The reactivity of rare-earth metallocenes towards alkynes
Quiroga Norambuena, Victor

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2006

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Download date: 01-01-2019
5. The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metalloccenes

5.1. Introduction

The rare-earth metalloccene-catalyzed oligomerization of phenylacetylene has been studied in detail (Scheme 5-1) and the factors determining the regio- and chemoselectivity have been identified (Chapter 4). High selectivities and activities for the formation of (E)-1,4-diphenylbut-1-en-3-yne (12a) were found for reactions with the precatalyst Cp*₂LaCH(SiMe₃)₂, while 2,4-diphenylbut-1-en-3-yne (11a) was formed selectively in reactions with Cp*₂YCH(SiMe₃)₂. However, significant catalyst deactivation via Cp* abstraction and the formation of oligomers higher than dimers was observed at relatively large substrate-to-catalyst molar ratios. A survey of the reported catalytic behavior towards phenylacetylene places the permethylanthanocene alkyl derivative Cp*₂LaCH(SiMe₃)₂ among the most active and selective precatalysts for the formation of the trans-head-to-head dimer.¹

Scheme 5-1. The rare-earth metalloccene-catalyzed oligomerization of phenylacetylene.

From the desire to apply the catalytic linear dimerization of 1-alkynes to bifunctional substrates in order to prepare conjugated polymers (Chapter 6), it was considered important to assess the scope of variation in the aromatic moiety of this reaction. In this context, the tolerance of the catalyst towards sterically hindered substrates (viz. ortho-substitution of phenyl group) and substrates with heteroatoms was of particular interest. Because large excesses of Lewis basic heteroatom-containing substrates are well-known to inhibit olefin and alkyne interactions with strongly Lewis acidic metal centers and lead commonly to a significant decrease in catalyst activity or even rapid catalyst deactivation, the compatibility of Lewis acidic metal catalysts with Lewis basic heteroatom-containing functionalities is an ongoing challenge in the development of catalytic carbon-carbon bond-forming transformations based on early transition and f-block metals.

The scope and mechanism of the catalytic oligomerization reaction of substituted (hetero)aromatic 1-alkynes, mediated by rare-earth metalloccenes, is described in this chapter. The factors governing the activity and selectivity of the catalytic oligomerization reactions with selected (hetero)aromatic 1-alkynes are determined, based on a kinetic and mechanistic study of both catalytic and stoichiometric reactions.
5.2. Synthesis of (hetero)aromatic 1-alkynes

Introduction

Six representative (hetero)aromatic 1-alkynes were synthesized to probe the scope of the permethylanthanocene-catalyzed 1-alkyne dimerization (Scheme 5-2). Several general routes are available for the preparation of hetero(aromatic) 1-alkynes, including (i) the palladium-catalyzed coupling (the Negishi reaction) of ethynylzinc, prepared in situ from the ethynyl Grignard reagent, and the corresponding halo(hetero)arene, (ii) the palladium-copper-catalyzed coupling (the Castro-Stephens/Hagihara-Sonogashira reaction) of trimethylsilylacetylene (TMSA) and halo(hetero)arene, followed by desilylation, and (iii) the palladium-catalyzed coupling of 2-methyl-3-butyne-2-ol and halo(hetero)arene, followed by base-induced cleavage of α-acetylenic alcohol (the reverse Favorskii reaction) into the corresponding carbonyl and ethynyl compounds. Although some 1-alkynes were commercially available, they were found to contain impurities that were reactive towards the present catalyst (e.g. aryl halide, 2-methyl-4-arylbut-3-yn-2-ol) and difficult to remove completely from the substrate.

The Negishi reaction

The Negishi reaction (route i, Scheme 5-2) proved to be unsuitable in the present study, because the commercially available ethynylmagnesium bromide contained trace amounts of the magnesium salt of 2,6-di-tert-butyl-4-methylphenolate (BHT). Experiments indicated that the small amounts of this compound in the substrate reacted with the catalyst to yield catalytically inactive, phenolate derivatives, as identified by 1H NMR spectroscopy. Taking into account that subsequent catalytic oligomerization experiments are performed in the presence of 2-0.08 mol% (pre)catalyst, contamination of BHT is undesirable, as it affects substrate reactivity. The complete separation of BHT from 2-ethynylanisole was found to be detrimental to the yield.

The solvent most commonly used in the Negishi reaction constitutes a second drawback of this procedure, especially for the preparation of 2-ethynyltoluene. Traces of THF in 2-ethynyltoluene were difficult to remove completely by several techniques. Contamination of THF in the substrate has adverse effects on the catalytic performance, as it leads to catalyst deactivation (Chapter 5). Other solvents did not give satisfactorily conversions, thereby contaminating the substrate with halide (hetero)arenes (1) which are known to react with rare-earth metalloocene derivatives.

Scheme 5-2. The synthesis of (hetero)arylalk-1-ynes.

![Scheme 5-2](image-url)

Reagents: (i) HC≡CMgBr, ZnBr₂, Pd(PPh₃)₂Cl₂, THF, RT. (ii) HC≡CSI-Me₂, Pd(PPh₃)₂Cl₂, CuI, HNPr₂, THF/toluene, 80 °C; (iiia) K₂CO₃, THF/MeOH; (iib) nBu₄NF, THF. (iii) HC≡CMc₂OH, Pd(PPh₃)₂Cl₂, CuI, HNPr₂, THF/toluene, 80 °C; (iia) Δ, toluene, KOH.
The Sonogashira reaction

The Sonogashira reaction (route ii, Scheme 5-2), on the other hand, produced 1-alkynes which were contaminated by varying amounts of 1,4-bis(trimethylsilyl)butadiyne. Diynes are a common by-product of palladium-catalyzed 1-alkyne cross-coupling methodologies. The contaminating small amounts of butadiyne reacted with the present catalyst forming organic products that were not studied further. Complete removal of the butadiyne proved to be difficult and the use of substoichiometric amounts of TMSA led to substrate which was contaminated with halide precursors.

The synthesis of desired (hetero)aromatic 1-alkynes

The substrates 2b-g were prepared satisfactorily by palladium-catalyzed coupling of (hetero)aryl iodide with 2-methyl-3-butyn-2-ol (route iii, Scheme 5-2), according to a published general procedure. Additional purification steps were found necessary to obtain the requisite purity for the present catalytic reactions. In most cases, the acetylenic carbinol (3) was purified by vacuum distillation, column chromatography and repeated crystallizations, while deprotection involved base-catalyzed cleavage followed by vacuum distillation and flash column chromatography.

The properties of the substrates

It must be noted that the prepared 1-alkynes should be handled with care. Especially the heteroaromatic 1-alkynes, such as 2-ethynylthiophene and 1-methyl-2-ethynylpyrrole, are thermally unstable. Thermal decomposition was accompanied by a coloration which was apparent within several hours after storage as pure oils or as solutions at room temperature and within minutes at higher temperatures. The (thermal) instability of terminal acetylenes is well-documented in literature, especially for 1-alkynes containing electron-withdrawing substituents. For example, it has been reported that 2-ethynylthiophene polymerizes at room temperature within 5 days to insoluble dark brown resins. IR and solid 13C NMR of the formed solid indicated that most acetylenic carbons had been converted to olefinic carbons. Some 1-alkynes are, in addition, fairly volatile and must be handled accordingly. The colored liquids, obtained after synthesis, were dried on CaH2 and produced colorless liquids after vacuum transfer. If stored under nitrogen at -30 °C, these liquids remained indefinitely stable and colorless.

