3. The cyclodimerization of 1-methylalk-2-yynes catalyzed by rare-earth metallocenes

3.1. Introduction

Transition-metal catalyzed oligomerization reactions of alkynes constitute an effective synthetic method for forming new carbon-carbon bonds between unsaturated organic compounds. Important examples include linear oligomerization, (co-)cyclotrimerization and cyclotetramerization reactions, catalyzed by a variety of transition-metal complexes. Current mechanistic understanding of these reactions entails carbon-carbon bond formation via oxidative coupling or metal alkyne π-bonding which activates the carbon-carbon triple bond towards nucleophilic attack.

Scheme 3-1. The catalytic cyclodimerization of 1-methylalk-1-yynes.

Catalytic alkyne cyclodimerization reactions that produce alkylidenecyclobutenes are scarce and only a few examples exist in literature. Alkyl-substituted 1-methylalk-2-yynes CH₃CCR (R = Me, Et, nPr) have been reported to undergo catalytic cyclodimerization in the presence of Cp*₂LnCH(SiMe₃)₂ (Ln = La, Ce), yielding mixtures of substituted 3-alkylidenecyclobutenes (Scheme 3-1). Unfortunately, further development of this catalytic system was inhibited by the small scope of substrates (i.e. 1-methylalk-1-ynes bearing small alkyl groups) and the low catalytic activities (e.g. 2-butyne is converted with a turnover frequency $N_t$ of 2.0 h⁻¹ at 80 °C) and (regio)selectivities. The use of Me₂Si(C₅Me₄)₂CeCH(SiMe₃)₂ resulted in lower catalytic rates and failed to broaden the scope of substrates. In contrast to most metal-catalyzed alkyne reactions, a mechanism involving α-methyl C-H activation, forming a lanthanide propargyl Cp*₂LnCH₂CCR, was proposed.

Due to the inherent reactivity of functionalized four-membered carbocycles and the possibility of a variety of further synthetic manipulations, the discovery of new methods for their construction is an active area of research. Contrary to other four-membered carbocycles, the synthetic access to alkylidenecyclobutenes is not straightforward and has been approached through the thermal coupling of alkynes and allenes or copper-mediated cyclization of 1,4-enynes. Mainly because of their high reactivity and their limited synthetic access, alkylidenecyclobutenes belong to a relatively unexplored class of molecules, their reported reactivity being limited to scattered examples of thermolysis, singlet oxygenation, electrophilic addition and polymerization reactions.

A study involving the synthesis, structure and reactivity of aryl-substituted η¹-allenyl/propargyl metallocene complexes Cp*₂Ln(η¹-CH₂CCAr) of the rare-earth metals revealed that 1-phenyl-1-propyne undergoes permethylanthanocene-catalyzed cyclodimerization, forming mainly (E)-3-benzylidene-2-methyl-1-phenylcyclobutene (Chapter 2). The goal of the investigations described in this Chapter was to further explore the scope and selectivity of the permethylanthanocene-mediated cyclodimerization reaction of propynylaromatics, searching for highly selective catalytic pathways general to the construction of four-
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membered carbocycles. First, the catalytic cyclodimerization of 1-phenyl-1-propyne is described, including reaction kinetics and mechanistic pathways to the observed products. Then, the effect of temperature, metal ion radius, substrate substituent pattern and ancillary ligation on the rate and selectivity is examined. Finally, the possibility of applying the cyclodimerization reaction as a method to prepare novel (cross-)conjugated polymers is investigated.

3.2. The cyclodimerization of propynylaromatics

3.2.1. Lanthanocene-catalyzed cyclodimerization

Catalyst precursors

When a benzene-d₆ solution of Cp*₂LaR [R = CH(SiMe₃)₂ (1a), H (2a), η₃-CH₂CCPh (3a)] was heated to 80-120 °C in the presence of an excess amount of 1-phenyl-1-propyn (10-25 equiv.), slow consumption of 1-phenyl-1-propyn was observed. NMR analysis of the reaction mixture indicated the conversion of 1-phenyl-1-propyn (4) into mainly (E)-3-benzylidene-2-methyl-1-phenylcyclobutene (5) (eq. 3.1). The catalytic nature of the cyclodimerization reaction was confirmed by performing a control experiment without metal complex. A solution of 1-phenyl-1-propyn in perdeuteriobenzene remained unchanged after 12 days at 120 °C, as indicated by NMR and GC-MS analysis.

\[
\begin{align*}
\text{Ph} & \quad \text{Cp*}_2\text{LaR} \quad 5 \text{ mol\%} \\
& \quad \text{C₆D₆} \quad 120 \degree C \\
\text{Ph} & \quad \text{Ph} \\
4 & \quad \text{Ph} \\
& \quad 75\% \\
\end{align*}
\]

5 \(75\%\)

6 \(10\%\)

7 \(9\%\)

The product mixtures obtained with the complexes 1a-3a were identical (NMR, GC/GC-MS) and the only lanthanocene species observed by In situ ¹¹¹H NMR spectroscopy during substrate conversion was the complex Cp*₂La(η₃-CH₂CCPh) (3a). The mixtures containing 1a showed lower rates of substrate conversion than mixtures containing of 2a and 3a, consistent with the relative rate of propargylic metalation of 1-phenyl-1-propyn of 1a as compared to 2a (Chapter 2). The rates of substrate conversion for mixtures containing 2a and 3a in the presence of a 20-fold molar excess of 1-phenyl-1-propyn are invariant within experimental error. In both cases, complete substrate conversion was observed within 7 days at 120 °C.

Reaction intermediates

When the substrate was completely consumed, ¹¹¹H NMR resonances attributable to 3a disappeared and new resonances were observed. The identities of these new organometallic species could not be established unequivocally, but NMR and GC-MS analysis of reaction mixtures, treated with trimethylsilylchloride (TMSCl), point to the cyclobutenyl derivatives C and F (Scheme 3-2). For example, the formation of two sets of characteristic ¹³C NMR resonances at δ 43.66 and 41.01 ppm and δ 12.22 and 11.36 ppm was observed after addition of TMSCl. The former set is assigned to the endocyclic CH group of the silylated alkylidenecyclobutenes 9 and 10, while the latter set is assigned the exocyclic methyl group, consistent with literature values (vide infra). Because the formed methylenecyclobutenes undergo decomposition during GC-MS analysis (vide infra), the product mixtures were subjected to catalytic hydrogenation prior to GC analysis. This methodology allowed for the quantitative analysis of stable derivatives by means of FID-GC. GC-MS analysis of the above mixtures after treatment with TMSCl and catalytic hydrogenation indicated the presence of two C₆H₅Si isomers (in a 71:29 ratio according to FID-GC), corresponding to the expected hydrogenated derivatives of 9 and 10. Attempts to prepare the proposed cyclobutenyl organolanthane derivatives F and G by reacting 3a with a two-fold molar excess of 1-phenyl-1-propyn gave reaction mixtures in which 3a was the major organometallic species.
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Scheme 3-2. The reactions of the organometallic species present during the catalytic cyclodimerization of 1-phenyl-1-propyne.

**Mechanism**

Catalytic cyclodimerization of alkyl-substituted 1-methyl-alk-1-yynes was previously observed for \( \text{Cp}^*\text{LnCH(SiMe}_3\text{)}_2 \) (Ln = La, Ce) and a catalytic cycle was proposed.\(^5\) Analogous reaction sequences (i-v) can be envisioned for the present catalytic system (Scheme 3-3). Additional experimental evidence is provided by the following observations: (i) the reactions of \( 1\text{a} \) and \( 2\text{a} \) with 1-phenyl-1-propyne afford \( 3\text{a} \) (Chapter 2), (ii) the product mixtures obtained with the complexes \( 1\text{a}-3\text{a} \) are identical, (iii) the only organolanthane species observed during cyclodimerization in the presence of excess substrate is \( 3\text{a} \), (iv) the reaction rate of substrate conversion is first-order in \( 3\text{a} \) (vide infra), (v) the observation of an alk-4-en-1-ynyl permethyllanthane derivative in the reaction of \( \text{Cp}^*\text{Y(\eta^3-CH}_2\text{CCPh)} \) (3b) with an excess amount of 1-phenyl-1-propyne (vide infra) and (vi) the ability of a permethyllanthane alk-1-en-1-y1 to undergo propagyllic C-H activation with 1-

Figure 3-1. 400 MHz \(^1\text{H} \) NMR spectra of a benzene-\( \text{d}_6 \) solution of \( 3\text{a} \) and a 20-fold molar excess of 1-phenyl-1-propyne, before (lower spectrum) and after substrate conversion (upper spectrum). Proton resonances denoted by an asterisk (*) are assigned to lanthanocene reaction intermediates.
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phenyl-1-propyne (as demonstrated by the reaction of \( \text{Cp}^* \), LaC(Ph)=C(Ph)H with 1-phenyl-1-propyne, giving \( 3a \) and cis-diphenylethene, Chapter 2). The observation of \( 3a \) as the resting state of the active catalyst argues for slow, rate-limiting alkyne insertion (\( ii \), Scheme 3-3), followed by rapid intramolecular cyclization (\( iv \)) and protonolysis (\( v \)). This picture is consistent with \( 3a \) being the major organometallic species after reaction of \( 3a \) with a two-fold molar excess of 1-phenyl-1-propyne and the rate of substrate conversion being first-order in substrate (\textit{vide infra}).

**Product analysis**

The major product \( 5 \) exhibits three broad singlets at \( \delta 6.45, 3.02 \) and 1.75 ppm in a 1:2:3 ratio in the \(^1H\) NMR spectrum of the reaction mixture, assigned to CHPh, endocyclic CH\(_2\) and exocyclic CH\(_3\), respectively. The proton resonances are broadened, because of long-range couplings, typical of substituted cyclobutenes.\(^{11}\) Characteristic \(^{13}C\) NMR resonances were observed at \( \delta 15.10 \) (q, \( J_{\text{CH}} = 125.6 \) Hz), 40.16 (t, \( J_{\text{CH}} = 139.2 \) Hz) and 111.68 (d, \( J_{\text{CH}} = 125.6 \) Hz) ppm, assigned to the CH\(_3\), endocyclic CH\(_2\) and CHPh groups, respectively. Both the proton and carbon chemical shifts are consistent with literature values of analogous substituted 3-methylenecyclobut-1-enes.\(^{11}\) The \textit{trans} stereochemistry of the exocyclic double bond was indicated by the absence of a NOE cross peak between \( \delta 6.45 \) (CHPh) and 3.02 (CH\(_2\)) ppm, while that between 3.02 and 1.75 ppm (CH\(_3\)) was observed. The proposed structure of \( 5 \) was furthermore corroborated by correlations observed with 2D NMR spectroscopy (i.e. \(^{1}H,^{1}H\)-COSY, \(^{1}H,^{13}C\)-gHSQC, \(^{1}H,^{31}C\)-gHMBC).

Attempts to isolate (\( E \))-3-benzylidene-2-methyl-1-phenylcyclobutene on a preparative scale were unsuccessful, as decomposition into unidentified compounds was observed upon contact with air (thereby excluding the facile use of chromatographic techniques) and at high temperatures during \textit{in vacuo} distillation attempts (>200 °C). In addition, suitable crystallization conditions employing a variety of solvents and solvent mixtures (\textit{e.g.} acetonitrile, toluene, hexanes) were not found. Considerable precedent exists for the highly reactive nature of alkylidenecyclobutenes.\(^{3,11,12}\) Although some exceptions are known which are reported to exhibit limited stability in air, most alkylidenecyclobutenes undergo extensive decomposition or polymerization on exposure to air or attempted purification by chromatographic techniques or distillation and are only stable under an inert atmosphere and in the absence of acids, bases or radical reagents.

