

# Dehydrogenative Coupling of Diorganostannanes Using Amido-Lanthanide Catalysts

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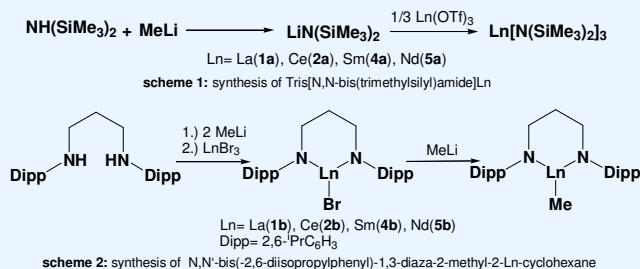
## Introduction

Dehydrogenative coupling of diorganotin dihydrides  $R_2SnH_2$ , is a popular way to build tin polymers.<sup>1</sup> As a consequence, this reaction finds widespread applications of tin containing polymer syntheses. Different catalysts with a focus on lanthanides as reactive centers were tested and the reaction products were characterized by  $^{119}Sn$ -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  $^tBu_2SnH_2$ ,  $Ph_2SnH_2$  and  $^tBu_2SnH_2$  are presented.

## Synthesis and Reactions

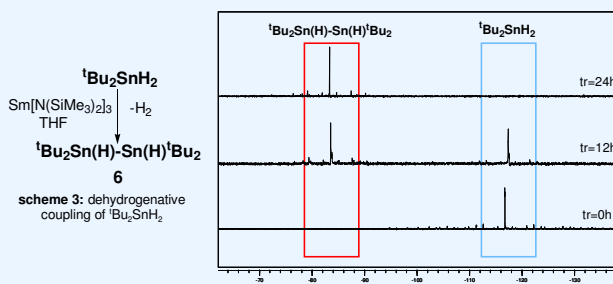
A wide range of transition metal and lanthanide catalysts have been tested for their reactivity in dehydrogenative coupling of various organostannanes.<sup>1</sup> For example,  $Cp^*_2SmCH(SiMe_3)_2$  was reported as an active catalyst in this context.<sup>2</sup>

In contrast to earlier work, which is mainly based on metallocenes, we focused on the amido lanthanide compounds **1a/b-5a/b** (scheme. 1 and 2).



### 1. Dehydrogenative coupling of $^tBu_2SnH_2$

The outcome of the dehydrogenative coupling reaction was reported to be highly sensitive to steric hindrance in the proximity of the tin atoms.<sup>3</sup> E.g. in the case of  $^tBu_2SnH_2$  no polymer formation was initiated by  $[RhCl(PPH_3)_3]$ . However, we found that the amido lanthanide catalysts **1a-5a** lead to a 100% monomer conversion to exclusively yield 1,1,2,2-tetra- $^t$ butyldistannane **6** ( $\delta^{119}Sn(1H)$ -NMR= -83,3 ppm, D<sub>2</sub>O-cap./THF) as shown in scheme 3.



So far, the dehydrogenative coupling of  $^tBu_2SnH_2$  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.<sup>4</sup>

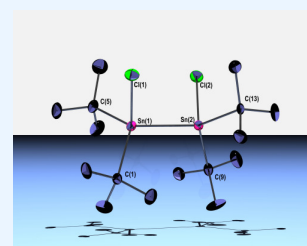
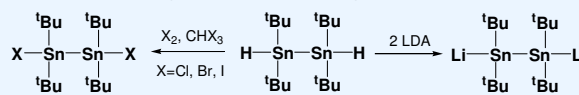
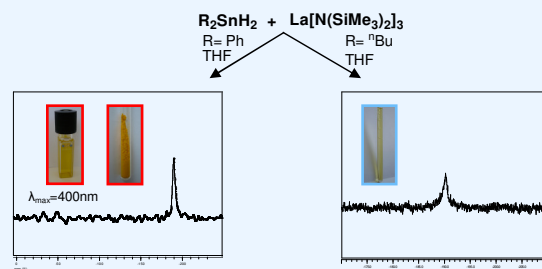


figure 1: x-ray-crystalstructure of  $^tBu_2Sn(Cl)-Sn(Cl)^tBu_2$

### 2. Dehydrogenative coupling of $Ph_2SnH_2$ and $^tBu_2SnH_2$

Dehydrogenative coupling of  $Ph_2SnH_2$  and  $^tBu_2SnH_2$  initiated by **1a/b-5a/b** leads to formation of polymers together with smaller amounts of cyclic products ( $R_2Sn$ )<sub>n</sub> (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 diorganostannanes. Future investigations will focus on monomers bearing two different organic substituents ( $RR'SnH_2$ ) and the stereochemistry of the dehydrogenative coupling reaction.

## References

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