The reactivity of rare-earth metallocenes towards alkynes
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The permethylcyclopentadienyl ligand (Cp*) has played a very important role in the development of organo rare-earth metal chemistry. The application of the bis-Cp* ligation has allowed for the preparation of well-defined derivatives, exhibiting interesting physical and chemical properties. Motivated by their catalytic properties towards unsaturated substrates (such as polymerization, hydrogenation, hydrosilylation, hydroamination, hydrophosphination, hydroboration of olefins and polyene cyclization reactions), many of the reactive features of these compounds have been developed. The chemistry of rare-earth metalloocene derivatives is characterized by a relative ease of C-H bond activation in combination with a high kinetic lability, as compared to early transition metals. This provides a unique possibility to develop catalytic transformations involving C-H activation steps in the presence of Lewis basic functionalities. Compared to the catalytic transformations of alkenes, alkynes have received much less attention as substrates. In this thesis, a detailed look is taken at the catalytic dimerization of 1-methylalk-2-ynes and 1-alkynes. For both of these processes, the scope of reaction, substrate selectivities, the kinetics and mechanism have been investigated. Furthermore, these catalytic dimerization reactions were explored, using bifunctional substrates, as carbon-carbon bond-forming reaction steps in the preparation of new (cross-)conjugated oligomers and polymers.

Scheme 7-1. The η^3-propargyl/allenyl derivatives (Ln = La, Y; R = H, Me, iPr) of rare-earth metallocenes.
Scheme 7-2. The catalytic cyclodimerization of 1-phenyl-1-propyne.

1-propyne decreased both the rate and selectivity of the reaction. Opening the coordination sphere around the metal center by the use of the Me₂Si(C₅Me₄)₂ ligation increased the rate, but decreased the selectivity of the reaction. As a result, the poor regioselectivity, slow conversion rate and the instability of the resulting products make this reaction not very attractive for the synthesis of (cross-)conjugated polymers (Scheme 7-3). Nevertheless, attempts to polymerize bifunctional substrates were carried out, and the resulting products were characterized spectroscopically.

Scheme 7-3. The formation of (cross-)conjugated polymers via catalytic cyclodimerization of 1,4-dipropynylbenzenes.

The rare-earth metalloocene-catalyzed linear dimerization of phenylacetylene is discussed in Chapter 4 (Scheme 7-4). The effect of substrate concentration, ancillary ligation (C₆Me₅ versus Me₂Si(C₅Me₄)₂), catalyst precursor and metal ion radius (La versus Y) on the rate and selectivity was investigated. An increase of the initial substrate concentration was found to promote the formation of higher oligomers, while the rate of catalyst deactivation was found to parallel that of catalytic dimerization. Replacing the bis-C₆Me₅ ligation by Me₂Si(C₅Me₄), on the one hand, and relatively small rare-earth metal centers (Y) by relatively large ones (La, Ce), on the other hand, revealed that the precatalyst C₆Me₅LaCH(SiMe₃)₂ performs best in the catalysis, combining a high activity with a high selectivity for trans-head-to-head dimerization. A plausible mechanism is proposed to account for the reaction products, the reaction intermediates and the kinetic behavior.

Six representative (hetero)aromatic 1-alkynes were synthesized to probe the scope of the permethyllanthanocene-catalyzed 1-alkyne dimerization reaction. The observed substrate effects are discussed in Chapter 5. Appropriate acetylenic substitution leads to enhanced reaction rates and selectivities for (E)-but-1-en-3-yne formation. In particular, substrates containing five-membered heterocycles, such as 2-ethynylthiophene and 2-ethynyl-1-methylpyrrole, were converted both rapidly and selectively to their trans-head-to-tail dimer. Even 2-ethynylpyridine was converted rapidly and exclusively to its trans-head-to-tail dimer, but at relatively low substrate concentrations competing reactions between the catalyst and the pyridyl moiety took place.
Summary

kinetic and mechanistic study in combination with stoichiometric reactions of catalyst precursors revealed that the increased reactivity and selectivity are the result of electronic alkyne substituent effects and metal-heteroatom interactions. The presumed active catalyst species \( \text{Cp}^* \text{LaCCR} \) is not stable, as it dimerizes into an alkynyl bridged, dinuclear derivative \( [\text{Cp}^* \text{La(µ-CCR)}]_2 \) that undergoes C-C coupling to form a butatrienyl derivative \( [(\text{Cp}^* \text{La})(\mu-\eta^5: \eta^5-\text{RC}_4\text{R})] \). The formation of butatrienyl derivatives from dimeric alkynyl derivatives was found to be governed by a combination of steric and electronic factors.

The application of the catalytic 1-alkyne dimerization reaction to the preparation of conjugated polymers is discussed in Chapter 6 (Scheme 7-5). The effect of the (hetero)arene moiety, with and without solubilizing aliphatic substituents, on the regioregularity of the polymers has been investigated. The application of 3-\( \eta \)-hexyl-2,5-diethynylthiophene, in particular, was found to afford conjugated polymers that were highly regioregular with respect to the formed butenynyl linkage. Monoethynyl substrates were used to control the molecular weight of the polymers. The formed conjugated polymers and their physical properties have been studied by a variety of spectroscopic methods.

Scheme 7-5. The formation of (cross-)conjugated polymers via catalytic dimerization of 1,4-diethynylbenzenes.