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Department of Chemistry

Special Seminar

1 p.m. Wednesday, September 25, 2013 • 402 Walter Library



Professor

Laurent Maron

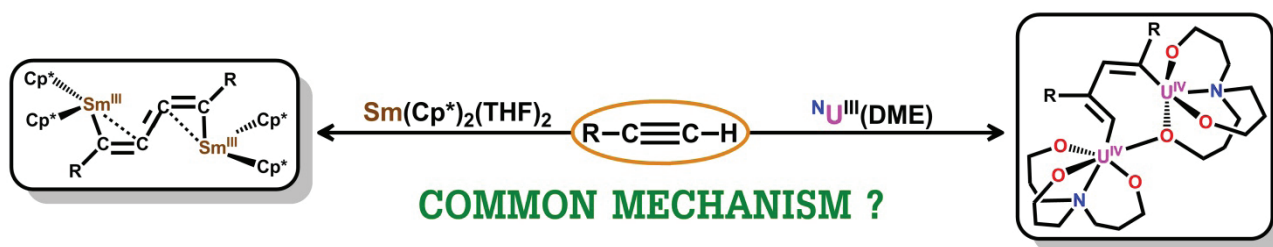
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*Can Redox Chemistry of Divalent Lanthanide and
Trivalent Uranium Complexes be Catalytic?
Some Insights from Theory.*

Website: <http://pcno.insa-toulouse.fr/spip.php?article422&lang=en>

Abstract

Uranium complexes are capable of producing some of the most extraordinary reactions, which are most of the time impossible to form with other type of metals (e.g. main group or transition metals). This is mainly due to the oxophilicity, Lewis acidity, and highly reducing nature of U(III) congeners. From the other side, samarium low-valent complexes can give the same peculiar reactions, in order to form a variety of new classes of organosamarium compounds. In both cases, the products of these reactions can serve as active catalysts or intermediates in catalytic transformations (CO and CO₂ activation), or/and oligomerization processes. For example, addition of terminal mono-alkynes to ^NU^{III}(DME) complexes, lead to the immediate formation of vinyl bridged dinuclear complexes of uranium (IV), [1] while addition of the same substrates to Sm(Cp*)₂(THF)₂ complexes will furnish the corresponding bimetallic allyl complexes [2] (cf. below):



Based on experimental observations, DFT calculations were conducted, in order to predict the corresponding reaction mechanisms. After briefly discussing, the reactions mechanism for CO₂ transformation, we will discuss the mechanism of alkyne dimerization. We will in particular compare the theoretically determined reaction profiles for both U(III) and Sm(II) that share some common features but also so differences that we will be underlined.

[1] B. Kosog, C.E. Kefalidis, F.W. Heinemann, L. Maron, K. Meyer, J. Am. Chem. Soc. 2012 [2] W.J. Evans, R.A. Keyer, J.W. Ziller, Organometallics 1990, 9, 2628.

Host: Professor Laura Gagliardi