5.3. Catalytic oligomerization of (hetero)aromatic 1-alkynes

5.3.1. Introduction

To study the effects of 1-alkyne substituents on the rate and selectivity of the 1-alkyne oligomerization reaction catalyzed by Cp*₂LaCH(SiMe₃)₂ (5D), a selected group of (hetero)aromatic 1-alkynes was applied under standardized reaction conditions. However, the relative amount of trimerization was found to increase upon increasing the substrate-to-catalyst ratio. Significant substrate and product inhibition was observed as well at relatively high substrate-to-catalyst ratios. As a consequence, two standardized reaction conditions (i.e. substrate-to-catalyst molar ratios of 50 and 400) at constant catalyst concentration were chosen to evaluate the substrate effects on rate and selectivity of the 5D-catalyzed 1-alkyne oligomerization reaction.

The organic products were identified by multinuclear 1D and 2D NMR spectroscopy and MS, while their relative amounts were determined by normalized, in situ 1H NMR spectroscopy, using appropriate long pulse delays to avoid signal saturation under the present anaerobic conditions. Other methods to determine the relative amount of products yielded values that corresponded only moderately with those determined by in situ 1H NMR analysis (Section 4.2.3).

5.3.2. Substrate effects at relatively low initial substrate concentration

As discussed previously, the reaction of Cp*₂LaCH(SiMe₃)₂ (5D) with a 50-fold molar excess of phenylacetylene (2a) takes place both rapidly and selectively to form trans-1,4-diphenylbut-1-en-3-yne (12a) (Table 5-1). Complete substrate conversion was observed within 10 min, accompanied by the formation of three
Cp* 1H NMR resonances, assigned to [(Cp*2La)µ-µ-PhC(Ph)] (δ 2.04 ppm), Cp*2LaC(Ph)=C(H)CCPh (δ 1.97 ppm) and Cp*2LaC(H)=C(Ph)CCPh (δ 1.92 ppm), present in a 1.0:1.4:1.3 ratio, respectively (Chapter 4).

The application of ortho-substituted analogues, i.e. 2-ethyl/hydroxene (2b) and 2-ethylthiylisole (2e), led to a decreased catalytic activity, accompanied by an increased selectivity for the formation of the head-to-tail dimer (9) and a decreased selectivity for trimerization. This catalytic behavior is most likely due to their larger steric requirements of the substrate. The steric effects of 1-alkyne substituents are discussed in more detail in Section 5.5.3. Unfortunately, the ortho-methyl 1H NMR resonances of 2b and its oligomers 11b and 12b overlapped with the Cp* 1H NMR resonances of the organometallic reaction intermediates, thereby impeding attempts to determine the nature and number of reaction intermediates during and after substrate conversion.

In the case of 2c, two major Cp* 1H NMR resonances were observed at δ 1.96 and 1.86 ppm during and after substrate conversion. In analogy to the reactions with phenylacetylene (vide supra), these resonances are presently assigned to [(Cp*2La)µ-µ-RC4R], Cp*2LaC(R)=C(H)CCR and Cp*2LaC(H)=C(R)CCR, respectively (R = C6H6OMe-2). After substrate conversion, these resonances were present in a 10.0:1.0:0.8 ratio, respectively. Monitoring the substrate concentration by means of normalized, single-pulse in situ 1H NMR spectroscopy revealed that the rate of dimerization is first-order in substrate for at least three half-lives ($R_1 = 0.9974, k_{obs} = 4.25(5) \text{ M}^{-1}\text{min}^{-1}$).

When five-membered heteroaromatic 1-alkynes, i.e. 2-thienylacetylene (2d), 3-thienylacetylene (2e) and 1-methyl-2-ethylpyrrole (2g), were employed, the observed catalytic rates and selectivities for the formation of the trans-head-to-head dimer (12) resembled those previously observed for phenylacetylene (Table 5-1). After complete conversion of 2d, the precatalyst 5D was quantitatively converted into a single new lanthanocene derivative, as indicated by one Cp* 1H NMR resonance at δ 1.97 ppm. Stoichiometric reactions provided evidence that the observed Cp* 1H NMR resonance corresponds to the but-1-en-3-yn-1-yl derivative Cp*2LaC(R)=C(H)CCR (R = C6H6OMe-2) (Section 5.4.1).

In marked contrast, the Cp* 1H NMR region of the reaction mixture after conversion of 2e was considerably more complex. Four major Cp* 1H NMR resonances at δ 2.17 (broad), 2.03, 1.95 and 1.91 ppm in a 1.0:3.7:0.4:1.0 ratio were observed, representing only ~80% of the total amount of organometallic species present. In analogy to the reactions with phenylacetylene, the latter three resonances may be assigned to [(Cp*2La)µ-µ-RC4R], Cp*2LaC(R)=C(H)CCR and Cp*2LaC(H)=C(R)CCR, respectively. After consumption of 2g, the reaction mixture resembled that of the analogous reaction with phenylacetylene in the sense that 5D was quantitatively converted into three species, as evidenced by three Cp* 1H NMR resonances at δ 2.03, 2.01 and 1.99 ppm in a 1.0:3.3:0.4 ratio, respectively. Based on this analogy, the resonances were tentatively assigned to [(Cp*2La)µ-µ-RC4R], Cp*2LaC(R)=C(H)CCR and Cp*2LaC(H)=C(R)CCR, respectively (R = 2-C6H4OMe-2).

Encouraged by the displayed tolerance of the catalyst towards 1-alkynes possessing relatively weakly coordinating heteroatoms (Section 5.4.3), it was decided to study the reactivity of 5D towards 2-ethylpyridine (2f) as well. In the light of the well-recognized kinetic lability of permethyllanthanidocene derivatives and their preference to coordinate hard heteroatoms, 2f represents an interesting substrate to probe the competition between strong Lewis base coordination to the catalyst and catalytic substrate conversion. Gratifyingly, 2f (50 equiv.) was converted for 95% within 30 min under the present reaction conditions, affording the corresponding trans-head-to-head dimer (12f) as the only observed organic product (Table 5-1). However, substrate conversion was very slow beyond this point and full conversion was only achieved after 16 h. A more detailed discussion of the reactions of 5D with 2f is deferred to Section 5.3.5.

5.3.3. Substrate effects at relatively high initial substrate concentration

Introduction

To determine the influence of the 1-alkyne substituent on the rate of 1-alkyne oligomerization catalyzed by Cp*2LaCH(SiMe3)_2 (5D) and monitor substrate conversion conveniently by means of in situ 1H NMR spectroscopy, the reaction time was increased by applying relatively large substrate-to-catalyst ratios. Unfortunately, the kinetic behavior of the 5D-catalyzed 1-alkyne oligomerization reaction under these reaction conditions was complicated by significant catalyst deactivation and product/substrate inhibition to varying degrees, depending on the substrate. In spite of these complications, the use of a substrate-to-catalyst molar ratio of 400 was found to allow for the convenient evaluation of reaction rates for all of the studied substrates. The
The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metallocenes

standardized reaction conditions were performed at constant catalyst concentration. Substrate conversion was monitored by single-pulse, in situ $^1$H NMR spectroscopy, using appropriate delay times to avoid signal saturation under the present anaerobic conditions. In most cases, normalization of substrate and product $^1$H NMR resonances against cyclooctane as an internal standard provided consistent kinetic data and product distributions (Table 5-1).

