

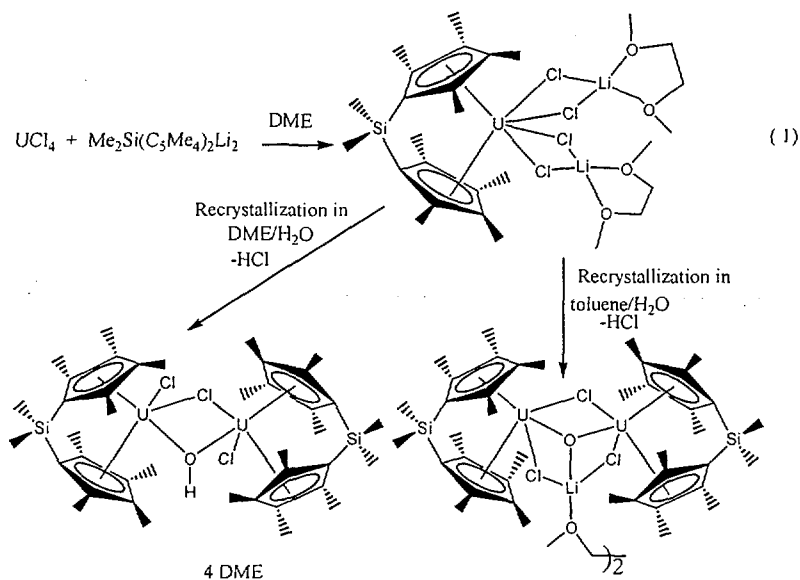
CATALYTIC EFFECT IN OPENING THE COORDINATION SPHERE OF AN ORGANO-f-COMPLEX

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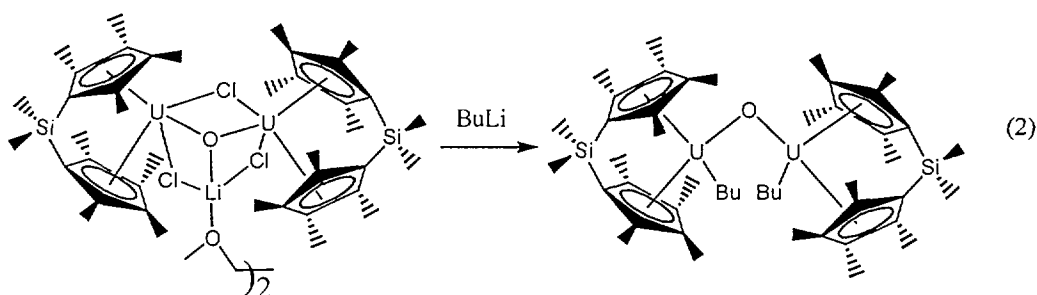
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Organo-f-complexes have been studied in the last decade showing unique stoichiometric and catalytic properties, which are deeply influenced by the nature of the π ancillary ligands. Opening of the metal center coordination sphere is obtained by replacing the pentamethylcyclopentadienyl ligation in Cp^*_2MR_2 ($\text{Cp}^* = \text{C}_5\text{Me}_5$, $\text{M} = \text{f}$ -element metal, $\text{R} = \sigma$ -bonded ligand) by the bridged ancillary ligation $\text{ansa-Me}_2\text{SiCp}''_2\text{MR}_2$ ($\text{Cp}'' = \text{C}_5\text{Me}_4$). For organolanthanides, this change allows an increase (10-100 fold) in rates for the olefin insertion into the M-R bond [1] and in organoactinides; this modification has been shown to cause an increase (10^3 fold) in their catalytic activity for the hydrogenation of 1-hexene [2]. Recently, we have shown that organoactinides of the type Cp^*_2MR_2 ($\text{Cp}^* = \text{C}_5\text{Me}_5$; $\text{M} = \text{Th}, \text{U}$; $\text{R} = \text{CH}_3$) are active catalysts for both the oligomerization and hydrosilylation of terminal alkynes [3]. Thus, a conceptual question arises regarding the use of an open organoactinide such as $\text{Me}_2\text{SiCp}''_2\text{U}^n\text{Bu}_2$ as compared to Cp^*_2UR_2 . This opening in the coordination sphere at the metal center should be unique in such a way that it is reasonable expected the increase of the reactivity towards product formation in the hydrosilylation and metathesis catalytic processes of terminal alkynes.

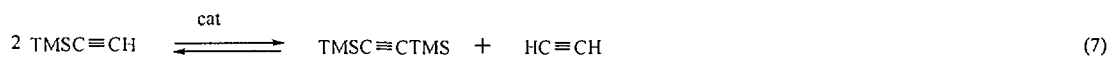
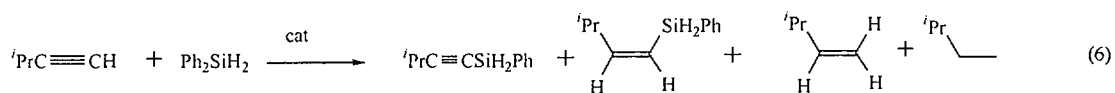
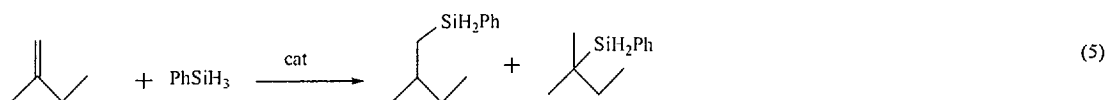
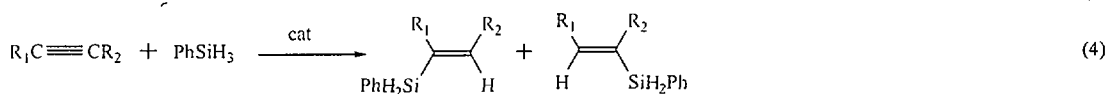
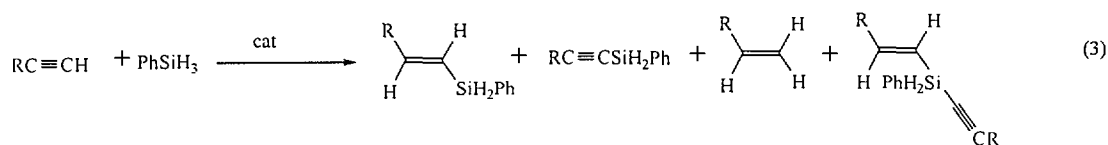
In this poster we report, and quantitatively compare, the effects of the *ansa*-organouranium complex ($\text{Me}_2\text{SiCp}''_2\text{U}^n\text{Bu}_2$)₂O. The synthesis of the complex was achieved as described in equations 1 and 2.



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The catalytic processes here described comprise the hydrosilylation of terminal and internal alkynes (equations 3 and 4) and alkenes with PhSiH_3 (equation 5), the hydrosilylation of terminal alkynes with secondary silanes (equation 6) and the metathesis of terminal alkynes toward mixed acetylenes (equation 7). The different yields obtained by changing the reaction conditions will be presented. The results obtained offer an insight into the different organoactinide-plausible mechanistic scenarios.



References

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