Organometallic chemistry of lanthanides: oxidation states in trompe l'oeil and magnetic sandwiches

Jules Moutet,^a Maxime Tricoire,^a Ding Wang,^a Valeriu Cemortan,^a Mathieu Xémard,^a Violaine Goudy^a, Ding Wang^a and <u>Grégory Nocton</u>^{*a}

LCM, Ecole polytechnique, CNRS, Route de Saclay, 91128, Palaiseau cedex, France greg.nocton@polytechnique.edu

Organolanthanide complexes are a class of organometallic compounds that have been developed since the seminal work of Wilkinson in the 1950's¹ and that now concern most of the rare earths in their trivalent states but also their divalent states.² Depending of their oxidation state, the applications for such compounds are numerous because of their optical³ and magnetic properties⁴ but also for single electron transfer reactivity.^{5a} However, the establishment of a clear cut electronic structure is often difficult in these compounds because of the propensity of the surrounding ligands to behave as redox non-innocent ligands and therefore masking the spectroscopic (or realistic) oxidation state.⁵ This electronic picture is however extremely important in order to better understand and manipulate their physical properties (magnetic, optical) but also their reactivity. We will present a short overview of our methodology to develop the synthesis of original organolanthanide complexes as well as their deep study using multiple spectroscopic and theoretical tools. Notably, the presentation will highlight recent coordination studies on divalent sandwich complexes with the cyclononatetraenyl (Cnt) ligand (Fig 1. left)⁶, on the coordination chemistry of divalent thulium (Fig 1. center)⁷ and on heterometallic complexes of organolanthanides and transition metals (Fig 1. right).⁸



Figure 1 Left, Structure of $(Cnt)_2$ Yb. Center, structure of TmI₂(18C6). Right, structure of Cp*₂Sm(bipym)PdMe₃I

1 G. Wilkinson, J. M. Birminham J. Am. Chem. Soc. 1954, 76, 6210.

2 F. Nief Dalton Trans. 2010, 39, 6589

3 E. G. Moore, A. P. S. Samuel, K. N. Raymond, Acc. Chem. Res. 2009, 42, 542

4a) F.-S. Guo, B. M. Day, Y.-C. Chen, M. –L. Tong, A. Mansikkamäki, R. A. Layfield Science 2018, 362, 1400

- 5 a) G. Nocton, W. W. Lukens, C. H. Booth, S. S. Rozenel, S. A. Medling, L. Maron, R. A. Andersen J. Am. Chem. Soc.,
- **2014**, *136*, 8626. b) M. Xemard, A. Jaoul, M. Cordier, F. Molton, O. Cador, B. Le Guennic, C. Duboc, O. Maury, C. Clavaguéra, G. Nocton Angew. Chem. Int. Ed. **2017**, *54*, 4266

6. M. Xémard, S. Zimmer, M. Cordier, V. Goudy, L. Ricard, C. Clavaguéra, G. Nocton, G. J. Am. Chem. Soc. 2018, 140, 14433.

7 M. Xemard, M. Cordier, F. Molton, C. Duboc, B. Le Guennic, O. Maury, C., O. Cador, G. Nocton *Inorg. Chem.* 2019, 58, 2872

8 Goudy, V.; Jaoul, A.; Cordier, M.; Clavaguéra, C.; Nocton, G. J. Am. Chem. Soc. 2017, 139, 10633