Table 5-1. The product distribution of the 5D-catalyzed 1-alkyne oligomerization reactions conducted at relatively low and high substrate concentrations.*

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>2 (equiv.)</th>
<th>11</th>
<th>12</th>
<th>15</th>
<th>16</th>
<th>time (conv.)</th>
<th>Cat. deact. b (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>a</td>
<td>50</td>
<td>0.1</td>
<td>97.8</td>
<td>0.5</td>
<td>1.6</td>
<td>&lt;10 min (100%)</td>
<td>0.7</td>
</tr>
<tr>
<td>2</td>
<td>b</td>
<td>400</td>
<td>0.2</td>
<td>89.1</td>
<td>8.4</td>
<td>2.4</td>
<td>22 min (100%)</td>
<td>5.0</td>
</tr>
<tr>
<td>3</td>
<td>c</td>
<td>50</td>
<td>4.9</td>
<td>92.9</td>
<td>2.2</td>
<td>0.0</td>
<td>1 h (100%)</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>d</td>
<td>400</td>
<td>4.4</td>
<td>89.3</td>
<td>6.3</td>
<td>0.0</td>
<td>6.3 h (100%)</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>e</td>
<td>50</td>
<td>37.0</td>
<td>63.0</td>
<td>0.0</td>
<td>0.0</td>
<td>2.5 h (100%)</td>
<td>0.6</td>
</tr>
<tr>
<td>6</td>
<td>f</td>
<td>400</td>
<td>23.2</td>
<td>76.6</td>
<td>0.1</td>
<td>0.0</td>
<td>10.1 h (94%)</td>
<td>7.3</td>
</tr>
<tr>
<td>7</td>
<td>g</td>
<td>50</td>
<td>0.0</td>
<td>99.4</td>
<td>0.6</td>
<td>0.0</td>
<td>&lt;10 min (100%)</td>
<td>0.8</td>
</tr>
<tr>
<td>8</td>
<td>h</td>
<td>400</td>
<td>0.1</td>
<td>98.3</td>
<td>1.2</td>
<td>0.5</td>
<td>37 min (100%)</td>
<td>9.6</td>
</tr>
<tr>
<td>9</td>
<td>i</td>
<td>50</td>
<td>1.8</td>
<td>97.8</td>
<td>0.3</td>
<td>0.1</td>
<td>&lt;10 min (100%)</td>
<td>0.7</td>
</tr>
<tr>
<td>10</td>
<td>j</td>
<td>400</td>
<td>0.0</td>
<td>87.5</td>
<td>7.7</td>
<td>4.8</td>
<td>6.6 h (93%)</td>
<td>12.1</td>
</tr>
<tr>
<td>11</td>
<td>k</td>
<td>50</td>
<td>0.0</td>
<td>100.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1 h (95%)</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>l</td>
<td>400</td>
<td>0.0</td>
<td>100.0</td>
<td>0.0</td>
<td>0.0</td>
<td>8.2 h (83%)</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>m</td>
<td>50</td>
<td>0.1</td>
<td>99.2</td>
<td>0.5</td>
<td>0.1</td>
<td>&lt;10 min (100%)</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>n</td>
<td>400</td>
<td>0.2</td>
<td>97.3</td>
<td>2.0</td>
<td>0.5</td>
<td>26 min (100%)</td>
<td>-</td>
</tr>
</tbody>
</table>

* Reaction conditions: [5D] = 4.1-4.4 mM, C₆D₆ and 25 °C. Yields are determined by normalized in situ $^1$H NMR spectroscopy and represent average values of two or more runs. The experimental error was found to be ±0.2. b Percentage of catalyst deactivated based on the amount of Cp*H formed relative to CH₂(SiMe₃)₂, as determined by in situ $^1$H NMR spectroscopy. c Not determined, due to overlapping $^1$H NMR resonances.

NMR spectroscopy and represent average values of two or more runs. The experimental error was found to be ±0.2. Percentage of catalyst deactivated based on the amount of Cp*H formed relative to CH₂(SiMe₃)₂, as determined by in situ $^1$H NMR spectroscopy. Not determined, due to overlapping $^1$H NMR resonances.
Phenylacetylene

The reaction of Cp*₂LaCH(SiMe₃)₂ (5D) with a 400-fold molar excess of phenylacetylene is rapid. ¹H NMR spectroscopy revealed that phenylacetylene was completely converted within 22 min, thereby allowing the acquisition of four data points. Even so, the rate of substrate conversion is more likely to be zero-order in substrate ($k_{obs} = 20(1) \text{ min}^{-1}$) than first-order in substrate, as seen from plots of substrate concentration $[S]$ versus time (Figure 5-1) and $\ln([S]/[S]₀)$ versus time (Figure 5-2). In addition, catalyst deactivation via Cp* ligand abstraction took place to a relatively small extent (5%).

A detailed kinetic and mechanistic study of the reaction of 5D with phenylacetylene revealed that the rate of substrate conversion may plausibly be described by saturation kinetics involving a rate-limiting pre-equilibrium of a monomeric, alkynyl derivative Cp*₂LaCCPh (20a) with its Lewis base adduct Cp*₂LaCCPh·PhCCH (20a·2a) (Chapter 4). In accord with this model, the rate is zero-order in substrate at high substrate concentration and becomes first-order in substrate at lower substrate concentrations.

2-Ethynyltoluene

Substrate conversion in the catalytic oligomerization of 2-ethynyltoluene (2b) was followed in time by monitoring the intensity decrease of the substrate ¹H NMR resonance C≡C₇H (δ 2.92 ppm) relative to that of cyclooctane. Full conversion of 2b was observed after 6.2 h and the rate of reaction was found to be first-order in substrate for at least 4 half-lives ($k_{obs} = 9.46(8) \text{ M}^{-1} \text{·min}^{-1}$). Unfortunately, the product ¹H NMR resonance at δ 2.01 ppm obscured Cp* ¹H NMR resonances and in situ ¹H NMR spectroscopy did not provide insight into the organometallic reaction intermediates during and after substrate conversion.

The formed products reveal that more head-to-tail dimerization and less trimerization take place in the reaction of 2b as compared to the analogous reaction with phenylacetylene. The selectivity for head-to-tail dimerization versus trans-head-to-head dimerization in the present oligomerization reaction was rationalized in terms of a competition between 1,2- and 2,1-insertion of substrate into a monomeric alkynyl derivative (Chapter 4). The present results show that the presence of an ortho-methyl group diminishes the preference for 2,1-insertion. The selectivity for dimerization versus trimerization was rationalized in terms of an alkynyl derivative (formed from substrate insertion into a monomeric alkynyl derivative) undergoing either protonolysis by substrate or insertion of substrate, respectively. It seems that the presence of an ortho-methyl group decreases the rate of substrate insertion into the alkynyl derivative relative to that of protonolysis by substrate. The presence of an ortho-methyl group affects the regioselectivity of catalytic trimerization as well, as trimer 15b was formed exclusively.
The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metalloccenes

2-Ethynylanisole

The catalytic oligomerization of 2-ethynylanisole (2c) is considerably slower than that of 2-ethynyltoluene (2b) and phenylacetylene. The substrate was found to be converted for 94% after 10.1 h. In spite of significant catalyst deactivation (10%), the kinetic data indicate that the rate of substrate conversion is first-order in substrate during the first 1.5 half-lives ($R^2 = 0.9981, k_{obs} = 3.51(2) \text{ M}^{-1} \text{ min}^{-1}$). Significant deviation from first-order kinetic behavior in substrate was observed after 204 min at which point 72% of the substrate had been converted (1.9 half-lives). In contrast to the four Cp* 1H NMR resonances observed during the analogous reaction of 5D with excess phenylacetylene, only two major Cp* 1H NMR resonances (at $\delta$ 1.98 and 1.87 ppm in a 1.0:1.5 ratio, respectively, after substrate conversion) were observed during and after conversion of 2-ethynylanisole (2c).