Quantitative \(^1H\) NMR analysis of the cyclodimerization catalyzed by \( 1a\)-\( 3a \) by means of an internal standard (hexamethyldisiloxane) and appropriate long pulse delays indicated that the formation of \( 5 \) was accompanied by that of several by-products. GC-MS analysis indicated the presence of phenyllallene-\( d_1 \), 1-phenyl-1-propyne-\( d_6 \) and a variety of \( C_{18}H_{16} \) isomers (at least fifteen of which the three major isomers

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**Figure 3-2.** The conversion of \( 4 \) (18 equiv.) and the formation of \( 5-7 \) during the cyclodimerization reaction catalyzed by \( 3a \) (30.9 mM) in benzene-\( d_6 \) at 120 °C, as monitored by 400 MHz \(^1H\) NMR spectroscopy. The lines drawn connecting the experimental points represent fitted first-order exponential functions.
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corresponded to 61, 15 and 13% of the total amount of the C_{18}H_{16} isomers, as indicated by uncorrected FID-GC values) after quenching the reaction mixture with methanol-d_4.

The formation of phenylallene-d_1 and 1-phenyl-1-propyne-d_1 can be ascribed to the deuterolyis reaction of 3a which is known to give a mixture of acetylenic and allenylc deuterolysis products (Scheme 3-2, Chapter 2). The observation of the large amount of C_{18}H_{16} isomers with GC-MS is inconsistent with the composition of the product mixture as observed with NMR spectroscopy and can be explained by thermal, oxygen- and/or acid-induced decomposition of the formed methylenecyclobutenes during GC analysis (vide infra). In fact, the electrocyclic ring-opening of alkylidenecyclobutenes, forming vinylallene and ultimately benzene derivatives as major products, has been implicated by several studies. Because extensive decomposition of the present alkylidenecyclobutenes during GC analysis was only observed to a relatively small degree, GC-MS could still be used to characterize the major reaction products.

Because purification of the reaction products and reliable quantitative GC analysis were frustrated by the reactivity of the formed alkylidenecyclobutenes, a methodology was sought to convert the reaction products into stable derivatives. To distinguish the reaction products, furthermore, from the organic products formed from the organometallic species present, the crude reaction mixture was first treated with trimethylsilychloride (TMSCl), producing (Cp*2LaCl)_n and silylated organic derivatives (vide supra). Catalytic hydrogenation of crude reaction mixtures, quenched with TMSCl, afforded the desired cyclobutane derivatives, based on the presence of six C_{18}H_{20} isomers (in a 12:72:2:1:13:1 ratio, according to FID-GC) and two C_{21}H_{28}Si isomers (in a 71:29 ratio) as indicated by GC-MS, but these products could not be purified by column chromatography or characterized unambiguously by standard spectroscopic methods.

Gratifyingly, careful analysis of the crude reaction mixture by means of multinuclear 1D and 2D NMR spectroscopy led to the identification of the two major by-products. The presence of ^1H NMR resonances at δ 6.06, 3.27 and 1.73 in a 1:2:3 ratio pointed to the presence of (E)-3-benzylidene-1-methyl-2-phenylcyclobutene (6) which was formed with a selectivity of 10-13%, depending on the reaction conditions (vide infra, Table 3-1). This proposal is supported by the corresponding ^13C NMR resonances, 2D NMR

Scheme 3-3. The proposed catalytic cycle of the cyclodimerization reaction of 1-phenyl-1-propyne catalyzed by 1a-3a.
spectroscopy and the similarity with reported alkylidenecyclobutenes. The formation of 6 can, furthermore, be explained by 1,2-insertion of 1-phenyl-1-propyne into the propargylic La-CH₂ bond (vi and vii, Scheme 3-3), consistent with the catalytic sequences proposed for the formation of 5.

Other by-products could, in principle, result from competing protonolysis relative to intramolecular ring-closing, giving rise to linear alk-4-en-1-ynes. The absence of acetylenic carbons (δ ~80-90 ppm) argues against the (significant) presence of these compounds, however. The absence of multiplets, having a ~7 Hz proton-proton coupling, in the vinylic region of the ¹H NMR spectrum excludes, moreover, the presence of linear alk-4-en-1-ynes. Competing intermolecular alkyne insertion into B can also be discarded (Scheme 3-3), because organic products having masses higher than that of 1-phenyl-1-propyne dimers were not observed with GC-MS. It seems, therefore, that intramolecular alkyne insertion of B is rapid under the applied reaction conditions, competing effectively with substrate protonolysis and insertion.

The ¹H NMR spectrum of the reaction mixture displayed three characteristic proton resonances at δ 5.07, 4.57 and 4.12 ppm in a 1:1:1 ratio. A ¹H-¹³C gHSQC experiment revealed that the former two resonances corresponded to a triplet (J_CH = 158.0 Hz) at δ 95.88 ppm in the ¹³C NMR spectrum, while the latter corresponded to a doublet (J_CH = 158.0 Hz) at δ 56.50 ppm. The carbon resonance at δ 95.88 ppm is suggestive of an allenylic methylene group (i.e. =C=CH₂), but is too far downfield to correspond to a terminal allenylic methylene group and no resonance attributable to a central allenylic carbon resonance could be observed with ¹³C{¹H} NMR spectroscopy.¹⁴ Methylene groups resonating in the δ 110-90 ppm region of the ¹³C NMR spectrum are observed for methylenecyclobutane derivatives, however. Based upon these findings, the presence of 1,3-diphenyl-2-methyl-4-methylidenecyclobutene (7) was inferred which was formed with a selectivity of 9-11% (Table 3-1). The proposed structure is supported by the observed correlations with 2D NMR spectroscopy and the similarity of the NMR spectral data with reported analogous substituted methylenecyclobutenes (vide supra).

In order to account for the (catalytic) formation of 1,3-diphenyl-2-methyl-4-methylidenecyclobutene (7), insertion of 1-phenyl-1-propyne into the La-C bond of the σ-allylic tautomer of 3a seems to be the most plausible mechanistic scenario. Indirect evidence for the kinetic accessibility of a σ-allyl tautomer of 3a has been presented previously, as the reaction of 3a with methanol and phenylacetylene furnished mixtures of acetylenic and allenylic protonolysis products (Chapter 2). Accordingly, the reaction of 3a and 1-phenyl-1-
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propyne may give rise to a lanthanum vinylallene species (H) after 2,1-insertion into the σ-allenylic tautomer (i and ii, Scheme 3-4). Further reactivity, most likely, involves protonolysis with 1-phenyl-1-propyne, forming a substituted vinylallene, or four-electron electrocyclic ring closure (vide infra), forming 1,3-diphenyl-2-methyl-4-methylidenecyclobutene (7) after protonolysis (iii).

Electrocyclization of vinylallenes is a well-studied reaction, but its synthetic use has been limited by the high reaction temperatures required (i.e. 200-500 °C) and the fact that equilibrium mixtures of starting material and product are obtained. Over the last decade, however, appropriate substitution has been found to result in mild and unidirectional electrocyclization of vinylallenes. In fact, several titanated vinylallenes undergo facile isomerization to cyclobutenytitanium compounds at room temperature. As a consequence, electrocyclization of H is considered to be more facile than that of the vinylallene formed upon protonolysis of H. This view is supported by the absence of NMR resonances attributable to such a vinylallene or derivatives thereof in the reaction mixture (during and after substrate consumption). These considerations led us to propose that 7 is formed via route (i)-(iv) (Scheme 3-4). It should also be noted that no indirect evidence for the 1,2-insertion of 1-phenyl-1-propyne into the La-C bond of the σ-allenylic tautomer of 3a was found, which is consistent with the observed predominant 2,1-insertion mode of 1-phenyl-1-propyne in the σ-propargylic tautomer (vide supra).

Other minor by-products were formed with a combined selectivity of 1-2% (1H NMR), depending on the reaction conditions. Although their low relative concentration impeded unambiguous characterization, structures similar to (E)-3-benzyldiene-2-methyl-1-phenylcyclobutene (5) and (E)-3-benzyldiene-2-phenyl-1-methylcyclobutene (6) can be proposed on the basis of the comparable proton (i.e. δ 6.05, 6.01, 3.53, 3.46, 1.80 and 1.70 ppm) and carbon resonances (i.e. δ 15.09, 15.09, 41.45, 42.43, 117.45 and 116.27 ppm). Mechanistic pathways to these products may consist of transmetallation of 3a with 1-phenyl-1-propyne yielding phenyllallene (as observed for 3b, vide infra), followed by regiorandom insertion of phenyllallene into 3a. It should be noted that no experimental evidence for the formation of 8 was found in this study (Scheme 3-4).

Kinetic study

The kinetics of the cyclodimerization of 1-phenyl-1-propyne (4) catalyzed by Cp*2La(η3-CH2CCPh) (3a) were studied by means of normalized 1H NMR spectroscopy, using long pulse delays to avoid signal saturation under the present anaerobic conditions. Substrate consumption was monitored by normalizing the intensity of the methyl proton resonance (δ 1.65 ppm) against that of hexamethyldisiloxane (δ 0.11 ppm) as an internal standard. However, the methyl resonance of the substrate overlapped partially with those of the products at relatively high substrate conversion, thereby lowering the accuracy of the kinetic data. Improved kinetic data were obtained by means of line-fitting procedures. Due to the slow rate of the cyclodimerization reaction, the progress of reaction could not be monitored at a constant reaction temperature by NMR spectroscopy. The NMR tubes were heated in an electric oven and transferred to the spectrometer after appropriate time intervals. It
seems that this methodology limited the accuracy of the kinetic analysis to some extent, especially for the slower reactions.\textsuperscript{17} Even so, the rate of substrate consumption could be fitted convincingly (\(R^2 > 0.98\)) to first-order rate dependence on substrate concentration in most cases.

For the reaction of \(\text{Cp}^*\text{L}a(\eta^3\text{-CH}_2\text{CCPh})\) (3a) and 1-phenyl-1-propyne (4) in benzene-\(d_6\) solution, Figure 3-3 presents kinetic data typical of many runs, which show the rate to be first-order in substrate for at least 3 half-lives. The rate of substrate conversion was observed to be first-order in substrate over a 5-fold concentration range (0.76-3.81 M) at constant catalyst concentration (Entries 5 and 7, Table 3-1). When the initial substrate concentration was maintained constant and the concentration of 3a was varied over a 5-fold concentration range (16.2-76.4 mM), a plot of the reaction rate versus catalyst concentration ([3a]) indicates that the reaction is first-order dependent on 3a (Figure 3-3). Thus, the empirical rate law for the cyclodimerization of 4 catalyzed by 3a can be formulated as \(v = k_{\text{obs}}[3a][4]\).

Influence of the reaction temperature

The cyclodimerization reaction of 1-phenyl-1-propyne (20 equiv.) catalyzed by 3a was performed at different temperatures in order to investigate the effect of temperature on both the rate and selectivity. Complete conversion of 1-phenyl-1-propyne was observed after 7 days at 120 °C. When the reaction was conducted at 100 °C, complete substrate conversion was observed after 28 days. In both cases, the kinetic data obtained agreed well with first-order rate dependence on substrate. The accuracy of the kinetic data for the reaction performed at 80 °C was limited by the slow rate of substrate conversion. After following the reaction for 30 days (1.7 half-lives) the substrate consumption was fitted only moderately to first-order kinetic behavior in substrate (\(R^2 = 0.9678\)). Repeated experiments involving fewer measurements (i.e. better temperature control) did not lead to kinetic data of higher accuracy. Thus, the present results clearly indicate that the rate of cyclodimerization is enhanced by increasing the reaction temperature, but the experimental error of the present methodology does not allow for an accurate determination of activation parameters by means of standard Eyring and Arrhenius analyses.

The selectivity for the formation of (\(E\))-3-benzylidene-1-methyl-2-phenylenecyclobutene (5) decreased with increasing reaction temperature (Table 3-1). The increased formation of (\(E\))-3-benzylidene-1-methyl-2-phenyl-cyclobutene (6, from 1,2-insertion into the propargylic La-CH\(_2\) bond of 3a, \textit{vide supra}) and 1,3-diphenyl-2-methyl-4-methylidenecyclobutene (7, from 2,1-insertion into the allenylidene L-La-C bond of 3a, \textit{vide supra}) indicates that other processes compete more effectively with 2,1-insertion of 1-phenyl-1-propyne into the La-CH\(_2\) bond of 3a at higher reaction temperatures.

