Dehydrogenative Coupling of Diorganostannanes
Using Amido-Lanthanide Catalysts

Kathrin Schittelkopf, Roland C. Fischer, Frank Uhlig
a) TU Graz, Institut für Anorganische Chemie, Stremayrgasse 16, A-8010 Graz, Austria

Introduction

Dehydrogenative coupling of diorganotin hydrides R₂SnH₂ is a popular way to build tin polymers. As a consequence, this reaction finds widespread applications on tin containing polymer syntheses. Different catalysts with a focus on lanthanides as reactive centers were tested and the reaction products were characterized by ¹¹³Sn-NMR-spectroscopy and UV-VIS-spectroscopy. Depending on the steric demand of the substituents, the catalysts employed in our studies initiate dehydrogenative coupling leading to polymers or well defined low molecular weight products, respectively. To exemplify the differences, the dehydrogenative coupling chemistry of Bu₂SnH₂, Ph₂SnH₂ and Bu₂SnH₂ is presented.

Synthesis and Reactions

A wide range of transition metal and lanthanide catalysts have been tested for their reactivity in dehydrogenative coupling of various organostannanes. For example, Cp₂SmCl(SiMe₃)₂ was reported as an active catalyst in this context. In contrast to earlier work, which is mainly based on metalloccenes, we focused on the amido lanthanide compounds 1a-b,5a-b (scheme 1 and 2).

1. Dehydrogenative coupling of Bu₂SnH₂

The outcome of the dehydrogenative coupling reaction was reported to be highly sensitive to steric hindrance in the proximity of the tin atoms. E.g, in the case of Bu₂SnH₂, no polymer formation was initiated by [RhCl(PPh₃)₃]. However, we found that the amido lanthanide catalysts 1a-b lead to a 100% monomer conversion to exclusively yield 1,1,2,2-tetra-butyldistannane 6 (δ¹¹³Sn(THF)= -83.3 ppm, D₂O-cap./THF) as shown in scheme 3.

So far, the dehydrogenative coupling of Bu₂SnH₂ with this class of catalysts has not been reported in literature. Nevertheless, it offers a straightforward and clean access to 6 which is a useful synthon in organotin chemistry as the hydrogen substituents are readily replaced by halogens. 6 may also be converted into the respective 1,2-dianionic species.

2. Dehydrogenative coupling of Ph₂SnH₂ and Bu₂SnH₂

Dehydrogenative coupling of Ph₂SnH₂ and Bu₂SnH₂ initiated by 1a-b,5a-b leads to formation of polymers together with smaller amounts of cyclic products (R₂Snₙ, n=5,6).

Conclusion and Outlook

Besides the already known lanthanide and transition metal catalysts, simple amido based lanthanide (Ln= La, Ce, Sm, Nd) catalysts were found useful in the dehydrogenative coupling of organostannanes. Future investigations will focus on monomers bearing two different organic substituents (RR'SnH₂) and the stereochemistry of the dehydrogenative coupling reaction.

References