Currently, we do not have an explanation as to why the selectivity factor is not higher \((s > 200)\) in this reaction as could be expected from Figure 2. A possible explanation is that the kinetics are more complicated with \(\text{Me}_2\text{Zn}\) than with the other zinc reagents in which case the formula given in reference [9] is no longer valid.


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**[3] Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.
Figure 1. GC yield Y [%] (a) and enantiomeric excesses ee [%] (b) of compounds 2 (-•–), 3a (-••–), 4a (-•••–) present in the reaction mixture at different conversions X of 2. Values determined by GC using a β-cyclodextrin column (see Supporting Information).

Scheme 2. Postulated mechanism of the regiodivergent PKR.

The efficient catalytic conversion of a racemic compound to two different and separable chiral products of high isomeric purity has been accomplished also by the use of a vinyloxirane having a blocked s-cis conformation such as 1,3-cyclohexadiene monoepoxide 5 (Scheme 3). The addition of Me₂Zn (1.5 equiv) to (-•••–) 5 catalyzed by [Cu(OTf)₂]/(R,R,R)-1 afforded a 60:40 mixture of (1R,2S)-6b (S₅₂-adduct, 64% ee) and (1S,2S)-7b (S₅₂-adduct, >97% ee).[15] The catalyzed addition of Et₂Zn (1.5 equiv) to the same racemate afforded a 76:24 mixture of regioisomer (1R,2S)-6a (34% ee) and (+)-(1S,2S)-7a (>98% ee). Evidently with this substrate, while keeping the corresponding kᵢ for one enantiomer of the substrate, the rates of reductive elimination versus isomerization for the other one (kᵢ vs. k₄ of Scheme 2) are not very different, thus allowing the formation of regioisomeric S₅₂ adducts 7a, b with very high ee, together with large amounts of S₅₂ substitution products 6a, b with a reduced enantioselectivity.

Scheme 3. Enantioselective and regiodivergent addition of R₂Zn to racemic 5 catalyzed by [Cu(OTf)₂]/(R,R,R)-1.
The mechanism of this reaction and the exact nature of the copper species involved in this highly efficient catalytic process still need to be established. Nevertheless, this unprecedented regiodivergent catalytic parallel kinetic resolution with an organometallic reagent supports the notion that the oxidative addition might be a very fast process and reductive elimination is instead a regio- and stereodetermining step.

Experimental Section


[12] The reaction was also carried out in CH₂Cl₂ instead of toluene to establish a practical parallelism between the two species, namely in the triple bond cleavage[20-22] or in their use in material science. In the latter context, the polymeric forms of acetylene, such as polyacetylene and related cumulenes, have a relevant importance.[14, 15] This report deals with the oligomerization of the metalla–dinitrogen functionality and with a perspective to polymerize this moiety. This entry into material science using dinitrogen opens a new avenue in this domain. We report herein how we were able to achieve the unprecedented oligomerization of the metalla–dinitrogen functionality and thereby anticipating and planning the formation of the corresponding polymers.

The alkylation of [WCl₄(dme)] (DME = dimethoxyethane) using MesMgBr (Mes = 2,4,6-(CH₃)₃C₆H₂) under a nitrogen atmosphere occurs with a fast absorption of dinitrogen

From Oligomers to Conducting Polymers of the Metal–Dinitrogen Functionality**

Euro Solari, Joëlle Hesschenbrouck, Rosario Scopelliti, Carlo Floriani,* and Nazzareno Re

This report opens, in the use of dinitrogen, a completely new avenue, which is derived neither from any of the bioinspired processes[1] nor from the objectives pursued so far in the metal-assisted dinitrogen chemistry.[2, 3]

Although $\text{N}_2 = \text{N}_2$ and [C≡C]¹⁻, the deprotonated form of acetylene, are iso electronic, this similarity has not helped in establishing a practical parallelism between the two species, namely in the triple bond cleavage[20-22] or in their use in material science. In the latter context, the polymeric forms of acetylene, such as polyacetylene and related cumulenes, have a relevant importance.[14, 15] This report deals with the oligomerization of the metalla–dinitrogen functionality and with a perspective to polymerize this moiety. This entry into material science using dinitrogen opens a new avenue in this domain.

We report herein how we were able to achieve the unprecedented oligomerization of the metalla–dinitrogen functionality and thereby anticipating and planning the formation of the corresponding polymers.

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