3.2.2. Influence of the metal ion size

The effect of changing the metal in organometallic compounds of rare-earth metals is predominantly steric in nature and many examples exist in literature where the selectivity and rate of reactions can be tuned by...
varying the ionic metal radius along the lanthanide and group 3 triad. The available metal sizes range from 0.870 Å for trivalent scandium to 1.160 Å for trivalent lanthanum in formally eight-coordination. Yttrium (1.019 Å), representing an intermediate size in this range, was chosen to evaluate the effect on the rate and selectivity of the rare-earth metalocene-catalyzed cyclodimerization reaction upon decreasing the metal ionic radius of the catalyst Cp*₂LnCH₂CCPh (3a).

When a reaction mixture of Cp*₂YCH₂CCPh (3b) and an excess amount of 1-phenyl-1-propyne (10-20 equiv.) was heated to 100 °C in benzene-d₆ for several days, no significant substrate consumption was observed with ¹H NMR spectroscopy. Instead, small amounts of phenylallene (0.31 equiv. per Y) and (E)-3-benzyldiene-2-methyl-1-phenylcyclobutene (0.16 equiv. per Y) were formed after several hours, while 3b was slowly consumed. Further heating did not change the amount of phenylallene and (E)-3-benzyldiene-2-methyl-1-phenylcyclobutene, but 3b was completely converted within three days at 100 °C into a 85:15 mixture of the pent-1-en-4-yn-1-yl yttrocene derivatives 11b and 12b, respectively, according to ¹H NMR spectroscopy (Scheme 3-9). The major species 11b was characterized by multinuclear ¹D and ²D NMR spectroscopy (see Experimental Section). A particularly interesting feature is the observation that the ¹³C NMR resonances of the acetylenic carbons in 11b exhibit yttrium-carbon coupling. Attempts to isolate 11b on a preparative scale by fractional crystallization have not yet been successful. The proposed structures of 11b and 12b are, furthermore, supported by the identity of their quenching products with methanol-d₄, i.e. (E)-1,5-diphenyl-1-deuterio-2-methyl-1-penten-4-yne (13-d₄) and (Z)-3,6-diphenyl-2-deuterio-2-penten-5-yne (14-d₄).

When the reaction mixture was allowed to react further at 100 °C, proton resonances in the Cp* (δ 2.5-1.5 ppm) and aliphatic region (δ 1-0 ppm) appeared, while the intensities of resonances due to 11b and 12b diminished slowly. Unfortunately, NMR spectra were not structurally diagnostic due to overlapping signals. The reaction mixture was quenched with methanol-d₄ after 24 days at 100 °C and analyzed with GC-MS. Besides 13-d₄ and 14-d₄, the presence of small amounts of unidentified oligodeuterated, organic compounds C₉H₆ (several isomers of m/z 232, consistent with the mass of a dimer of 1-phenyl-1-propyne) and C₉H₈ (three isomers of m/z 252) was indicated.

These findings indicate that insertion of 1-phenyl-1-propyne into the Y-C bond of 3b is feasible. In spite of the larger steric constraints of 3b, due to the smaller metal size, the electronically favored 2,1-insertion (i) predominates over the sterically favored 1,2-insertion (ii) of 1-phenyl-1-propyne at 100 °C (Scheme 3-9). The presence of phenylallene can be explained by transmetallation of the σ-allenyl tautomer of 3b with 1-phenyl-1-propyne (Scheme 3-6), as previously observed for sterically hindered propynylenes and Cp*₂LnCH₂CCAr complexes (Chapter 2). Clearly, transmetallation of the σ-propargyl tautomer of 3b with 1-phenyl-1-propyne is nonproductive. In contrast to 3a (Chapter 2), no further reactivity is observed for phenylallene and 3b.
The lack of catalytic substrate consumption can be attributed to the high stability of the pent-1-en-4-yn-1-yl yttrocene derivatives 11b and 12b towards both intramolecular cyclization and substrate protonolysis. It seems that the yttrium metal is too small to allow intramolecular alkyne insertion, although an intramolecular metal-to-alkyne interaction is evident from the observed yttrium-carbon couplings of the acetylenic carbon resonances. This intramolecular alkyne coordination is most likely responsible for the absence of substrate protonolysis, as it effectively competes with intermolecular alkyne coordination. Upon prolonged heating, however, evidence for intramolecular ligand metallation was found.

The observation of organic compounds C19H24 is consistent with the coupling products, originating from insertion of 1-phenyl-1-propyne into the Y-CH2 bond of the fulvene species (15b). Insertion of unsaturated bonds into the metal-methylene bond of a fulvene species have been reported for analogous Cp*FvM (M = Zr, Ti) complexes.20 Extensive H/D scrambling and the observation of proton resonances in the aliphatic region was also observed, when benzene-d6 solutions of Cp*2Ln(η3-CH2CCPh) and Cp*2LnCH(SiMe3)2 were heated to 120 °C (Chapter 2).21 The formation of fulvene derivatives [Cp*(C5Me4CH2-η5:η2)Ln] was put forward to account for these observations. The fact that the functionalized Cp* derivatives are not deuterated after quenching with methanol-d4 implies that the insertion products are not stable under the reaction condition. Regiorandom insertion of 1-phenyl-1-propyne and a 1,3-H shift of the insertion product can be proposed to rationalize the formation of three different isomers.

In conclusion, no catalytic cyclodimerization of 1-phenyl-1-propyne was observed with Cp*2Y(η3-CH2CCPh) (3b). Although the present data indicate that 1-phenyl-1-propyne insertion into the Y-C bond of 3b does take place, both intramolecular alkyne insertion and intermolecular alkyne protonolysis of the formed insertion product are practically absent upon substituting the lanthanum metal center in the catalyst Cp*2LnCH2CCPh with the smaller yttrium.

### 3.2.3 Influence of the ancillary ligation

Introduction

Structurally, a considerable opening of the metal coordination sphere at the σ-ligand equatorial girdle is obtained by replacing the bis(pentamethylcyclopentadienyl) ligation in Cp*LnR by the ansa-ligation Me2SiCp*=LnR (Cp*= C5Me4) and it has been shown that linking the cyclopentadienyl ligands by a Me2Si group greatly influences the rates of insertion and σ-bond metathesis.22 The present results revealed that intermolecular alkyne insertion is rate limiting in the cyclodimerization reactions and that steric interactions between substrate and catalyst influence the observed selectivity. Reactions of Me2SiCp*=LnCH(SiMe3)2 (Ln = Y 23b, Ce 23c) with 1-phenyl-1-propyne (20 equiv.) were conducted in order to investigate the effects on the rate and selectivity of the cyclodimerization reaction upon opening the metal coordination environment of the catalyst. Previous attempts to apply the catalyst precursor 23c in the catalytic cyclodimerization of 2-propyne did not lead to catalytic substrate conversion. Instead, a catalytically inactive product was formed, tentatively formulated as the 2-alkynyl derivative (Me2SiCp*=CeCH2CCMe).2b

![Scheme 3-6. Transmetalation reaction of 3b with 1-phenyl-1-propyne.](image-url)
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When a benzene-d6 solution of Me2SiCp"2YCH(SiMe3)2 (23b) was heated to 120 °C in the presence of a 20-fold molar excess of 1-phenyl-1-propyne, slow propargylic metalation took place, as seen from the slow formation of CH2(SiMe3)2. 1H NMR spectroscopy indicated that complete substrate conversion into several products took place after 16 days at 120 °C. Upon complete substrate conversion, 12% of 23b was present in the reaction mixture. GC-MS analysis indicated the presence of dimers (m/z 232) and tetramers (m/z 464), but did not provide information on the number of formed products, due to thermal, oxygen- and/or acid-induced decomposition of the products during GC analysis (Section 3.2.1). Assuming a linear relationship between the response factors and the carbon numbers of the oligomers, FID-GC values of the reaction products could be expressed in terms of monomeric units. These normalized FID-GC values revealed that the reaction displayed a 89% selectivity for dimerization and a 11% selectivity for tetramerization. Even though the product mixture was too complex for conclusive NMR analysis, the major products could be identified as (E)-3-benzyldiene-1-methyl-2-phenylcyclobutene (5) and 1,3-diphenyl-4-methyl-2-methylene-cyclobutene (7) (eq. 3.2).

![Equation 3.2](image)

The observed catalytic cyclodimerization of 1-phenyl-1-propyne in the presence of Me2SiCp"2YCH(SiMe3)2 (23b) is in marked contrast with that of Cp*2YCH(SiMe3)2 (1b) for which no catalytic reactivity was observed. It seems that the increased coordination sphere of the catalyst allows for intramolecular alkyne insertion. The observed major products 5 and 7 are formed from 2,1-insertion into the propargylic Y-CH2 and allenic Y-CHPh bond of the active catalyst, respectively (Section 3.2.1.). The observed regioselectivity corresponds to the electronically favored, but sterically more hindered insertion at the metal center and reflects the decreased steric demands of alkyne insertion in the more open coordination sphere of the catalyst. The similar preference for 2,1-insertion into both the propargylic Y-CH2 and allenic Y-CHPh bond is remarkable, because products originating from substrate insertion into the allenic metal-carbon were only minor by-products in the reactions of Cp*2La(η3-CH2CCPh) with 1-phenyl-1-propyne.

![Equation 3.3](image)

Me2SiCp"2CeCH(SiMe3)2

Heating a benzene-d6 solution of Me2SiCp"2CeCH(SiMe3)2 (23c) and 1-phenyl-1-propyne (20 equiv.) to 120 °C resulted within several minutes in a clear color change from purple to brown-red. Monitoring the progress of reaction by 1H NMR spectroscopy revealed that the substrate was completely converted after 16 h. On the basis of NMR and GC-MS analysis, the products were identified as 5 (25%), 6 (27%), 7 (14%) and an unknown tetramer (m/z 464, 30%) (eq. 3.3). Although the complexity of the product mixture hampered attempts to determine the structure of the tetramer unequivocally by means of NMR spectroscopy, the presence of new, non-overlapping 1H NMR resonances did allow for quantitative 1H NMR analysis. After quenching the product mixture with methanol (3 equiv.), FID-GC revealed a 64% selectivity for dimerization and a 36% selectivity for tetramerization. These values agree only moderately with those obtained from quantitative 1H NMR analysis (i.e. 52% selectivity for dimerization and 48% selectivity for tetramerization), even after taking the decomposition product(s) of the catalyst (5%) into account. Apparently, a nonlinear relationship between response factors and carbon numbers exists for the present oligomers. Hence, the normalized FID-GC values represent only an estimate for the degree of oligomerization. When the analogous reaction was performed at 80 °C, complete substrate conversion into 5 (9%), 6 (28%) and 8 (58%) was observed after 18 days. In this case, normalized FID-
GC analysis after methanolyis of the reaction mixture revealed a 41% selectivity for dimerization and a 59% selectivity for tetramerization.

These results indicate that Me₂SiCp"₂CeCH(SiMe₃)₂ (23c) is a more active (pre)catalyst for cyclodimerization of 1-phenyl-1-propyne than Cp*₂LaCH(SiMe₃)₂ (1a) and Cp*₂La(η³-CH₂CCPh) (3a). Monitoring the reaction at 80 °C with ¹H NMR spectroscopy revealed quantitative propargylic metalation within 6 h. The rate of CH₂(SiMe₃)₂ formation was found to be first-order in substrate concentration (R² = 0.9914, kobs = 0.293(2) M⁻¹·min⁻¹). This observation suggests that propargylic metalation of 23c is more rapid than that of 1a (i.e. quantitative within 5.4 h at 120 °C). Even so, the observed 6-fold rate increase of substrate conversion for the reaction with 23c relative to that with 1a most likely reflects an increased rate of alkyne insertion in a more open metal coordination sphere of the catalyst. Unfortunately, the increased catalytic activity is accompanied by a lower selectivity. As compared to 3a, 2,1-insertion of substrate into the propargylic metal-carbon bond to form 5 seems to be less favored in this system relative to other modes of substrate insertion into the active catalyst, such as 1,2-insertion into propargylic Ln-CH₂ to form 6 and 2,1-insertion into allenyl Ln-CH to form 7. In analogy to the reactions of 3a with 1-phenyl-1-propyne, the formation of products originating from the sterically more hindered insertion at the metal center (i.e. 5 and 8) decreased upon decreasing the reaction temperature. It is interesting to note that the relative formation of tetramer increased upon decreasing the reaction temperature. Apparently, the rate of protonolysis by substrate increases relative to that of multiple alkyne insertions upon increasing the reaction temperature.

