



3^{èmes} Journées de Catalyse de Paris Saclay

5-6 avril 2018
Auditorium IMAGIF, Centre de Recherches de Gif-sur-Yvette

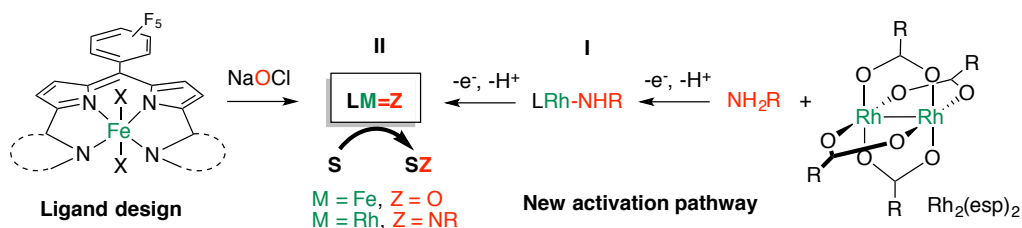
Playing with reactive transition metal oxo and nitrene species: From ligand design to new mechanistic pathway

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The development of new efficient catalytic methods allowing the formation of C-O and C-N bonds in a sustainable way is of primary importance in synthetic chemistry. Strategies aiming at investigating structure-activity relationship by the design of new ligand platforms, but also new activation pathways leading to catalytically active species often offer a fertile ground to the emergence of such methodologies. With this mind-set, we have been investigating on the design of new planar N₄ ligands able to contain highly oxidized iron-oxo species.¹ The electronic properties of the latter present some similarity with those of the enzymatic site of the P450, enlightening the role of the ligand redox non-innocence in the stabilization of such intermediates. Preliminary reactivity studies show encouraging results concerning the oxygen atom transfer reaction but more demanding C-H activation may require ligand optimization. In parallel, we have been investigating on amination reactions catalyzed by the well known Rh₂(esp)₂ dimer, focusing on the improvement of the generation of the nitrene active species. Indeed, most strategies so far involve nitrene transfer from an *in situ* generated imidoiodinane (PhI=NR), thereby releasing undesired halogenated by-products. Alternatively, encouraged by a study published by Berry in 2011, we wondered if a Rh-nitrene complex could be generated from a Rh-amine adduct instead, via two proton-coupled electron transfers (PCET). Indeed, following this strategy we were able to generate and characterize species I and II. They differ from intermediates postulated so far, in that they present two coordinatively saturated Rh centers. These results clearly evidence that highly oxidized metal-nitrene species can be generated through sequential PCET, paving the way to photo-induced nitrene transfer reactions.²



References

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