metals (M) like Ti, Fe, Co, Ni or Cu as replacements.^[4]

My PhD project, carried out in collaboration with Versalis S.p.A. company, will focus on “green” catalysts based on first-row transition metals and 2,6-diiminopyridines (PDI) as tridentate NNN-

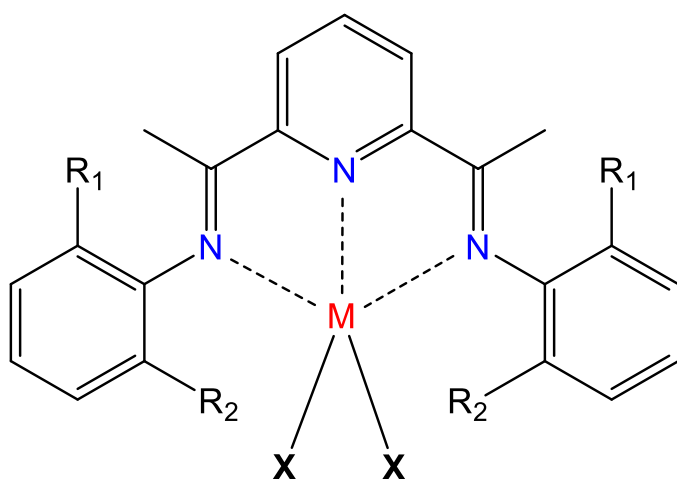


Figure 2. Structure of organometallic catalysts with 2,6-diiminopyridine (PDI) ligands (X: alkyl, halide, etc.).

as NMR, FT-IR, SC-XRD, PXRD, MS, EPR and magnetic measurements. Key aspects to be investigated during this project are: the role of 2,6-diiminopyridines as *non-innocent* ligands with redox activity; the catalytic role played by the number and steric hindrance of the substituents on the aryl groups (R_1 and R_2) in the presence of complex substrates (e.g. organic polymers); the development of “green” preparation methods suitable for industrial scale-up.

My PhD will include a research period at Versalis S.p.A. company to investigate the application of such organometallic compounds in the field of homogeneous catalysis (eight months), and a further research period at the Molecular Materials & Magnetism (M_3) team of Prof. Rodolphe Clérac (Pessac, France) to study the electronic structure of the compounds using the most advanced magnetometric techniques available (six months).

References: ^[1] N. Supanchaiyamat, A. J. Hunt, *ChemSusChem* **2019**, *12*, 397–403; ^[2] A. J. Hunt, T. J. Farmer, J. H. Clark, in *Element Recovery and Sustainability*, ed. A. J. Hunt, Royal Society of Chemistry, London, **2013**, ch. 1, pp. 1–28; ^[3] A. Fürstner, *ACS Cent. Sci.* **2016**, *2*, 778–789; ^[4] J. V. Oblacion, P. J. Chirik, *Nat. Rev. Chem.* **2018**, *2*, 15–34.

donor ligands (*Fig. 2*). PDI complexes often display an outstanding catalytic activity in various organic reactions and can contribute to the environmental sustainability of productive processes employed in polymer industry.^[4] In particular, my PhD project will entail a systematic study of the molecular and electronic structure, and catalytic properties of these first-row transition metal complexes as a function of the PDI and X ligands used. The syntheses of the complexes, often requiring low-temperature and inert atmosphere operations, will be validated by a manifold of characterization techniques such