Concluding remarks
The results for Me₂SiCp"₂LnCH(SiMe₃)₂ (Ln = Y, Ce) reveal that the ancillary ligation influences not only the reaction rate by enhancing both the rate of propargylic metalation and alkyne insertion reaction sequences, but the reaction selectivity to a significant degree as well. Linking the cyclopentadienyl ligands with a Me₂Si group led to a decreased relative formation of 5 and an increased tendency to form oligomers higher than dimers. It seems therefore that lowering the steric demands of alkyne insertion decreases the preference for the electronically preferred 2,1-insertion mode (to give 5) over the sterically preferred 1,2-insertion mode (to give 6) and decreases the preference for dimerization over higher oligomerization.

The present findings suggest also that alkyne insertions into the allenylic Ln-CH(Ph) bond of the active catalyst are more facile in a Me₂SiCp"₂ ligand environment than in Cp*₂ ligand environment. This observation is consistent with the higher steric requirements for the formation of an initial η¹-allenyl-like Lewis base adduct relative to that of an initial η¹-propargyl-like Lewis base adduct (Chapter 2).

3.2.4. Reactions with 2-propynyltoluene

Introduction
In order to assess the effect of ortho-substituents on the rate and selectivity of the lanthanide-catalyzed catalytic cyclodimerization of 1,4-dipropynylphenyl derivatives (Section 3.3), the reaction of 3a with 2-propynyltoluene (16) was investigated as a model substrate.

Cp*₂LaCH₂CCPh

When Cp*₂LaCH₂CCPh (3a) was heated in benzene-d₆ to 100 °C for several days in the presence of a 20-fold molar excess of 2-propynyltoluene (16), slow substrate consumption was observed with ¹H NMR spectroscopy. The progress of reaction could be followed in time by monitoring the intensity of the substrate CH₃ ¹H NMR resonance in time with ¹H NMR spectroscopy, thereby revealing first-order rate dependence on substrate concentration (R² = 0.9974, kobs = 1.64(2) M⁻¹·day⁻¹) for at least 3 half-lives. After heating for 37 days, the reaction was stopped by quenching the reaction mixture with methanol-d₄. GC/GC-MS analysis indicated the presence of several isomeric dimers (m/z 260, at least fifteen of which the two major isomers corresponded to 34 and 27% of the total amount of the C₂₀H₂₀ isomers, according to normalized FID-GC values), two isomers of C₁₀H₁₄ (m/z 246, corresponding to the mass of a cross-coupled dimer of 1-phenyl-1-propyne and 2-propynyltoluene) and three isomeric trimers (m/z 390). The multitude of minor isomers can plausibly be ascribed to oxygen- and/or acid-induced decomposition during GC-analysis (Section 3.2.1). Normalized FID-GC revealed a 96% selectivity for dimerization and a 4% selectivity for trimerization.

¹H NMR analysis of the reaction mixture indicated that the propargyl derivative Cp*₂LaCH₂CCPh (3a) was completely converted into Cp*₂LaCH₂CC₆H₄Me-2 within 1 day. Further heating led to slow substrate
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consumption and the formation of a complex reaction mixture, exhibiting several vinylic ($\delta$ 7.5 and 4.3 ppm) and aliphatic ($\delta$ 2.5-1.5 ppm) proton resonances. The two major products could be identified with NMR spectroscopy by comparison with previous alkylidene cyclobutenes as $(E)$-3-(2-methylbenzylidene)-2-(2-methylphenyl)-1-methylcyclobutene (17) and $(E)$-3-(2-methylbenzylidene)-2-methyl-1-(2-methylphenyl)cyclobutene (18). After 37 days, 88% of the substrate was consumed and the two major products 17 (4.7 equiv. relative to 3a) and 18 (5.6 equiv.) were formed with a selectivity of 27 and 32%, respectively. The identity of the other dimers and the trimers is presently unknown, but $^{13}$C NMR analysis of the reaction mixture indicated several acetylenic signals, suggesting the presence of linear dimers or trimers.

$$\text{Cp}^*\text{LaCH}_2\text{CCPh} \quad (3a)$$

5 mol% $\text{C}_6\text{D}_6$ 100 °C

These findings reveal that the rate of cyclodimerization is decreased ~3-fold upon substituting the phenyl group of 1-phenyl-1-propyne with an ortho-methyl group. Increasing the steric bulk of the phenyl group also affects the selectivity of the reaction to a significant degree. The selectivity for the cyclodimer, resulting from 2,1-insertion of the propynylarene into the La-CH$_2$ bond, decreased from 75 to 27%, while the major product formed from 1,2-insertion of the propynylarene into the La-CH$_2$ bond of the catalyst. In contrast to analogous reactions with 1-phenyl-1-propyne, ortho-substitution led also to the formation of oligomers higher than dimers.

$$\text{Me}_2\text{SiCp'}^*\text{CeCH(SiMe}_3\text{)}_2 \quad (23c)$$

Upon heating a benzene-$d_6$ solution of Me$_2$SiCp’$^*$CeCH(SiMe$_3$)$_2$ (23c) and 2-propynyltoluene (20 equiv.) to 120 °C, the purple solution turned brown-red within several minutes. Monitoring the progress of reaction by $^1$H NMR spectroscopy revealed quantitative propargylic metalation after 4 h and complete substrate conversion after 55 days. Because the formation of the active catalyst is rapid as compared to subsequent catalytic reaction sequences, the rate of reaction could reasonably well be modeled by first-order rate
dependence on substrate concentration ($R^2 = 0.9807, k_{obs} = 2.09(1) \text{ M}^{-1} \text{ day}^{-1}$) for at least 3 half-lives. Several products formed and the major products were identified as $17$ ($33\%$), $18$ ($1\%$), $19$ ($2\%$) and $20$ ($2\%$) with NMR spectroscopy (eq. 3.5). Normalized FID-GC revealed a $85\%$ selectivity for dimerization (at least 7 isomers, of which the 4 major isomers were present in a 8:8:41:5 ratio) and a $15\%$ selectivity for trimerization (2 major isomers in a 1:1 ratio).

$$\text{(3.5)}$$

These results indicate that the rate of cyclodimerization is decreased dramatically upon substituting the phenyl group of 1-phenyl-1-propyne with an ortho-methyl group. The reaction of $23c$ with a 20-fold molar excess of 1-phenyl-1-propyne is complete after 16 h at 120 °C, whereas the analogous reaction with 2-propynyltoluene requires 55 days under identical reaction conditions for complete substrate conversion. Concomitantly, the selectivity for dimerization increased from 64% to 85%, while the nonspecific regioselectivity of cyclodimerization changed into a preference for cyclodimerization via the sterically favored 1,2-insertion mode. Substrate insertion into the allenyllic Ln-CH bond is also possible in this catalytic system.

Concluding remarks

The increased relative formation of the cyclodimer formed from 1,2-insertion rather than 2,1-insertion of substrate into the active catalyst can be rationalized, when the insertion of the carbon-carbon triple bond into the lanthanide-carbon bond of the propargyl is taken into account (Scheme 3-1). Insertion most likely takes place via a concerted, four-centered transition state (Scheme 3-7).\textsuperscript{27} When 1-aryl-1-alkynes or 1-aryl-1-alkenes add to the metal-carbon bond of electrophilic metal complexes, the electronically preferred 2,1-insertion mode commonly outweighs the sterically preferred 1,2-insertion mode.\textsuperscript{24} The higher observed preference for 1,2-insertion suggests that the steric hindrance resulting from ortho-methyl substitution decreases the rate of 2,1-insertion relative to that of 1,2-insertion.

Another effect of ortho-methyl substitution is the occurrence of trimerization in the reactions of $3a$. The reaction of $3a$ with 2-propynyltoluene displayed a $8\%$ selectivity for trimerization and a $92\%$ selectivity for dimerization, whereas exclusive dimerization was observed for the analogous reaction with 1-phenyl-1-propyne. Apparently, ortho-methyl substitution leads also to a decrease of the relative rate of intramolecular alkyne insertion (ii) and/or alkyne protonolysis (ii, Scheme 3-1), thereby favoring intermolecular alkyne insertion. A decreased relative rate of intramolecular insertion is also consistent with the observation of acetylenic carbons in the reaction mixture with $^{13}$C NMR spectroscopy, indicative of linear dimers and/or trimers.

Scheme 3-7. The insertion of propynylarene into the Ln-CH$_2$ bond of a rare-earth metalloocene propargyl.
Interestingly, ortho-methyl substitution has a different effect on the degree of oligomerization in the reactions of 23c. The reaction of 23c with 1-phenyl-1-propyne displayed a 70% selectivity for dimerization and a 30% selectivity for tetramerization, whereas the analogous reaction with 2-propynyltoluene exhibited a 85% selectivity for dimerization and a 15% selectivity for trimemerization. In this case, the increased steric bulk of the substrate lowers the rate of multiple alkyne insertions into the active catalyst as compared to that of propargylic metalation and/or intramolecular alkyne insertion.

3.3. The cyclodimerization of dipropynlaromatics

3.3.1. Introduction

A catalytic system capable of catalyzing the cyclodimerization of propynylarenes selectively to head-to-head dimers (via 2,1-metal insertion into the propargylic metal-carbon bond) should, in principle, yield a cross-conjugated polymer M, when allowed to react with 1,4-dipropynylbenzene (Scheme 3-8). Similarly, a catalytic system capable of selective head-to-tail cyclodimerization (via 1,2-metal insertion into the propargylic metal-carbon bond) should give rise to a conjugated polymer N. Both type of polymers are unprecedented and represent as such an interesting new class of (cross)-conjugated polymer in this very active field of research.

These polymerization reactions involving bifunctional substrates may be considered as taking place via a step growth mechanism. Polymerization reactions taking place by a step growth mechanism give rise to high molecular weight polymers only at high degrees of monomer conversion and the average length of the polymer chain is mostly limited by the presence of side reactions, the solubility of the growing polymer and the viscosity of the reaction medium. As a consequence, step growth polymerization reactions place generally stringent requirements on any reaction to be used for polymerization, such as very high conversions and selectivities.

The factors that govern the rate and selectivity of the lanthanidocene-catalyzed cyclodimerization reaction of propynylarenes as model substrates has been investigated. Unfortunately, the observed selectivities were not high, the rates were low and the major products were not stable under ambient conditions. In some cases, minor products originating from substrate insertion into the allenyllic metal-carbon bond of the catalyst
were observed. Similar to propargylic coupling (insertion into the propargylic metal-carbon bond), allenyl coupling may take place in a 1,2- (head-to-tail) and 2,1-manner (head-to-head), thereby introducing structural defects into the polymer backbone (Scheme 3-8). Despite the above limitations, explorative reactions of several catalyst precursors with dipropynylarenes were performed in order to assess the feasibility of the present cyclodimerization reaction as a route towards novel (cross)-conjugated polymers.

3.3.2. **1,4-Dipropynylbenzene**

When \( \text{Cp}^\ast_2\text{LaCH(SiMe}_3\text{)_2} \) (1a) was allowed to react in benzene-\( \text{d}_6 \) at 100 °C with an 8-fold molar excess of 1,4-dipropynylbenzene (21) and monitored with \( ^1\text{H} \) NMR spectroscopy, slow metalation was observed, as evidenced by the formation \( \text{CH}_2(\text{SiMe}_3)_2 \). After 1 day 66% of 1a was converted and \( ^1\text{H} \) NMR analysis indicated that one major \( \eta^3 \)-propargyl/allenyl derivative (one propargylic \( \text{CH}_2 \) proton resonance at \( \delta 2.81 \) ppm and one new \( \text{Cp}^\ast \) resonance at \( \delta 1.89 \) ppm in a 1:15 ratio) and one cyclodimer (broad singlets at \( \delta 6.28, 2.88, 1.70, 1.70 \) and 1.71 in a ratio of 1:2:3:3:3, respectively) were present in the reaction mixture. Further heating led to substrate consumption (~90% after 4 days as determined by line-shape analysis) and the formation of broad signals around \( \delta 6.5, 3.0 \) and 1.7 ppm, accompanied by a gradual change of the initially light-yellow solution into a viscous deep-red liquid and ultimately the precipitation of a dark-red solid. Because the formed polymer was found to be insoluble in both aromatic (i.e. benzene-\( \text{d}_6 \), toluene-\( \text{d}_8 \)) and halogenated deuteriosolvents (i.e. dichloromethane-\( \text{d}_2 \), tetrachloroethylene-\( \text{d}_2 \), bromobenzene-\( \text{d}_5 \)), even after prolonged heating under an inert atmosphere, characterization of the formed polymer by means of \( ^1\text{C} \) NMR spectroscopy could not be performed. The soluble portion of the reaction mixture displayed a \( ^1\text{H} \) NMR spectrum too complex for unambiguous assignments, especially after exposure to air. Also, GC/GC-MS analysis was not diagnostic in this respect.