These results confirm the above notion that the presence of an ortho-substituent disfavors trimerization over dimerization, trans-head-to-head dimerization over head-to-tail dimerization and catalytic trimerization to produce 16 over catalytic trimerization to produce 15 relative to analogous reactions with phenylacetylene. Remarkably, the selectivity for head-to-tail dimerization of 2e seems to decrease with increasing substrate-to-catalyst molar ratios (Table 5-1, Entries 5 and 6). This behavior was studied in more detail and is discussed in Section 5.3.6. The slower rate of reaction as compared to analogous reactions with 2b and phenylacetylene and the observed deviation from first-order rate dependence on substrate concentration are presently attributed to substrate and/or product inhibition via La-O interactions (Section 5.5.3). More catalyst deactivation via Cp*ligand abstraction was observed for 2c than for phenylacetylene and 2b.

2-Ethynylthiophene

Complete conversion of 2-ethynylthiophene (2d) was observed after 40 min. Only one major 1H NMR resonance at $\delta$ 1.97 ppm was observed during substrate conversion in the Cp* region (6 2.5-1.5 ppm). Despite significant catalyst deactivation (10%), the first 7 data points (during which 99% of the substrate is converted, covering 6.6 half-lives of the reaction) indicate that the rate of reaction is first-order in substrate ($R^2 = 0.9981, k_{obs} = 36(1) \text{ M}^{-1} \text{ min}^{-1}$). The formed products reveal that less trimerization and more catalyst deactivation via Cp* abstraction take place in the reaction of 2d as compared to the analogous reaction with phenylacetylene.

The decreased tendency for catalytic trimerization as displayed by 2-ethynyltoluene (2b) and 2-ethynylthiophene (2d) relative to phenylacetylene was previously rationalized in terms of an increased steric bulk of the 1-alkyne substituent. This view is consistent with the larger steric requirements for 1-alkyne insertion relative to those for protonolysis by 1-alkyne, but contradicts the present result. In spite of its smaller size, 2-ethynylthiophene (2d) displays a significant lower tendency for catalytic trimerization than phenylacetylene.

Figure 5-2. Integrated rate plot of the substrate concentration versus time for the catalytic oligomerization reactions of 2a, 2d and 2g mediated by 5D. Lines represent fitted linear plots (see text for details).
Clearly, electronic effects play an additional role in determining the reactivity of the alkenyl derivative, undergoing either substrate insertion (to yield trimerization products) or protonolysis by substrate (to yield dimerization products).

The increased rate of catalyst deactivation as observed for 2d relative to phenylacetylene can be explained by the higher (kinetic) acidity, thereby promoting Cp*H abstraction (Section 5.5.3). Another explanation involves the more electron-withdrawing character and smaller size of the 2-thienyl group relative to the phenyl group, thereby rendering the metal center both electronically and sterically less saturated and therefore more reactive. The reactivity of lanthanide complexes is well-known to be correlated with steric and electronic saturation at the metal center, while the stability of alkynyl complexes decreases in general with the electron-withdrawing ability of the 1-alkyne substituent. The steric and electronic 1-alkyne substituent effects and their importance in the present catalytic reactions are discussed in more detail in later sections (Sections 5.5.1 and 5.5.3).

One major Cp* 1H NMR resonance at \( \delta = 1.97 \) ppm was observed during catalytic conversion of 2-ethynylthiophene (2d). Interestingly, this Cp* 1H NMR resonance was also observed in the product mixture resulting from the stoichiometric reaction of Cp*2LaCH(SiMe3)2 (5d) with 2d (Section 5.4.1). In the latter mixture, NMR spectroscopy showed the presence of two Cp* 1H NMR resonances at \( \delta = 2.00 \) and 1.97 ppm, assigned plausibly to the butatrienediyl derivative \( \{[\text{Cp}*_{2}\text{La}][\mu-(\text{C}_4\text{H}_3\text{S}-2)\text{C}_4(\text{C}_4\text{H}_3\text{S}-2)]\} \) (22d) and the but-1-en-3-yn-1-yl derivative \( \text{Cp}*_{2}\text{LaC}(2-\text{C}_4\text{H}_3\text{S})=\text{C}(\text{H})\text{C}(2-\text{C}_4\text{H}_3\text{S}) \) (24d), respectively. The but-1-en-3-yn-1-yl derivative 24d is formed from insertion of 2d into the metal-carbon bond of a monomeric alkynyl species \( \text{Cp}*_{2}\text{LaCC}(2-\text{C}_4\text{H}_3\text{S}) \) (20d) and seems to represent the resting state of the catalyst during the catalytic conversion of 2d. This finding implies that the reaction of 24d with 1-alkyne is rate-limiting in the present reaction, which is consistent with the observed first-order rate dependence on substrate concentration.

The reaction of 5d with 3-ethynylthiophene (2e) exhibited both a lower reaction rate and a lower selectivity towards the trans-head-to-head dimer 12e than the analogous reaction with 2-ethynylthiophene (2d) (Table 5-1). Remarkably, no head-to-tail dimer 11e was observed and the relatively low selectivity for 12e stems from an increased preference for trimerization. The first 2.13 h (5.6 half-lives) correspond to a region of first-order rate dependence on substrate concentration (\( R^2 = 0.9967, k_{\text{obs}} = 6.1(1) \text{ M}^{-1}\cdot\text{min}^{-1} \)) during which 97% of the substrate was consumed. After 6.6 h, only a conversion of 98% was reached and longer reaction times did not lead to complete substrate conversion. One dominant Cp* 1H NMR resonance at \( \delta = 2.10 \) ppm was observed.

![Figure 5-3. Integrated rate plot of the substrate concentration versus time for the 5D-catalyzed oligomerization reaction of 2b, 2c, 2e and 2f. Lines represent fitted linear plots (see text for details).](image-url)
The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metallocenes

Scheme 5-3. Model for competing Lewis base coordination via heteroatom-metal interactions during trans-head-to-head dimerization (S = heteroatom of substrate, P = heteroatom of product).

During the majority of the reaction which transformed into several new, unidentified Cp* 1H NMR resonances after ~2 h.

