Synthesis and Reactivity of Actinide Sandwich Complexes supported by the cyclo-butadienyl ligand.

Nikolaos Tsoureas,*^a Richard A. Layfield^a and Akselli Mansikkamäki^b

^a School of Life Sciences, Division of Chemistry, University of Sussex, Falmer Brighton, BN1 9QJ, United Kingdom; ^bNMR Research Unit, University of Oulu, P.O. Box 8000, Finland *e-mail: nt85@sussex.ac.uk

Organometallic sandwich complexes of the actinides continue to play an important role in understanding the diverse facets of bonding and reactivity of the 5f block elements. A plethora of molecular actinide complexes supported by cyclopentadienyl (C₅), arene (C₆), cycloheptatrienyl (C₇), cyclooctatetraenyl and pentalene (both C₈) ligands are known, as well as organometallic compounds featuring combinations of these ligands, often referred to as mixed sandwich complexes. By comparison the coordination chemistry of the cyclo-butadienyl ligand $[C_4(SiMe_3)_4]^{2-1}$ (Cb'''') with f-elements can only be described as scarce, with the first examples of its coordination to lanthanide(III) metal centres described by our group.¹ More recently we,² and others,³ have extended the coordination chemistry of the Cb^{''''} ligand to 5f block metals and specifically uranium and thorium. In this talk, our recent advances in the synthesis of An(IV)Cb''' organometallic complexes (An = U, Th) from simple starting materials as well as studies of their reactivity, are highlighted. These include new members of the U(IV) azulene family⁴ (e.g. $[U(\eta^8-C_8H_8)(\eta^4-Cb''')])$, observation of metal-ligand co-operativity in the activation of diethyl-ether, preparation of heteroleptic Th(IV) Cb''' complexes and finally preliminary results showing that the Cb''' scaffold can stabilise low-valent U(III) complexes. Our investigations point to a rich and diverse chemistry and reactivity engendered by the Cb''' ligand, the surface of which we have only begun to scratch, and which can have a significant impact in the fields of small molecule activation and molecular magnetism.⁵

References:

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