Similar results were obtained after increasing the amount of substrate or the use of \( \text{Cp}^\ast_2\text{LaCH}_2\text{CCPh} \) (3a). For instance, when 3a was allowed to react with an 50-fold molar excess of 1,4-dipropynylbenzene in benzene-\( \text{d}_6 \) at 100 °C, a dark red mixture was obtained after 14 days, containing a red precipitate. No solvents were found that allowed \( ^1\text{C} \) NMR analysis of the formed polymer.

3.3.3. **1,4-Dipropynyl-2,5-di-\( n \)-hexylbenzene.**

**Introduction**

In order to facilitate the characterization of the polymer, it was decided to increase the solubility of the polymer by substituting 1,4-diethynylbenzene with flexible aliphatic side chains. It is likely that the incorporation of substituents onto the monomer will influence both the reactivity of the monomer and the regioselectivity of the reaction, as observed for 2-propynyltoluene (16) relative to propynylbenzene in the analogous cyclodimerization reaction (Section 3.2.4). The choice of the substituent is not clear-cut, however. On the one hand, it can be expected that both solubility and the degree of polymerization will increase with the length of the side-chain. On the other hand, however, the steric size of the substituent will most likely hinder metal coordination, thereby diminishing the observed reactivity as well. The \( n \)-hexyl substituent was chosen based on reports that the degree of polymerization and the solubility of poly\((p\)-phenylethynylene) substituted with 2,5-di-\( n \)-hexyl groups did not increase significantly upon chain elongation of the substituents.

**Reactions with \( \text{Me}_2\text{SiCp}^\ast_2\text{CeCH(SiMe}_3\text{)_2} \) (23c)**

Encouraged by the high activity of the catalyst precursor \( \text{Me}_2\text{SiCp}^\ast_2\text{CeCH(SiMe}_3\text{)_2} \) (23c) in the catalytic cyclodimerization of 1-phenyl-1-propyne, reactions of 23c and a 20-fold molar excess of 1,4-dipropynyl-2,5-di-\( n \)-hexylbenzene (22) were performed in benzene-\( \text{d}_6 \) at 120 °C. \( ^1\text{H} \) NMR spectroscopy indicated the quantitative formation of \( \text{CH}_2(\text{SiMe}_3)_2 \) within 2 h, while the intensity of the aromatic CH and propargylic CH, \( ^1\text{H} \) NMR resonances of 22 decreased slowly upon further heating. Substrate conversion was accompanied by the formation of new resonances in the vinyllic (\( \delta 7.0-3.0 \) ppm) and aromatic region of the \( ^1\text{H} \) NMR spectrum. The newly formed \( ^1\text{H} \) NMR resonances became increasingly broad and their intensity slowly decreased upon further heating (Figure 3-5). Complete substrate conversion was observed after 15 days and continued heating led to the precipitation of a red solid after 22 days.
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The relatively large number of $^1$H NMR resonances in the vinylic region observed during the $23c$-catalyzed polymerization reaction of $22$ point to nonselective cyclodimerization (Figure 3-7). The $^1$H NMR resonances of the products formed from cyclodimerization of 1-phenyl-1-propyne can be used to identify the nature of the formed C-C linkages in the polymer of $22$. The resonances at $\delta$ 6.52 and 3.85 ppm are assigned to the CH and CH$_2$ groups formed from head-to-head propargylic C-C coupling, while the resonances at $\delta$ 6.24 and 3.29 ppm are assigned to CH and CH$_2$ groups formed from head-to-tail propargylic coupling. These assignments are supported by the analogous CH and CH$_2$ $^1$H NMR resonances of \( \text{(E)} \)-3-benzyldiene-1-methyl-2-phenylcyclobutene (5) (i.e. $\delta$ 6.45 and 3.03 ppm, respectively) and \( \text{(E)} \)-3-benzyldiene-2-methyl-1-phenylcyclobutene (6) (i.e. $\delta$ 6.10 and 3.27 ppm, respectively). Because only allenic coupling of 1-phenyl-1-propyne led to products resonating in the region of 5.1-4.1 ppm, the presence of $^1$H NMR resonances in the region of 6.0-4.0 ppm demonstrates that insertion of $23c$ into the allenic metal-carbon bond of the catalyst is also feasible in this system. These considerations imply that head-to-head propargylic coupling is the dominant mode of C-C coupling in the reaction of $23c$ and $22$.

**Reactions with Cp*$^\text{+}$La($n^\text{-CH$_3$CCPh}$) (3a)**

To determine the effect of catalyst structure on the mode of C-C coupling in the present polymerization reactions, the reaction of Cp*$^\text{+}$La($n^\text{-CH$_3$CCPh}$) (3a) and a 20-fold molar excess of 1,4-dipropynyl-2,5-di-$n$-hexylbenzene (22) was conducted in benzene-$d_6$ at 120 °C. $^1$H NMR spectroscopy indicated very slow substrate consumption. For example, only 82% substrate conversion was observed after 50 days. After 3 months, the reaction mixture was found to be completely solidified into a dark-red solid. $^1$H NMR resonances observed during polymerization indicated that allenic coupling was practically absent in this system and that propargylic head-to-head coupling was the dominant mode of C-C coupling in the reaction of 3a and 22.

**Product analysis**

In analogy to the methyleneacylclobutenes formed from cyclodimerization of 1-phenyl-1-propyne, the formed polymers were found to be both acid- and air-sensitive. When the polymer solution was opened to air or quenched with methanol, an instantaneous color change from dark-red to light-yellow was observed. Attempts to isolate and identify products from these yellow suspensions under aerobic conditions afforded complicated mixtures that defied characterization. Attempts to remove the catalyst from the reaction mixture by quenching the solidified reaction mixture with a small amount of dry methanol (3 equiv. relative to the precatalyst) also led...
to complicated mixtures of ill-defined compounds, accompanied by a color change from red to yellow. Catalyst removal in the absence of air and acids was accomplished successfully by quenching the reaction mixture with trimethylsilylchloride. This methodology did not lead to a color change of the product mixture.

Quenching with trimethylsilylchloride introduces trimethylsilyl groups onto the formed polymer. Because the resting state of the catalyst was found to be the $\eta^3$-propargyl/allenyl derivative $\text{Cp}^*\text{La(}\eta^1\text{-CH}_2\text{CPh)}$ in the permethylanthanocene-catalyzed cyclodimerization of 1-phenyl-1-propyne (Section 3.2.1), a similar species may reasonably be assumed to represent the resting state of the catalyst in the present polymerization reactions. In analogy to other electrophilic reagents (e.g. methanol, phenylacetylene, Chapter 2), the reaction of such an $\eta^3$-propargyl/allenyl derivative with trimethylsilylchloride is likely to produce both allenyl and propargylic quenching products. Hence, plausible end-group structures of the polymer formed after quenching with trimethylsilylchloride are believed to be: $\text{Me}_3\text{SiCH}_2\text{C}$, $\text{Me}_2\text{SiCH}=$CH, and $\text{CH}_3\text{CC}$ (Scheme 3-10).

Poly($3a+22$)

When the solidified reaction mixture of $3a$ and $22$ was treated with trimethylsilylchloride after polymerization, a dark-red solution was obtained containing a dark-red solid. The suspension was filtered and washed with chloroform, affording a chloroform-soluble and chloroform-insoluble polymer fraction. The chloroform-soluble polymer fraction poly($3a+22$) was isolated as a red solid in 27% yield, while the insoluble fraction was isolated as a darker red solid in 35% yield. Both fractions were analyzed by infrared spectroscopy and the close resemblance of the infrared spectra of both polymer fractions suggests a similar structure. The insolubility of the chloroform-insoluble polymer fraction may be due to its higher molecular weight and/or the occurrence of cross-linking reactions. It can be envisioned that C-C bond forming reaction sequences that give rise to the formation of higher oligomers in the reaction of the monofunctional substrates introduce oligofunctional structural defects in the polymer (Section 3.2.4). These defects are likely to produce cross-linked structures upon further reaction.

The infrared spectra of both polymer fractions did not display symmetrical C≡C stretching vibrations (observed at 2225 cm$^{-1}$ for the monomer), thereby suggesting a relatively high degree of polymerization and the absence of linear oligomeric structures (Figure 3-6). Both polymer fractions displayed absorptions at −1670, −1600 and 1015 cm$^{-1}$ that are not present in the infrared spectrum of the monomer. The absorptions near 1670 and 1600 cm$^{-1}$ are presently assigned to symmetric and asymmetric coupled C=C-C=C stretching vibrations of the four-membered carbocycles, respectively, while the absorption at 1015 cm$^{-1}$ is assigned to the out-of-plane $\text{=C-H}$ bending vibration of the exo-methylene group. The vibrations at 900 and 722 cm$^{-1}$ point to the presence of vinylidene ($R\text{C}=$CH$_2$) and cis-alkene (cis-R=CH=CH) groups, respectively (Figure 3-6). In addition, no evidence for the proposed end-group structures was obtained with infrared spectroscopy, however.

The chloroform-soluble polymer fraction could also be analyzed with NMR spectroscopy (Figure 3-7). Previous $^1$H NMR assignments observed during the polymerization reaction are supported by the observed $^{13}$C NMR resonances of the isolated, chloroform-soluble polymer fraction. The $^{13}$C NMR resonances at δ 110.4, 40.72 and 14.12 ppm are assigned to the CH, CH$_2$ and CH$_3$ groups, respectively, of the cyclodimer formed from head-to-head propargylic coupling, while the $^{13}$C NMR resonances at δ 116.71, 39.62 and 10.98 ppm are...
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assigned to the CH, CH₂ and CH₃ groups, respectively, of the cyclodimer formed from head-to-tail propargylic coupling. These assignment are consistent with the analogous ¹³C NMR resonances of (E)-3-benzyldiene-1-methyl-2-phenylcyclobutene (⁵) (i.e. δ 111.66, 40.16 and 14.16 ppm, respectively) and (E)-3-benzyldiene-2-methyl-1-phenylcyclobutene (⁶) (i.e. δ 112.42, 36.26 and 10.81 ppm, respectively).

Low-intensity ¹³C NMR resonances in the 100-90 ppm region are reminiscent of the resonance previously observed for the CH₂=C group of 1,3-diphenyl-2-methyl-4-methylene-cyclobutene (⁷) (i.e. δ 95.88 ppm). However, the presence of such groups, originating from 2,1-insertion into the allenyl metal-carbon bond of the catalyst, is ruled out by the absence of corresponding ¹H NMR resonances (i.e. δ 5.05, 4.55 and 4.12 ppm of the CHH=C, CH=C and CHPH groups in ⁷, respectively). The significance of the ¹³C NMR resonances in the 100-90 ppm region is therefore not understood at present.

Attempts to determine the number-average degree of polymerization \( P_n \) by means of end-group analysis were hampered by the fact that the existence of propynyl end-groups could neither be confirmed nor discarded spectroscopically. If propynyl end-groups are neglected, quantitative ¹H NMR analysis of the trimethylsilyl groups relative to the aromatic or methylene-cyclobutene CH and CH₂ groups (of the soluble polymer fraction in dichloromethane-d₂ at 80 °C) reveals a \( P_n \) of 36(2).³³ The solubility of the polymer was too low in aromatic and halogenated deuteriosolvents to allow quantitative ¹³C NMR analysis and its air-sensitive nature precluded MALDI-TOF and GPC analysis under aerobic conditions.