In view of the formation of multiple Cp* 1H NMR resonances at a relatively high substrate conversion, the deviation from first-order kinetic behavior in substrate at higher substrate conversion and the absence of other products after quenching with methanol-d1 (GC/GC-MS), reversible catalyst inhibition via metal sulfur interactions is believed to be responsible for the observed catalytic behavior. The preparation of Lewis base adduct of monomeric alkynyl derivatives Cp*2LaCCR (Section 5.4.3) and the observed reactivity of but-1-en-3-ynyl lanthocene derivatives with THF (Chapter 4) provide indirect evidence that the proposed reaction intermediates are capable of coordinating to substrate and product(s). Competing Lewis base coordination of substrate and product via metal heteroatom interactions during trans-head-to-head dimerization is shown schematically in Scheme 5-3. Deviation from first-order kinetic behavior in substrate at higher substrate conversion was also observed for analogous reactions with 2-ethynylanisole (2c) and 2-ethynylpyridine (2f), but was absent in reactions with phenylacetylene (2a), 2-ethynyltoluene (2b) and 1-methyl-2-ethynylpyrrole (2g). This finding suggests that competing Lewis base coordination via heteroatom metal interactions during trans-head-to-head dimerization is not observed in the oligomerization reactions of 2a and 2g (Section 5.5.3).

The 6-fold higher reaction rate and the absence of a significant deviation from first-order kinetic behavior in substrate at relatively high substrate conversion in the reaction of 2-ethynylthiophene (2d) as compared to 3-ethynylthiophene (2e) reveals that competing Lewis base coordination via heteroatom metal interactions depends on the substitution pattern of the thienyl ring. Indeed, the stronger σ-electron withdrawing character of the 2-thienyl group versus the 3-thienyl group is well-established (Appendix) and electronic substituent effects are presently believed to influence both catalytic rate and selectivity (Section 5.5.3). The lower degree of reversible catalyst inhibition via metal sulfur interactions in the reactions with 2d relative to reactions with 2e is also attributed to the close proximity of the ethynyl group and the sulfur atom in 2d. The proximity of the thienyl group and the sulfur atom in 2d is presently believed to assist catalytic reaction sequences (Section 5.5.3).

The present results for the reactions of 5D and 3-ethynylthiophene (2e) at relatively high initial substrate concentration indicate that the catalytic reaction sequences can compete effectively with Lewis base coordination at low degrees of substrate conversion. At a higher degree of substrate conversion, the substrate concentration decreases relative to the concentration of products, rendering nonproductive sulfur coordination more competitive with the catalytic reaction sequences. Because complete substrate conversion is achieved at a relatively low initial substrate concentration (Section 5.3.2), the extent of competing Lewis base coordination via metal heteroatom interactions seems to be determined by the absolute substrate concentration. Catalytic rate depression due to metal heteroatom interactions was demonstrated by catalytic reactions in the presence of exogenous Lewis bases (Sections 5.3.4 and 5.3.5) and is commonly observed in rare-earth metal-catalyzed reactions.17
2-Ethynylpyridine

The catalytic dimerization of 2-ethynylpyridine (2f) slowed down in a remarkable fashion after 1.4 h (57% conversion). In the first hour 44% of the substrate was converted, but only a conversion of 63% and 73% was reached after the second and third hour, respectively. Finally, after 3.9 days 89% of the substrate was found to be consumed. Exclusive trans-head-to-head dimerization was indicated by NMR spectroscopy and no evidence for the formation of the head-to-tail dimer and trimers was obtained with GC/GC-MS. Several major Cp* 1H NMR resonances were observed at low substrate conversion, giving rise to a multitude of Cp* 1H NMR resonances at higher substrate conversion.

The kinetic data of the first 1.4 h (1.2 half-lives) correspond to a region, exhibiting first-order rate dependence on substrate concentration ($R^2 = 0.9976$, $k_{obs} = 2.08(3)$ M$^{-1}$·min$^{-1}$). Exclusive trans-head-to-head dimerization is presently attributed to the high $\sigma$-electron withdrawing character of the 2-pyridyl group and precomplexation to the nitrogen atom, rendering the reaction a heteroatom-directed C-C coupling reaction (Section 5.5.3). The relatively low reaction rate and the failure to achieve full substrate conversion are ascribed to product inhibition and catalyst deactivation (Section 5.3.5). When the analogous reaction was performed at 50 °C, the high selectivity for trans-head-to-head dimerization was preserved, but full conversion was still not achieved (86% after 9.5 h). The reaction of 5D with 2f was studied in more detail and these results are discussed in Section 5.3.5.

1-Methyl-2-ethynylpyrrole

In marked contrast to the other five-membered heteroaromatic 1-alkynes, 1-methyl-2-ethynlypyrrole (2g) was completely converted within 26 min (allowing the acquisition of only four data points), while the selectivity was comparable to that of 2-ethynlythiophene (2d). In spite of the limited number of kinetic data, the rate of reaction can be modeled more accurately by zero-order rate dependence on substrate concentration ($R^2 = 0.9971$, $k = 14.2(4)$ min$^{-1}$) than by first-order rate dependence on substrate concentration, as seen from plots of substrate concentration $[S]$ versus time (Figure 5-1) and ln($[S]/[S]_0$) versus time (Figure 5-2). One major, broad Cp* 1H NMR resonance at $\delta$ 2.11 ppm was observed during substrate conversion which transformed into three Cp* 1H NMR resonances at $\delta$ 2.03, 2.01 and 1.99 ppm in a 0.9:3.4:0.5 ratio, respectively, after complete substrate conversion.

The Cp* 1H NMR resonances of the reaction intermediates are analogous to those observed during the corresponding reaction of Cp*$_2$La(CH(SiMe$_3$)$_2$ (5D) and phenylacetylene (Chapter 4). Also, the kinetics of the reaction of 5D with 2g resembles that of the corresponding reaction of 5D with phenylacetylene. These considerations imply that the nitrogen atom of 2g does not interact significantly with the metal center of the catalyst. This notion is, in fact, in accord with the common belief that the nitrogen lone pair in 1-methylpyrrole is part of the aromatic system and therefore not available for interaction with electrophiles.

5.3.4. Experiments with 2-ethynylthiophene

Effect of substrate and catalyst concentration

In view of the favorable catalytic behavior, combining a high selectivity for trans-head-to-head dimerization with a high activity, it was decided to study the reaction of Cp*$_2$La(SiMe$_3$)$_2$ (5D) with excess 2-ethynylthiophene (2d) in more detail. Monitoring the substrate consumption during the 5D-catalyzed oligomerization of 2d by normalized, single-pulse in situ 1H NMR spectroscopy revealed that the rate of reaction is first-order dependent on substrate concentration over a 3-fold substrate concentration range (0.6-1.6 M) and a 3-fold catalyst concentration range (1.4-4.4 mM) for at least 3 half-lives.

When the substrate concentration at constant catalyst concentration (1.4 mM) was increased from 0.601 M to 1.52 M, deviation from first-order rate dependence on substrate concentration was observed at a lower degree of substrate conversion (i.e. after 5.4 and 3.1 half-lives, respectively). This observation suggests that nonproductive product coordination to the catalyst competes effectively with productive substrate coordination to the catalyst at relatively high product concentrations and low substrate concentrations. Similar, but more pronounced behavior was also observed in the analogous reactions with 2-ethynylanisole, 3-ethynylthiophene and 2-ethynylpyridine (Section 5.3.3).

The product distribution of the oligomerization reaction of 2d at different reaction conditions revealed that the rates of catalytic trimerization and catalyst deactivation are promoted relative to catalytic
The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metallocenes

Table 5-3. The 5D-catalyzed oligomerization of 2-ethynylthiophene at different substrate and catalyst concentrations and in the presence of thiophene.

