

NOVEL REACTIVITY OF THE CATIONIC COMPLEX

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The catalytic chemistry of electrophilic d^0/f^n organometallic complexes is nowadays under intense investigation, reaching a high level of sophistication. General aspects concerning these complexes are concentrated for most studies to the functionalization of unsaturated organic molecules. To cite an instance, the actinide-promoted oligomerization of terminal alkynes is of essential present concern since it may introduce to a diversity of organic enynes and oligoacetylene products that are valuable synthons for the synthesis of natural products. Enynes are the simplest oligomerization products of alkynes. We have demonstrated that organoactinides complexes of the type $[\text{Cp}^*_2\text{AnMe}_2 \text{AnMe}_2]$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$; $\text{An} = \text{U}, \text{Th}$) are active catalysts for the linear oligomerization of terminal alkynes and the extent of oligomerization was found to be strongly dependent on the electronic and steric properties of the alkyne substituents. Bulky alkynes were reacted with high regioselectivity toward dimer and/or trimers whereas for non-bulky alkynes, these compounds were transformed into oligomers with a total deficiency of regioselectivity. The addition of primary amines to the catalytic cycle, for $\text{An} = \text{Th}$, granted the chemoselective formation of dimers, chemoselectively, whereas for $\text{An} = \text{U}$, this control was not succeeded. In distinction to the neutral organoactinide complexes, homogeneous cationic d^0/f^n actinide complexes have been used as in the homogeneous polymerization of olefins as extremely active catalysts. Hence, the catalytic alkyne oligomerization is a opportune route to explore insertions and σ -bond metathesis reactivity of complexes. We have recently shown that the reaction of terminal alkynes ($\text{RC}\equiv\text{CH}$), promoted by $[(\text{Et}_2\text{N})_3\text{U}][\text{BPh}_4]$, in toluene, produces efficiently mostly the *gem* dimers (for $\text{R} = \text{Me}$, *i*Pr and *n*Bu) as the major products, whereas for bulky alkynes ($\text{R} = \text{TMS}$ or *t*Bu) small amounts of the *cis* dimer was concomitantly obtained. A plausible mechanism was proposed for the dimerization of terminal alkynes, which was corroborated by kinetic, thermodynamic, equilibrium studies and trapping experiments of the first π -alkyne complex

Expanding the cationic organoactinide rich potential of the cationic organoactinide compounds as homogeneous catalysts, in this presentation we report on the reactivity and selectivity of a the well defined cationic actinide uranium complex $[(\text{Et}_2\text{N})_3\text{U}][\text{BPh}_4]$, as a catalytic precursor for the selective dimerization, oligomerization or/and hydroamination of a variety of terminal alkynes. In addition we present the reactivity of the complex towards the coupling of amine and silanes.

The three amido ancillary ligations in the cationic complex $[(\text{Et}_2\text{N})_3\text{U}][\text{BPh}_4]$, are highly reactive and are replaced when the complex is reacted with primary amines.



The reaction of $[(Et_2N)_3U][BPh_4]$, with an excess of $tBuNH_2$, allows the formation of the cationic complex $[(tBuNH_2)_3(tBuNH)_3U][BPh_4]$. X-ray diffraction studies (see below) on the complex indicate that 3 amido and 3 amine ligands are arranged around the cationic metal center in a slightly distorted octahedral *mer*-geometry. The cationic complex reacts with primary alkynes in the presence of external primary amines allowing the formation of the *unexpected cis*-dimer primordially and in some cases the hydroamination products are obtained concomitantly. The formation of *cis*-dimer is the result of an envelope isomerization through a metalla-cyclopropyl cationic complex. In the reaction of the bulkier alkyne $tBuC\equiv CH$ with the cationic uranium complex in the presence of various primary amines the *cis*-dimer, one trimer and one tetramer are obtained regioselectively as confirmed by deuterium labeling experiments. The trimer and the tetramer correspond to the consecutive insertions of an alkyne molecule into the vinylic CH bond *trans* to the bulky *tert*-butyl group. The reaction of $(TMS)C\equiv CH$ with the uranium catalyst in the presence of $EtNH_2$ followed a distinct course producing the *gem*-dimer and the hydroamination imine as the major product. Although, when other bulkier amines were used ($iPrNH_2$ or $tBuNH_2$) both hydroamination isomeric imines *Z* and *E* were obtained. During the catalytic reaction the *E* (kinetic) isomer is transformed into the most stable *Z* (thermodynamic) isomer. Remarkably is the unique reactivity of the alkyne $(TMS)C\equiv CH$ with the secondary amine Et_2NH , which afforded the *trans* dimer and the corresponding hydroamination enamine; this latter likely results from the insertion of the alkyne into a secondary metal-amide bond, followed by protonolysis. Moreover, we will present on the dehydrogenative coupling of silane and amines showing the unique effect of the course of the reaction based on the structure and stoichiometry of the substrates.