Poly(23c + 22)

When the solidified reaction mixture of 23c and 22 was treated with trimethylsilylchloride after polymerization, a dark-red, chloroform-insoluble solid was obtained in virtually quantitative yield. The infrared spectrum of the polymer (23a + 22) resembles that of poly(3a + 22), but the intensity of the vibrations at 900 and 722 cm⁻¹ point to an increased presence of vinylidene (R=C=CH₂) and cis-alkene (cis-R=CH=CH=CH) groups (Figure 3-6).³³ Hence, infrared spectroscopy supports previous notion, based on ¹H NMR resonances observed during polymerization (vide supra), that the reaction of 23c and 22 takes place via nonselective C-C bond forming reaction sequences.
3.4. Conclusions

The present mechanistic study has demonstrated that the cyclodimerization reaction of 1-methylalk-2-ynes catalyzed by rare-earth permethylmetalocenes proceeds via well-established elementary reactions, such as protonolysis of a metal-carbon σ-bond by the acidic propargylic hydrogen of 1-methylalk-2-ynes and insertion of carbon-carbon triple bonds into a metal-carbon σ-bond. Intermolecular insertion of substrate into the metal-carbon bond of an η³-propargyl/allenyl derivative was found to be rate-limiting. In accord with previous investigations of rare-earth metallocone η³-propargyl/allenyl derivatives, the involvement of both the η¹-allenyl and η¹-propargyl tautomer was implicated by the identities of the reaction products.

The practical utility of this catalytic reaction was found to be limited by the small scope of substrates, the modest selectivities and the low catalytic rate. The observed catalytic activity and selectivity were found to be governed by a delicate balance between the steric properties of both the catalyst and substrate. The combination of Cp*₂LaCH₂CCPh and 1-phenyl-1-propyne performed best in catalysis. Changes in the metal ion
size ($\text{Cp}*\text{La} \rightarrow \text{Cp}*\text{Y}$), the ancillary ligation ($\text{Cp}*\text{La} \rightarrow \text{Me}_2\text{Cp}^*\text{Ln}$) or substrate structure (propynylbenzene → 2-propynyltoluene) did not lead to improved catalytic behavior.

Explorative reactions of $\text{Cp}^*\text{LaCH}_2\text{CCH}_3$ with 1,4-dipropynylbenzenes indicated that the slow rate, the low selectivity and the reactive nature of the formed polymer hampered the use of the present cyclodimerization reaction considerably as a practical route towards novel soluble (cross)-conjugated polymers.

### 3.5. Experimental section

**General considerations.** For general remarks and physical and analytical measurements, see Section 2.7. The compounds Me$_2$ScCp$^*$LaCH$_2$(SiMe$_3$)$_2$ (La = Y$^{36}$, Ce$^{37}$) and 2,5-di-n-hexyl-1,4-propynylbenzene$^{38}$ were prepared according to literature procedures. 1-Phenyl-1-propyne (distilled over CaH$_2$) and chlorotrimethylsilane (distilled over KOH) were purchased from Aldrich and dried before use as recommended.$^{39}$

**General purification procedure for 1-methylalk-2-ynes.** The liquids obtained after synthesis or received after purchase were brought in a flask containing freshly ground CaH$_2$ and stirred at room temperature under nitrogen for at least 24 h after several freeze-thaw-pump degassing cycles. Vacuum transfer afforded colorless oils for 1-phenyl-1-propyne and 2-propynyltoluene. 1,4-Di(prop-1-ynyl)benzene was dried as a pentane solution with CaH$_2$ and filtered through a plug of alumina (neutral, activated) to afford a colorless oil after evaporation to dryness. These substrate samples were subsequently stored at -30 °C under a nitrogen atmosphere.

1,4-Di(prop-1-ynyl)benzene (21). A similar procedure as described for 2-propynyltoluene (Chapter 2) was applied, using 1,4-diodobenzene (4.29 g, 13.0 mmol), Pd(PPh$_3$)$_4$ (0.75 g, 0.65 mmol), and anhydrous ZnBr$_2$ (8.10 g, 36.0 mmol). After 6 h stirring at room temperature, the reaction mixture was quenched with 50 mL of a saturated aqueous NaCl solution. Filtration, separation of the organic layer, drying over MgSO$_4$ and flash column chromatography (silica, petroleum ether) afforded yellow crystalline material after rotary evaporation. Sublimation (80 °C/1 mmHg) and repeated recrystallization from toluene produced colorless crystals. Yield: 1.84 g (92%).

$^1$H NMR (300 MHz, CDCl$_3$, 25 °C): δ 1.99 (s, CH$_3$, 3 H), 7.24 (s, CH$_3$, 2 H). $^{13}$C NMR (75 MHz, CDCl$_3$, 25 °C): δ 4.35 (CH$_2$), 79.49 (C= C), 87.28 (C=C), 123.14 (C=C), 131.28 (CH) ppm. IR (neat, [cm$^{-1}$]): 2950 (m), 2925 (s), 2845 (m), 2230 (w), 1465 (m), 1450 (m), 1425 (m), 1260 (w), 1020 (w), 990 (w), 905 (w), 870 (s), 725 (s). GC-MS, m/z (relative intensity): 154 (M$^+$, 100), 153 (M$^+$ - H, 43), 152 (65), 139 (19), 139 (9), 126 (6), 115 (22), 77 (5), 76 (17), 75 (7), 63 (11), 51 (7). Anal. Calcd. for C$_{12}$H$_{10}$ (154.21): C, 93.46%; H, 6.54%. Found: C, 93.75%; H, 6.62%.

**Reaction of $\text{Cp}^*\text{La}(\eta^3\text{C}_6\text{H}_5\text{CCH}_3)$ (3a) with 1-phenyl-1-propyne. NMR scale.** $\text{Cp}^*\text{La}(\eta^1\text{C}_6\text{H}_5\text{CCH}_3)$ (10.0 mg, 19.1 µmol) was dissolved in 0.50 mL of a benzene-$d_6$ solution of hexamethyldisiloxane (1.4 mM). After addition of 1-phenyl-1-propyne (47.7 µL, 401.3 µmol) with a microsyringe, the mixture was heated to 120 °C and monitored with $^1$H NMR spectroscopy. After 7 days at 120 °C, the substrate was consumed completely and the mixture was quenched with methanol-$d_6$. GC/GC-MS analysis indicated the presence of 1-phenylprop-1-ene, $\text{Cp}^*\text{D}, \text{phenylpropadiene}$-$d_1$, 1-phenyl-1-propyne-$d_4$ and at least 15 isomers of $\text{C}_6\text{H}_{10}$. The three major $\text{C}_6\text{H}_{10}$ isomers were assigned to the three major products, as observed with NMR spectroscopy. The major product of the reaction mixture could be characterized with HR-MS.

![Scheme 3-11. Numbering scheme of 5.](image-url)
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assigned due to considerable overlap with other signals. 1H-1H gCOSY (500-500 MHz, CD6, 25 °C): ABC, BC, CAB. 1H-1H gNOESY (500-500 MHz, CD6, 25 °C): ABD, BAC, DBC. 1H-1H gHSQC (500-500 MHz, CD6, 25 °C): AD, BD, AC, DC. GC-MS, m/z (relative intensity): 232 (M'9, 96), 231 (30), 217 (M' - CH3, 100), 216 (46), 215 (59), 203 (14), 202 (M' - 2 CH3, 49), 191 (13), 190 (6), 189 (17), 153 (8), 128 (8), 116 (8), 115 (31), 107 (6), 101 (6), 89 (7), 77 (6), 63 (6). GC-MS, m/z (calc., found): 235 (0.1, 0.1), 234 (1.8, 2.0), 233 (19.6, 20.7), 232 (100.0, 100.0). HR-MS: C18H16, calc.: 232.12520, found: 232.12585.

(E)-3-benzylidene-1-phenyl-2-methylcyclobutene (6): 1H NMR (CD6, 25 °C, 500 MHz): δ 1.73 (dt, J1,HH = 2.0 Hz, J2,HH = 6.0 Hz, CH3, 3 H, A), 3.27 (dq, J2,HH = 2.0 Hz, J3,HH = 1.5 Hz, CH2H, 2 H, B), 6.10 (q, J4,HH = 1.5 Hz, 1H, C) ppm. The aromatic signals could not be assigned due to considerable overlap with other signals. 13C NMR (CD6, 25 °C, 125.7 MHz): δ 10.81 (q, JCH = 126.8 Hz, CH3, 8), 36.26 (t, JCH = 137.8 Hz, CH2, 4), 112.42 (d, JCH = 151.2 Hz, =CH, 5) ppm. Due to overlapping signals, the aromatic and cyclobutenic carbon signals could not be assigned. 1H-1H gCOSY (500-500 MHz, CD6, 25 °C): ABC, BC, CAB. 1H-1H gNOESY (500-500 MHz, CD6, 25 °C): ABC, BAC, DBC, EBC. 1H-1H gHSQC (500-125.7 MHz, CD6, 25 °C): ABC, BAC, CAB, DBC, EBC. GC-MS, m/z (relative intensity): 235 (0.1, 0.3), 234 (1.8, 3.3), 233 (19.6, 26.3), 232 (100.0, 100.0). HR-MS: C18H16, calc.: 232.12520, found: 232.12585.


Reaction of Cp*2Y(η5-CH=CCPh) (3b) with 1-phenyl-1-propyne, NMR scale. Cp*2Y(η5-CH=CCPh) (18.1 mg, 38.1 µmol) was dissolved in benzene-d6 (500.0 µL) in a Teflon-capped NMR tube and 1-phenyl-1-propyne (480.0 µL, 384 µmol, 10.1 equiv.) was added with a microsyringe. The reaction mixture was heated to 100 °C and monitored with 1H NMR spectroscopy. After 3 days at 100 °C, when Cp*2Y(η5-CH=CCPh) was found to be completely converted into a 85:15 mixture of 11b and 12b, respectively, the mixture was evaporated to dryness, redissolved in benzene-d6 and analyzed with multinuclear 1D and 2D NMR spectroscopy. Subsequent addition of methanol-d6 (10 µL) was followed by NMR and GC/GC-MS analysis. GC/GC-MS analysis indicated the presence of Cp*D, C18H16D (two isomers 13-d1 and 14-d1 in a 86:14 ratio, respectively) and C17H15 (four isomers).

11b: 1H NMR (CD6, 25 °C, 500 MHz): δ 1.95 (s, 3CMe6), 2.08 (s, CH3), 3.46 (s, CH2, B) ppm. The aromatic signals could not be assigned due to overlap with other signals. 13C NMR (CD6, 25 °C, 125.7 MHz): δ 11.60 (dq, J1,CH = 125.4 Hz, J2,CH = 1.4 Hz, CH3, 3), 19.74 (q, J1,CH = 128.1 Hz, CH3, 7), 27.44 (t, J1,CH = 125.4 Hz, CH3, 3), 89.00 (d, JCH = 2.8 Hz, CH2, 5), 91.84 (d, JCH = 1.6 Hz, C), 110.40 (d, JCH = 6.1 Hz, C, 6), 118.20 (m, 10) 216.17 (d, JCH = 43.2 Hz, YCH, C) ppm. Due to overlapping signals, the aromatic carbon signals

$^{13}$H NMR (C$_6$D$_6$, 25 °C, 500 MHz): δ 1.99 (t, $^1$J$_{HH}$ = 0.6 Hz, CH$_3$), 3.54 (m, CH$_2$) ppm. The aromatic signals could not be assigned due to overlap with other signals. The proton and carbon NMR resonances are consistent with literature values of analogous alk-4-en-1-ynes. $^{13}$C NMR (C$_6$D$_6$, 25 °C, 75 MHz): δ 19.50 (CH$_3$), 235 (1.8, 1.8), 234 (19.6, 18.1), 232 (100.0, 100.0). GC-MS, m/z (relative intensity): 233 (M$^+$, 100), 232 (31), 218 (51), 217 (51), 216 (63), 215 (35), 203 (55), 202 (50), 189 (10), 156 (15), 155 (20), 154 (37), 153 (35), 128 (30), 118 (35), 116 (33), 115 (48), 91 (30), 28 (34). GC-MS, m/z (calc., found): 236 (0.1, 0.2), 235 (1.8, 1.8), 234 (19.6, 19.9), 232 (100.0, 100.0).