<table>
<thead>
<tr>
<th>Entry</th>
<th>[5D] (nM)</th>
<th>[2d] (M)</th>
<th>[Cp*H] (mM)</th>
<th>11d</th>
<th>12d</th>
<th>15d</th>
<th>16d</th>
<th>time (min)</th>
<th>Cat. deact. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.46</td>
<td>0.47</td>
<td>0.24</td>
<td>0.0</td>
<td>99.5</td>
<td>0.6</td>
<td>0.0</td>
<td>&lt;10</td>
<td>1.4(3)</td>
</tr>
<tr>
<td>2</td>
<td>4.41</td>
<td>1.63</td>
<td>0.79</td>
<td>0.1</td>
<td>97.0</td>
<td>2.5</td>
<td>0.4</td>
<td>32</td>
<td>9(1)</td>
</tr>
<tr>
<td>3</td>
<td>1.42</td>
<td>0.601</td>
<td>0.31</td>
<td>0.0</td>
<td>98.9</td>
<td>1.0</td>
<td>0.1</td>
<td>83</td>
<td>11(2)</td>
</tr>
<tr>
<td>4</td>
<td>1.35</td>
<td>1.52</td>
<td>0.77</td>
<td>0.0</td>
<td>96.8</td>
<td>2.7</td>
<td>0.6</td>
<td>105</td>
<td>27(2)</td>
</tr>
<tr>
<td>5d</td>
<td>1.35</td>
<td>1.52</td>
<td>0.95</td>
<td>0.0</td>
<td>96.8</td>
<td>2.6</td>
<td>0.6</td>
<td>282</td>
<td>34(2)</td>
</tr>
</tbody>
</table>

* Reaction conditions: benzene-\textit{d}_6 and 25 °C. Yields are determined by normalized \textit{in situ} \textit{H} NMR spectroscopy and represent average values of two or more runs. The experimental error in the relative amounts and [Cp*H] were found to be ±0.2 and ±0.05 mM, respectively. Catalyst deactivation, calculated from [Cp*H] and [5D]. ‡ Not determined, due to rapid substrate conversion. § In the presence of 1130 equiv. of thiophene.

Substrate and product inhibition

To obtain additional evidence for the proposal that nonproductive metal heteroatom interactions play a role in the catalytic oligomerization reactions of 2-ethynylthiophene (2d), the reaction of 5D and 2d (1200 equiv.) was performed in the presence of thiophene (Entry 5, Table 5-3). The rate of 2d conversion was found to be first-order in 2d for only 2.7 half-lives and a ~1.6-fold rate decrease was observed (Figure 5-4). This result clearly demonstrates that nonproductive metal heteroatom interactions lead to catalyst rate depression by competing for and blocking coordination sites at the metal center of the catalyst in the present catalytic system. As thiophene is capable of competing effectively with productive Lewis base coordination of the substrate to the catalyst, it seems likely that both substrate and product are engaged in competitive inhibition of the catalyst (Scheme 5-3).

Additionally, the observation that the presence of thiophene leads to more catalyst deactivation (34% versus 26%, Table 5-3) suggests that the nonproductive coordination of thiophene to the catalyst retards the rate of catalytic dimerization relative to that of catalytically dimerization.

Mechanism

In analogy to the oligomerization reactions of Cp*\text*\textsubscript{2}LaCH(SiMe\textsubscript{3})\textsubscript{2} (5D) with phenylacetylene, the proposed mechanism for the analogous oligomerization of 2-ethynylthiophene (2d) is believed to involve the reaction of Cp*\text*\textsubscript{2}LaCC(2-C\textsubscript{4}H\textsubscript{3}S)=CHCC(2-C\textsubscript{4}H\textsubscript{3}S) (20d) with substrate to form the substrate adduct 20d-2d which may undergo intramolecular protonolysis leading to catalyst deactivation or intramolecular substrate insertion leading to Cp*\text*\textsubscript{2}LaC(2-C\textsubscript{4}H\textsubscript{3}S)=CHCC(2-C\textsubscript{4}H\textsubscript{3}S) (24d) (Scheme 5-4). Protonolysis of the formed but-1-en-3-ynyl derivative 24d by 2d leads to the formation of 12d and 20d, while insertion of 2d into 24d leads to catalytic trimerization.

It can also be envisaged that protonolysis of 24d by substrate proceeds \textit{via} the formation of an alkyne coordinated substrate adduct or \textit{via} the formation of a sulfur coordinated substrate adduct which may give rise to an alkyne coordinated substrate adduct (Scheme 5-15). Although these possibilities are neither supported nor discarded by the present data (\textit{vide infra}), sulfur and alkyne coordination to the metal center in substrate adducts of the catalyst are treated separately in the following analysis. Recognizing that the reaction of 2d and 24d is rate-limiting in the present oligomerization reaction leads to the following empirical rate law: \( v = k_{\text{cat}}[2d][5D] \)

When the effects of reversible, nonproductive coordination of the substrate (substrate self-inhibition) and product (competitive product inhibition) to the catalyst are included, a standard rapid equilibrium analysis reproduces the observed kinetic behavior, as increasing substrate and product concentrations lead to decreasing reaction rates and deviations from first-order rate dependence on substrate concentration.** It is difficult to determine the significance of non-productive substrate coordination to the catalyst during catalytic conversion of 2d based on the present data, however.***
In analogy to the oligomerization reactions of Cp*₂LaCH(SiMe₃)₂ (5D) with phenylacetylene, catalyst deactivation may be modeled by the irreversible formation of a catalytically inactive complex from the catalyst precursor (Chapter 4). A standard steady-state approximation reveals that the rate of catalyst deactivation may be zero-, first- or mixed-order dependent on substrate concentration. The observation that the ratio between the final concentration of Cp*H and that of 12d is invariant (within experimental error) suggests that catalyst deactivation is first-order rate dependent on substrate concentration under the studied reaction conditions. For this scenario implies that the ratio of reaction products of catalyst deactivation (d[Cp*H]/dt = \( k_d \cdot [ET][S] \)) and catalytic dimerization (d[P]/dt = \( k_p \cdot [ET][S] \)) is determined solely by the ratio of the corresponding reaction constants. The experimental error in the final concentration of Cp*H does not allow an accurate determination of \( k_p/k_d \), however (e.g. \([12d]/[Cp*H] = 2.0(4) \times 10^3\), based on selected data presented in Table 5-3). It should be noted that a scenario in which the rate of catalyst deactivation is zero- or mixed-order dependent on substrate concentration entails a \([12d]\)-to-[Cp*H] ratio that is not constant, but varies with substrate concentration.

