

Rh₂(esp)₂ : Toward photocatalytic Nitrogen Atom Transfer

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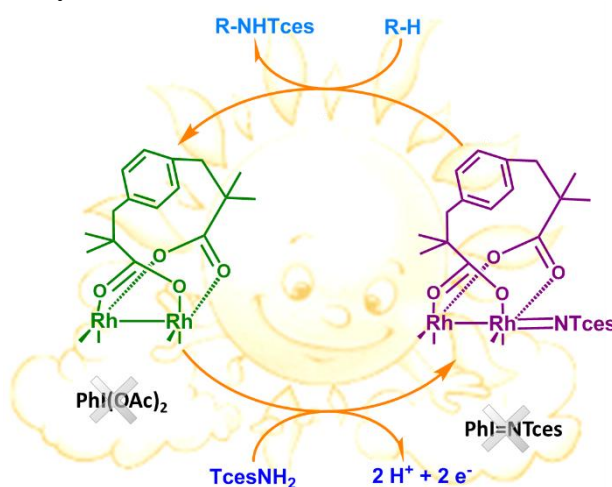
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Amination has a great importance both for the living and at the industrial level. Current methods use powerful and toxic oxidants in harsh conditions. To find suitable catalytic systems, reactions by transfer of Nitrogen atom (NAT) have been studied. Promoted by a metal-nitrene species, these reactions require a high ligand design. Some complexes have a catalytic activity but still require the use of toxic oxidants. An alternative approach is to switch from chemical energy to light energy. A better understanding of the mechanism is necessary in order to develop photoactivation.

We studied the activation mechanism of a Rhodium complex: the Rh₂(esp)₂ dimer.^[1] This complex is known to promote NAT reactions selectively and efficiently. The presence of an iodine precursor is still required to generate the Rhodium-nitrene active species and its formation is still poorly understood. We showed that this species can be generated following a PCET process (coupled proton and electron transfer).^[2] A complete UV-visible spectro-electrochemical study combined with EPR analysis allowed us to form and identify the targeted intermediate species. To achieve these steps photochemically, the best conditions were selected. Well-known [Ru(bpy)₃]²⁺ and methyl viologen were used respectively as chromophore and electron acceptor. As evidenced by transient absorption spectroscopy, electronic transfer between the chromophore and the catalyst actually takes place which is a first step toward photocatalysis.



References:

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