(1Z,4Z)-1,5-diphenyl-1-deutero-2-methyl-1-penten-4-yne (13-d$_2$). $^1$H NMR (C$_6$D$_6$, 25 °C, 300 MHz): δ 1.99 (t, $^1$J$_{HH}$ = 0.6 Hz, CH$_3$), 3.54 (m, CH$_2$) ppm. The aromatic signals could not be assigned due to overlap with other signals. $^{13}$C NMR (C$_6$D$_6$, 25 °C, 75 MHz): δ 19.50 (CH$_3$), 25.95 (CH$_3$), 82.71 (CC), 87.03 (CC) ppm. The aromatic carbon signals could not be assigned due to considerable overlap. $^{13}$C NMR (C$_6$D$_6$, 25 °C, 125.7 MHz): δ 21.26 (CH$_3$), 30.18 (CH$_2$) ppm. The acetylenic and aromatic carbon signals could not be assigned. The proton and carbon NMR resonances are consistent with literature values of analogous alk-4-en-1-ynes. $^{33}$C NMR, m/z (relative intensity): 233 (M$^+$, 62), 232 (34), 218 (100), 217 (76), 216 (92), 215 (39), 203 (65), 202 (40), 155 (25), 116 (25), 115 (32), 103 (31). GC-MS, m/z (calc., found): 236 (0.1, 0.1), 235 (1.8, 1.8), 234 (19.6, 18.1), 232 (100.0, 100.0).

Reaction of Cp$^*$_2Y([η$^6$]CH$_2$CCPh) (3b) with 1-phenyl-1-propyne after prolonged heating. NMR scale. Cp$^*$_2Y([η$^6$]CH$_2$CCPh) (9.1 mg, 19.2 µmol) was dissolved in 0.50 mL of a benzene-d$_6$ solution of hexamethyldisiloxane (1.4 mM). After addition of 1-phenyl-1-propyne (48.0 µL, 381 µmol) with a microsyringe the mixture was heated to 100 °C and monitored with $^1$H NMR spectroscopy. After 24 days at 100 °C, no significant changes were observed with $^1$H NMR spectroscopy and the reaction mixture was quenched with methanol-d$_6$. GC/GC-MS analysis indicated the presence of Cp$^*$_D, 1-phenyl-1-propyne, 13-d$_2$-1, 14-d$_2$-C$_{19}$H$_{18}$ (at least fifteen isomers of m/z 252) and C$_{19}$H$_{18}$ (several isomers of m/z 232).

C$_{19}$H$_{20}$: GC-MS, m/z (calc., found): 255 (0.1, -), 254 (2.0, 1.9), 253 (20.8, 21.6), 252 (100.0, 100.0); 255 (0.1, -), 254 (2.0, 2.9), 253 (20.8, 21.4), 252 (100.0, 100.0); 255 (0.1, -), 254 (2.0, 2.1), 253 (20.8, 21.0), 252 (100.0, 100.0).

Reaction of Cp$^*$_2La([η$^3$]CH$_3$CCPh) (3a) with 2-propynyltoluene. NMR scale. Cp$^*$_2La([η$^3$]CH$_3$CCPh) (10.1 mg, 19.3 µmol) was dissolved in 0.50 mL of a benzene-d$_6$ solution of hexamethyldisiloxane (1.4 mM). After addition of 2-propynyltoluene (50.0 mg, 384 µmol) the mixture was heated to 100 °C and monitored with $^1$H NMR spectroscopy. After 37 days at 100 °C, no significant changes were observed with $^1$H NMR spectroscopy and the reaction mixture was quenched with methanol-d$_6$. GC/GC-MS analysis indicated the presence of Cp$^*$_D, 2-propynyltoluene-d$_2$, 2-methylphenyllallene-d$_1$, C$_{20}$H$_{20}$ (at least fifteen isomers of m/z 130), C$_{19}$H$_{18}$ (two isomers of m/z 246) and C$_{19}$H$_{19}$ (three isomers of m/z 390) in the major products. The two major products were observed with NMR spectroscopy.

2-Propynyltoluene-d$_2$: GC-MS, m/z (relative intensity): 130 (M$^+$, 100), 129 (M$^+$ - H, 62), 128 (65), 127 (29), 116 (9), 115 (M$^+$ - CH$_3$, 83), 102 (8), 89 (7), 77 (10), 64 (11), 63 (14), 51 (14), 50 (7), 39 (7). GC-MS, m/z (calc., found): 132 (0.5, 0.7), 131 (11.0, 11.1), 130 (100.0, 100.0). The observed values differ somewhat from those obtained after synthesis (Chapter 2) due to the presence of 2-propynyltoluene-d$_2$.

2-Methylphenyllallene-d$_1$: GC-MS, m/z (relative intensity): 131 (M$^+$, 10), 130 (M$^+$ - H, 89), 129 (100), 128 (88), 127 (38), 116 (10), 115 (93), 103 (4), 102 (11), 91 (6), 89 (9), 77 (15), 74 (7), 65 (9), 64 (14), 63 (20), 51 (11), 39 (14). GC-MS, m/z (calc., found): 133 (0.5, 0.9), 131 (11.0, 10.7), 130 (100.0, 100.0).

(E)-3-(2-methylbenzylidene)-2-methyl-1-(2-methylphenyl)cyclobutene (17). $^1$H NMR (C$_6$D$_6$, 25 °C, 500 MHz): δ 1.66 (br. s, CH$_3$, 3 H), 2.16 (s, CH$_3$, 3 H), 2.33 (s, CH$_3$, 3 H), 3.53 (br. s, CH$_3$, 2 H), 6.28 (br. s, =CH, 1 H) ppm. The aromatic signals could not be assigned due to considerable overlap. $^{13}$C NMR (C$_6$D$_6$, 25 °C, 125.7 MHz): δ 10.86 (q, $^1$J$_{CH}$ = 124.9 Hz, CH$_3$), 20.18 (q, $^1$J$_{CH}$ = 125.8 Hz, CH$_3$), 20.41 (q, $^1$J$_{CH}$ = 125.8 Hz, CH$_3$), 39.36 (t, $^1$J$_{CH}$ = 137.6 Hz), 109.16 (d, $^1$J$_{CH}$ = 151.5 Hz, =CH) ppm. The aromatic signals and
cyclobutenic carbon signals could not be assigned due to considerable overlap. GC-MS, m/z (relative intensity): 260 (M', 100), 246 (M - CH₃, 61), 231 (18), 230 (M - 2 CH₃, 58), 229 (33), 228 (13), 219 (8), 217 (19), 216 (24), 215 (31), 204 (12), 203 (18), 202 (22), 165 (8), 155 (16), 153 (16), 152 (13), 130 (10), 129 (27), 128 (38), 127 (14), 116 (8), 115 (40), 105 (17), 77 (9). GC-MS, m/z (calc., found): 263 (0.1, 0.2), 262 (2.2, 2.5), 261 (22.0, 23.0), 260 (100.0, 100.0).  

(E)-3-(2-methylbenzylidene)-2-(2-methylphenyl)-1-methylcyclobutene (18). ¹H NMR (CD₂Cl₂, 25 °C, 500 MHz): δ 1.77 (br. s, CH₃, 3 H), 2.19 (s, CH₃, 3 H), 2.28 (s, CH₃, 2 H), 6.35 (br. s, =CH, 1 H) ppm. The aromatic signals could not be assigned due to considerable overlap. ¹³C NMR (CD₂Cl₂, 25 °C, 125.7 MHz): δ 15.47 (q, J_CH = 126.7 Hz, CH₃), 20.28 (q, J_CH = 126.5 Hz, CH₃), 21.28 (q, J_CH = 126.2 Hz, CH₃), 40.22 (t, J_C = 139.3 Hz, CH₃), 109.24 (d, J_C = 151.3 Hz, =CH) ppm. The aromatic and cyclobutenic carbon signals could not be assigned due to considerable overlap. GC-MS, m/z (relative intensity): 260 (M', 100), 246 (16), 245 (M - CH₃, 65), 231 (13), 230 (M - 2 CH₃, 49), 229 (88), 228 (11), 217 (8), 216 (16), 215 (46), 213 (13), 202 (8), 155 (16), 153 (14), 152 (10), 143 (8), 142 (8), 141 (10), 130 (14), 129 (35), 128 (42), 127 (15), 116 (10), 115 (50), 114 (12), 105 (26), 91 (12), 77 (10). GC-MS, m/z (calc., found): 263 (0.1, 0.2), 262 (2.2, 3.0), 261 (22.0, 25.5), 260 (100.0, 100.0). 

C₉H₈: GC-MS, m/z (calc., found): 249 (0.1, 0.3), 248 (2.0, 2.3), 247 (20.8, 20.6); 249 (0.1, 0.2), 248 (2.0, 2.0), 247 (20.8, 21.0), 246 (100.0, 100.0). 

C₆H₅: GC-MS, m/z (calc., found): 393 (0.5, -), 392 (5.2, 7.0), 391 (32.8, 35.5), 390 (100.0, 100.0); major isomer: 393 (0.5, 0.8), 392 (5.2, 5.8), 391 (32.8, 34.3), 390 (100.0, 100.0). 

Reaction of Cp*₂LaCH(SiMe₃)₂ (1a) with 1-phenyl-1-propyne, followed by treatment with trimethylsilylchloride and catalytic hydrogenation. NMR scale. 

Trimethyl[(E)-2-(2-methyl-3-phenyl-2-cyclobuten-1-ylidene)(phenyl)methyl]silane (9): ¹H NMR (CD₂Cl₂, 25 °C, 500 MHz): δ -0.02 (s, SiCH₃) ppm. The methyl, methylene and aromatic signals were obscured by overlapping signals. ¹³C NMR (CD₂Cl₂, 25 °C, 125.7 MHz): δ -2.16 (SiC₃H₂), 122.2 (CH₂), 43.66 (CH₃), 111.6 (CH₃SiMe₃) ppm. The cyclobutenic and aromatic carbon signals could not be assigned unambiguously. The carbon NMR resonances are consistent with reported values of alkylidenecyclobutenes (vide supra). 

Trimethyl[(E)-3-methyl-2-cyclobuten-1-ylidene]phenyl)methyl]silane (10): ¹H NMR (CD₂Cl₂, 25 °C, 500 MHz): δ -0.02 (s, SiCH₃), 3.24 (CH₂) ppm. The methyl and aromatic signals were obscured by overlapping signals. ¹³C NMR (CD₂Cl₂, 25 °C, 125.7 MHz): δ -2.16 (SiC₃H₂), 113.6 (CH₂), 41.01 (CH₃), 111.6 (CH₃SiMe₃) ppm. The cyclobutenic and aromatic carbon signals could not be assigned unambiguously. The proton and carbon NMR resonances are consistent with reported values of alkylidenecyclobutenes (vide supra). 

**Reaction of Me₃SiCp*₂YCH(SiMe₃)₂ (19b) with excess 1-phenyl-1-propyne. NMR scale.** Me₃SiCp*₂YCH(SiMe₃)₂ (12.2 mg, 22.3 µmol) was dissolved in 0.50 mL of a benzene-d₆ solution. After heating 6 h to 50 °C, the deep red solution was found to be converted into a light-yellow solution. After 7 days at 120 °C, the substrate was completely consumed and trimethylsilylchloride (3.0 µL, 24 µmol) was added. Upon heating 6 h to 50 °C, the deep red solution was found to be converted into a light-yellow solution. The filtrate was subjected to catalytic hydrogenation (room temperature, 12 h, 4 atm. of H₂) using Pd/C (~100 mg). The reaction mixture was filtered through a plug of neutral alumina, analyzed with NMR spectroscopy and quenched with methanol-d₆. GC/GC-MS analysis indicated the presence of CH₂(SiMe₃)₂, 1,2,3,4,5-pentamethylcyclopentane, six C₁₈H₂₀ isomers (in a 12:72:1:13:1 ratio) and two C₃₀H₃₀ isomers (in a 71:29 ratio). 