**Influence of the reaction temperature**

Interestingly, the preference for *trans*-head-to-head dimerization decreased only to a small extent, when the reaction of Cp*₂LaCH(SiMe₃)₂ (5D) with a 400-fold molar excess of 2-thienylacetylene (2d) was performed at 80 °C (i.e. \(11d:12d:15d:16d = 1.25:97.10:1.10:0.56\)). Because 2d was found to be somewhat thermally unstable (Section 5.2), control experiments without catalyst were performed in order to determine the rate of thermal oligomerization of 2d. Experiments conducted at 80 °C revealed that thermal oligomerization is not competitive with 5D-catalyzed oligomerization. For example, under identical reaction conditions, but in the absence of metal (pre)catalyst, a substrate conversion of 28% was indicated by \(^1\)H NMR spectroscopy after 17 h at 80 °C. Longer reaction times did not lead to a significantly higher degree of substrate conversion. After 26 days (92% conversion) the sample was analyzed with GC- and GC-MS. Unidentified compounds were found having the following mass-to-charge ratios and relative flame ionization detector responses (FID-GC yields): a dimer (\(m/z\) 216, 31%), an unknown compound (\(m/z\) 298, 50%) and three trimers (\(m/z\) 324, 78/5/5%). The radical nature of the thermal polymerization of arylacetylenes was established several decades ago, but the exact mechanism is not known presently.\(^{21}\) Even so, there seems to be a general consensus that the low molecular weight fraction consists mainly of dimers and trimers, whose structures have been identified as substituted naphtalenes, and that the higher molecular weight fraction consists of oligo(ene)s.
5.3.5. Experiments with 2-ethynylpyridine

Introduction

Monitoring the substrate consumption during the reaction of $\text{Cp}^*\text{LaCH(SiMe}_3\text{)}_2$ (5D) with 2-ethynylpyridine (55 equiv.) by normalized, single-pulse *in situ* $^1$H NMR spectroscopy revealed three regions of kinetic behavior (Figure 5-6). The first region is defined by the first 18 min of substrate conversion in which 87% of the substrate is converted. Because the corresponding four data points can be modeled both to first- and zero-order rate dependence, the determination of the rate order in substrate is rather tentative, however. In analogy to the observed kinetic behavior of the reactions of $\text{Cp}^*\text{LaCH(SiMe}_3\text{)}_2$ (5D) with other coordinating heteroaromatic 1-alkynes (e.g., 2- and 3-ethynylthiophene), the first kinetic region is presently assumed to exhibit first-order kinetic behavior in substrate ($R^2 = 0.9935, k_{\text{obs}} = 14.4(8) \text{ M}^{-1}\text{·min}^{-1}$). A transition is observed between 22 and 52 min followed by a third kinetic region after 95% substrate conversion where the rate appears to be approximately zero-order in substrate ($R^2 = 0.9543, k_{\text{obs}} = 8.2(4) \times 10^{-3} \text{ min}^{-1}$).

Additional mechanistic information for this reaction was obtained by monitoring the $^1$H NMR resonances in the Cp* region during substrate conversion. During the first 30 min of the reaction, corresponding to a substrate conversion of 91%, one major Cp* $^1$H NMR resonance at $\delta = 2.16$ ppm was observed. Further substrate conversion led to its disappearance, accompanied by the formation of at least eight new Cp* $^1$H NMR resonances. The complexity of the $^1$H NMR spectrum after substrate conversion thwarted attempts to identify the organometallic reaction products. Upon addition of D$_2$O or MeI to the reaction mixture after substrate conversion, most of the $^1$H NMR resonances in the Cp* region ($\delta = 2.5-1.5$ ppm) disappeared and the amount of Cp*H formed could be determined (by $^1$H NMR integration versus CH$_2$(SiMe$_3$)$_2$ formed *in situ* from 5D and substrate). Catalyst deactivation resulting in cyclopentadienyl ligand abstraction occurred only to a small extent (0.5%), thereby advocating that the observed catalytic rate depression at a relatively high substrate conversion is not due to catalyst deactivation via Cp* H abstraction.

The above results argue that catalytic dimerization of 2-ethynylpyridine (2f) represents the only productive pathway in the reaction of 5D with a 55-fold molar excess of 2-ethynylpyridine. Upon reaching a substrate conversion of 87%, however, nonproductive, competing reaction sequences become increasingly important, thereby altering the observed kinetic behavior of the reaction of 5D with 2f and giving rise to several organometallic reaction products. In view of the formation of several Cp* $^1$H NMR resonances at a relatively high substrate conversion, the deviation from first-order kinetic behavior in substrate at higher substrate
Chapter 5

conversion and the absence of other products after quenching with methanol-d$_6$ (GC/GC-MS), it seems natural to ascribe the nature of these nonproductive, competing reaction sequences to reversible heteroatom coordination of the reaction intermediates to substrate and/or product, as proposed previously for the reactions of 5D with 3-ethynylthiophene (Section 5.3.3) and 2-ethynylthiophene (Section 5.3.4).

Product and substrate inhibition

In order to provide additional evidence for the proposed competition between nitrogen coordination of substrate and/or product to the catalyst and catalytic reaction sequences, analogous reactions of Cp*$_2$LaCH(SiMe$_3$)$_2$ (5D) with 2-ethynylpyridine (2f) were performed in the presence of product and pyridine. When a second portion of substrate (55 equiv.) was added to the above reaction mixture, in situ $^1$H NMR spectroscopy revealed the slow conversion of substrate. The kinetic profiles of the reactions in the presence (run 2) and absence of product (run 1) were similar (Figure 5-5), but the rates of substrate conversion during the first and third region were lower and the third region started at a lower degree of substrate conversion (71% versus 95%). Instead of a single, major Cp* $^1$H NMR resonance at $\delta$ 2.16 ppm, two major Cp* $^1$H NMR resonances were observed at $\delta$ 1.75 and 1.71 ppm during substrate conversion. It seems therefore that other organometallic reaction intermediates are involved in the catalytic conversion of 2f, when a second portion of substrate is added to the reaction mixture. Catalyst deactivation via Cp* abstraction took place only to a small extent (~1%) and no products other than those expected from exclusive trans-head-to-head dimerization of 2f were observed with GC/GC-MS after quenching the reaction mixture with D$_2$O.

Under the assumption that the degree of irreversible catalyst deactivation can be neglected (vide infra), the catalytic conversion of 2f in the presence of product (~25 equiv. relative to catalyst) indicates that the presence of product lowers both the catalytic rate and the attainable degree of substrate conversion. In order to investigate the possibility of irreversible catalyst deactivation during the catalytic conversion of 2f, product inhibition was modeled by pyridine by performing the reaction of 5D with 2-ethynylpyridine (55 equiv.) in the presence of pyridine (55 equiv.). In situ $^1$H NMR spectroscopy revealed slow substrate conversion and a kinetic profile (run 3) similar to those observed before (Figure 5-5). The observed Cp* $^1$H NMR resonances were reminiscent of those observed during the reaction of 5D and 2f (55 equiv.) in the sense that one major species ($\delta$ 2.15 ppm, ~50% of the total amount of organometallic species present) was present during the first stage of substrate conversion which transformed into a multitude of unidentified species at higher substrate conversion.

The rates of substrate conversion for the reaction of 5D in the presence of product (run 2) and pyridine (run 3) are similar during the first kinetic region and this finding reveals that the decreased reaction rate at higher degrees of substrate conversion is due to reversible catalyst inhibition and not irreversible catalyst deactivation. The observation that a higher degree of substrate conversion is achieved in the presence of pyridine (93%) than in the presence of product (71%) implies also that the dimerization product inhibits catalytic activity more effectively than pyridine. The above reactions of 5D and 2f in the presence of product and pyridine clearly

Figure 5-5. Plot of the substrate concentration versus time for the 5D-catalyzed dimerization of a single portion of 2f (50 equiv., run 1), a second portion of 2f (50 equiv., run 2) and 2f (50 equiv.) in the presence of pyridine (50 equiv., run 3). Curves connecting the data points are fitted second-order exponentials.
The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metallocenes

establish that competing reversible nitrogen coordination to the catalyst results in both a lower rate and a lower degree of substrate conversion. Similar catalytic consequences from competing metal heteroatom interactions during catalytic oligomerization of heteroaromatic 1-alkynes were also observed in the reactions of 3-ethynylthiophene (Section 5.3.3) and 2-ethynylthiophene (Section 5.3.4), albeit less pronounced. The strong preference for nitrogen coordination over sulfur coordination is well-recognized in rare-earth metal chemistry (Sections 5.4.3 and 5.4.4).