C₉H₈: GC-MS, m/z (calc., found): 238 (1.8, 6.8), 237 (19.8, 20.0), 236 (100.0, 100.0); major isomer: 239 (0.1, 0.1), 238 (1.8, 2.5), 237 (19.8, 20.3), 236 (100.0, 100.0); 238 (1.8, 1.3), 237 (19.8, 22.9), 236 (100.0, 100.0); 238 (1.8, 2.0), 237 (19.8, 21.5), 236 (100.0, 100.0); 238 (1.8, 1.5), 237 (19.8, 20.3), 236 (100.0, 100.0); 238 (1.8, 2.4), 237 (19.8, 20.2), 236 (100.0, 100.0). 

C₉H₈: GC-MS, m/z (relative intensity): 393 (0.5, 0.8), 392 (5.2, 5.8), 391 (32.8, 34.3), 390 (100.0, 100.0).
addition of 1-phenyl-1-propyne (49.7 µL, 397 µmol, 17.8 equiv.) with a microsyringe, the mixture was heated to 120 °C and monitored with 1H NMR spectroscopy. After 16 days at 120 °C, the substrate was consumed completely and the mixture was quenched with methanol. GC-MS analysis indicated the presence of dimers (m/z 232) and tetramers (m/z 464). Normalized FID-GC values revealed a 89% selectivity for dimerization and a 11% selectivity for tetramerization. Even though the product mixture was too complex for conclusive NMR analysis, the major products could be identified as (E)-3-benzylidene-1-methyl-2-phenylcyclobutene (5) and 1,3-diphenyl-4-methyl-2-methylene-cyclobutene (7) in yields of 13 and 10%, by integration against the SiMe₃ 1H NMR resonances of CH₂(SiMe₃)₂ and intact Me₂SiCp''₂YCH(SiMe₃)₂.

**Reaction of Me₂SiCp''₂CeCH(SiMe₃)₂ (19c) with excess 1-phenyl-1-propyne. NMR scale.**

Me₂SiCp''₂CeCH(SiMe₃)₂ (11.8 mg, 19.7 µmol) was dissolved in 0.50 mL of a benzene-δ₆ solution. After addition of 1-phenyl-1-propyne (48.4 µL, 387 µmol, 20 equiv.) with a microsyringe, the mixture was heated to 120 °C and monitored with 1H NMR spectroscopy. Complete substrate conversion was observed after 55 days and the mixture was quenched with methanol. GC-MS analysis indicated the presence of dimers (m/z 464, 30%), while the yields were determined by integration against CH₂(SiMe₃)₂. Normalized FID-GC revealed a 64% selectivity for dimerization and a 36% selectivity for tetramerization. These values agree only moderately with those obtained from quantitative 1H NMR analysis (i.e. 52% selectivity for dimerization and 48% selectivity for tetramerization).

Tetramer (C₆H₁₂): major isomer, GC-MS, m/z (relative intensity): 464 (M⁺, 44), 450 (39), 449 (100), 343 (8), 265 (11), 253 (8), 252 (10), 241 (11), 239 (9), 215 (11), 202 (10), 191 (10), 178 (14), 165 (16), 153 (20), 128 (8), 115 (19), 105 (22), 91 (51), 77 (8), 28 (11). GC-MS, m/z (calc., found): 467 (0.9, 1.0), 466 (7.5, 7.2), 465 (39.3, 37.2), 464 (100.0, 100.0).

**Reaction of Me₂SiCp''₂CeCH(SiMe₃)₂ (19c) with excess 2-propynyltoluene. NMR scale.**

Me₂SiCp''₂CeCH(SiMe₃)₂ (11.1 mg, 18.6 µmol) was dissolved in 0.50 mL of a benzene-δ₆ solution. After addition of 2-propynyltoluene (54.5 µL, 395 µmol, 20 equiv.) with a microsyringe, the mixture was heated to 120 °C and monitored with 1H NMR spectroscopy. Complete substrate conversion was observed after 55 days and the mixture was quenched with methanol. The basis of NMR and GC-MS analysis, the products were identified as 17 (33%), 18 (1%), 19 (2%) and 20 (2%), while the yields were determined by integration against CH₂(SiMe₃)₂. Normalized FID-GC revealed a 85% selectivity for dimerization (at least 7 isomers, of which the 4 major isomers were present in a 8:8:41:5 ratio) and a 15% selectivity for trimerization (2 major isomers in a 1:1 ratio).

1,3-Di(2-methylphenyl)-2-methyl-4-methylenecyclobut-1-ene (19) and 1,2-di(2-methylphenyl)-3-methyl-4-methylene-cyclobut-1-ene (20). The complexity of the 1H NMR spectrum hampered unambiguous assignments, but characteristic 1H NMR resonances at δ 6.48, 4.61, 4.48 and 4.22 ppm in a 1:1:1:1 ratio are reminiscent of those of the exo-cyclic methylene group in 6 (i.e. δ 6.47 and 5.07 ppm). Under the assumption that these 1H NMR resonances correspond to 19 and 20, the yields of these dimers, based on 1H NMR, agree well with those of two new major isomeric cyclodimers (GC-MS) based on FID-GC. It was not possible to distinguish between these two isomers. Isomer 1. GC-MS, m/z (relative intensity): 260 (M⁺, 100), 246 (14), 245 (M⁺ - CH₃, 63), 230 (M⁺ - 2 CH₃, 65), 229 (37), 228 (15), 217 (18), 216 (26), 215 (75), 204 (14), 203 (21), 202 (25), 165 (11), 155 (22), 153 (23), 152 (18), 145 (26), 142 (14), 141 (13), 130 (14), 129 (41), 128 (58), 127 (22), 117 (12), 116 (11), 115 (58), 114 (23), 108 (10), 105 (29), 101 (14), 91 (17), 77 (15). GC-MS, m/z (calc., found): 263 (0.1, 0.2), 262 (2.2, 2.4), 261 (22.0, 22.7), 260 (100.0, 100.0). Isomer 2. GC-MS, m/z (relative intensity): 260 (M⁺, 29), 246 (21), 245 (M⁺ - CH₃, 100), 231 (20), 230 (M⁺ - 2 CH₃, 87), 229 (26), 228 (15), 217 (18), 216 (20), 215 (73), 202 (10), 153 (10), 152 (12), 129 (20), 128 (36), 127 (14), 117 (11), 115 (48), 114 (28), 101 (12), 91 (13), 77 (11). GC-MS, m/z (calc., found): 263 (0.1, 0.3), 262 (2.2, 2.8), 261 (22.0, 22.5), 260 (100.0, 100.0).

Trimers (C₁₂H₃₀): GC-MS, m/z (calc., found): 393 (0.5, 0.7), 392 (5.2, 5.9), 391 (32.8, 36.7), 390 (100.0, 100.0); 393 (0.5, 0.6), 392 (5.2, 5.9), 391 (32.8, 36.0), 390 (100.0, 100.0).

**Kinetic studies of the cyclodimerization reaction.** A catalyst stock solution was prepared by weighing the amount of precatalyst and dissolving the solid in a specified volume of benzene-δ₆, as determined by volumetric glassware. After preparation, the catalyst solution (typically 40 mM) was transferred into a pre-weighted vial with screw-cap and weighted. A specified amount of internal standard (hexamethyldisiloxane) was added with a microsyringe. After use, the catalyst stock solution was stored at -40 °C in the glovebox. A 1H NMR experiment of the sample containing the catalyst solution (prior to substrate addition) ensured the presence of the prerequisite amount of catalyst after long-term storage or handling.

In a typical experiment, an NMR tube was charged with 500.0 µL of a catalyst stock solution (40 mM) using a 500.0-µL microsyringe. The volume of substrate needed for the kinetic experiment was calculated,
from the density which was determined experimentally. The tube was heated in an electric oven at a specified temperature and taken out for NMR analysis after appropriate intervals. NMR data were acquired using appropriate long pulse delays (at least 60 s) in order to avoid signal saturation under anaerobic conditions. In most cases, the reaction kinetics were monitored from the normalized intensity changes in the substrate resonance over 3 or more half-lives. The substrate concentration was determined from the normalized intensity of the methyl substrate protons relative to the methyl protons of hexamethyldisiloxane.

Typical polymerization reaction. Cp*₄La(η⁴-CH₂CCPh) (10.2 mg, 19.4 µmol) was dissolved in 0.50 mL of a benzene-d₆ solution of hexamethyldisiloxane (1.4 mM). After addition of 2,5-di-n-hexyl-1,4-dipropynylbenzene (123.6 mg, 383.2 µmol, 19.8 equiv.), the mixture was heated to 120 °C and the progress of reaction was followed in time by means of ¹H NMR spectroscopy. After 3 months at 120 °C, the reaction mixture was completely solidified. The contents of the tube was transferred into a Teflon-capped reaction vial and suspended in toluene (3.0 mL). Addition of trimethylsilylchloride (24.6 µL, 194 µmol, 10 equiv.) was followed by heating to 120 °C and stirring for 7 days in a closed Teflon-capped flask. The formed red suspension was filtered over a small glass filter and washed with (dry) chloroform. The chloroform-soluble fraction was evaporated to dryness and washed with copious amount of pentane over a filter, affording a bright red rubbery solid after drying in vacuo. Yield: 33.4 mg (27%).

3.6 References and notes


Because the rate constant $k$ varies exponentially with temperature $T$ and activation energy $E_a$, the error in $k$ associated with a particular uncertainty in $T$ is proportional with $E_a/RT$ (i.e. $\delta k/k = E_a/RT \times \delta T/T$). The error due to poor temperature control will therefore increase with decreasing reaction temperature. Moreover, slow reactions have in general high activation energies $E_a$ and require more precise temperature control for decent precision in rate constants than fast reactions.

Ionic radii for eight-coordinate complexes: La$^{3+}$ (1.160 Å), Ce$^{3+}$ (1.143 Å), Y$^{3+}$ (1.019 Å) and Sc$^{3+}$ (0.870 Å), see: Shannon, R. D. Acta Crystallogr., Sect. A 1976, 432, 751.

The regiosomeric ratio of products arising from 1,2- and 2,1-insertion of phenylacetylene into the Ln-C bond of Cp*$_2$LnCCPh at 25 °C was found to be greatly influenced by the metal size (Chapter 4). For example, the use of a 50-fold excess of phenylacetylene gives a 95:5 ratio of products arising from 1,2- and 2,1-insertion, respectively, for Ln = Y, whereas a ratio of 0:100 was found for Ln = La.


A cross-conjugated compound may be defined as a compound possessing three unsaturated groups, two of which although conjugated to a third unsaturated center are not conjugated to each other, see: Phelan, N. F.; Orchin, M. J. Chem. Educ. 1968, 45, 633.


Typical examples of this approach include poly(thiophene)s, poly(arylenevinylene)s and poly(aryleneethynylene)s. Examples in which the degree of polymerization and the solubility of the polymer increased with side-chain elongation include poly(p-phenylenevinylene)s and poly(thiophene)s. For reviews on poly(p-phenylenevinylene)s, see: (a) Giese, R. J. M. S-Rev. Macromol. Chem. Phys. 1996, 36, 631. (b) Ref. 26c.

The cyclodimerization of 1-methylalk-2-ynes catalyzed by rare-earth metallocenes

Infrared spectral data of cyclobutenes containing substituted exo-methylene groups (=CHR) are lacking in literature, but cyclobutenes containing unsubstituted exo-methylene groups are reported to exhibit vibrations at 1670-1680 and 860-880 cm⁻¹, due to the exocyclic =CH₂ groups.⁵,¹² Characteristic vibrations reported for 1-(trimethylsilyl)-3-phenyl-1-propyne (i.e. 2180 (C≡C), 1250, 840 (C-Si) cm⁻¹) and 1-(trimethylsilyl)-1-phenylpropa-1,2-diene (i.e. 1912 (C=C=C) cm⁻¹) were not observed. For examples of infrared spectral data for these compounds, see: (a) Najafi, M. R.; Wang, M.-L.; Zweifel, G. J. Org. Chem. 1991, 56, 2468. (b) Ma, S.; Zhang, A. J. Org. Chem. 2002, 67, 2287.

The experimental error was obtained by repeated integration.