An inverse relationship between the degree of substrate conversion and the substrate-to-catalyst molar ratio was found. For example, the use of a 30-fold molar excess led to 100% substrate conversion (after 12 h at room temperature), whereas the use of a 200-, 400 and 1000-fold molar excess led to 95% (after 28 h), 89% (after 94 h) and 71% (after 102 h) substrate conversion, respectively. It seems therefore that the degree of catalyst inhibition increases upon increasing the substrate concentration at constant precatalyst concentration. This finding provides additional support to the above view that competing reversible nitrogen coordination of both product and substrate compete with catalytic reaction sequences (Scheme 5-3), thereby lowering the degree of substrate conversion. Similar catalytic behavior was also observed for the reactions of 5D with 3-ethynylthiophene (2d). Even though a 55-fold molar excess of 2d was converted completely, the use of a 400-fold molar excess led to incomplete substrate conversion (Section 5.3.3).

5.3.6. Experiments with 2-ethynylanisole

Substrate and product inhibition

Reactions with a 40-, 200- and 600-fold molar excess of 2e were conducted at constant precatalyst concentration and substrate conversion was followed in time by normalized, in situ 1H NMR spectroscopy (Figure 5-7). The reaction of 5D with a 40-fold molar excess of 2e exhibited first-order rate dependence on substrate concentration over at least 10 half-lives ($R^2 = 0.9974, k_{obs} = 20.6(2) \text{ M}^{-1} \cdot \text{min}$). Complete substrate conversion was observed after 150 min, accompanied by 0.6% catalyst deactivation via Cp*H abstraction. The analogous reaction with a 200-fold molar excess of 2e displayed first-order dependence on substrate concentration over at least 3 half-lives ($R^2 = 0.9983, k_{obs} = 4.70(3) \text{ M}^{-1} \cdot \text{min}$). Only 99.8% substrate conversion was observed after 10 h, accompanied by 5% catalyst deactivation via Cp*H abstraction, and longer reaction times did not lead to complete substrate conversion. When the reaction was performed in the presence of a 600-fold molar excess of 2e, the reaction rate was first-order dependent on substrate concentration for 1.5 half-lives ($R^2 = 0.9981, k_{obs} = 3.83(2) \text{ M}^{-1} \cdot \text{min}$) and only 94% substrate conversion was achieved after 13 h, accompanied by 10% catalyst deactivation via Cp*H abstraction.

Figure 5-6. Integrated rate plot of the substrate concentration versus time for the 5D-catalyzed dimerization of a single portion of 2f (50 equiv., run 1), a second portion of 2f (50 equiv., run 2) and 2f (50 equiv.) in the presence of pyridine (50 equiv., run 3). Lines drawn represent fitted linear plots (see text for details).
These results reveal a lower reaction rate and a lower degree of substrate conversion upon increasing the molar substrate-to-catalyst ratio. This catalytic behavior points to nonproductive metal oxygen interactions that compete with catalytic reaction sequences, as discussed previously for the reactions of 3-ethynylthiophene (Section 5.3.3), 2-ethynylthiophene (Section 5.3.4) and 2-ethynylpyridine (Section 5.3.5). No evidence for other products than those expected from catalytic oligomerization was obtained with GC/GC-MS after quenching the above product mixtures with D\textsubscript{2}O. This observation argues against the occurrence of irreversible catalyst deactivation via other routes than Cp*H abstraction and supports the notion that the above observed catalyst inhibition is due to reversible metal oxygen coordination of the catalyst with substrate and product (Scheme 5-3.).

**Figure 5-7.** Integrated rate plot of the substrate concentration versus time for the 5D-catalyzed oligomerization of 2c at different initial substrate concentrations. The lines connecting the data points represent fitted linear plots (see text for details).

These results reveal a lower reaction rate and a lower degree of substrate conversion upon increasing the molar substrate-to-catalyst ratio. This catalytic behavior points to nonproductive metal oxygen interactions that compete with catalytic reaction sequences, as discussed previously for the reactions of 3-ethynylthiophene (Section 5.3.3), 2-ethynylthiophene (Section 5.3.4) and 2-ethynylpyridine (Section 5.3.5). No evidence for other products than those expected from catalytic oligomerization was obtained with GC/GC-MS after quenching the above product mixtures with D\textsubscript{2}O. This observation argues against the occurrence of irreversible catalyst deactivation via other routes than Cp*H abstraction and supports the notion that the above observed catalyst inhibition is due to reversible metal oxygen coordination of the catalyst with substrate and product (Scheme 5-3.).

**Table 5-4:** The 5D-catalyzed oligomerization of 2-ethynylanisole at different substrate-to-catalyst ratios.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>(2c) (equiv.)</th>
<th>([2c]) (M)</th>
<th>11</th>
<th>12</th>
<th>15</th>
<th>16</th>
<th>(k_{obs}) (M\textsuperscript{-1}·min\textsuperscript{-1})</th>
<th>Cat. deact. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>0.072</td>
<td>36.9</td>
<td>63.1</td>
<td>0.0</td>
<td>0.0</td>
<td>20.6(2)</td>
<td>0.6</td>
</tr>
<tr>
<td>2</td>
<td>230</td>
<td>0.42</td>
<td>18.7</td>
<td>81.3</td>
<td>0.0</td>
<td>0.0</td>
<td>4.70(3)</td>
<td>5.4</td>
</tr>
<tr>
<td>3</td>
<td>593</td>
<td>0.99</td>
<td>10.1</td>
<td>89.9</td>
<td>0.1</td>
<td>0.0</td>
<td>3.83(2)</td>
<td>9.5</td>
</tr>
<tr>
<td>4</td>
<td>1108</td>
<td>2.00</td>
<td>4.8</td>
<td>95.2</td>
<td>0.3</td>
<td>0.0</td>
<td>c</td>
<td>15.2</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: [5D] = 1.6-1.8 mM, benzene-d\textsubscript{6} and 25 °C. Yields are determined by normalized in situ \(^1\)H NMR spectroscopy and represent average values of two or more runs. The experimental error was found to be ±0.2. The second-order reaction constants \(k_{obs}\) were determined from linear regression analysis.

\textsuperscript{b} Catalyst deactivation, calculated from the amount of Cp*H formed (\(^1\)H NMR).

**Effects of substrate-to-catalyst ratios on the regioselectivity**

As noted before in Section 5.3.3, the selectivity for head-to-head dimerization in the reactions of 5D with 2f increases with increasing substrate concentration (Table 5-4). This trend was also supported by the product distribution of an analogous reaction with a 1200-fold molar excess of 2e, but is not understood at present. Based on the reasonable assumption that substrate and/or product coordination to the catalyst will be favored at relatively high substrate-to-catalyst molar ratios, the relative increase of the sterically hindered 2,1-metal insertion mode with increasing initial substrate concentration seems counter intuitive.
The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metallocenes

5.3.7. Experiments with yttrium precatalyst

Introduction

The precatalyst Cp*₂YCH(SiMe₃)₃ (5A) was found to be an active and selective catalyst for the formation of the head-to-tail dimer 11a of phenylacetylene (Chapter 4). The formation of the dimer, arising from the sterically preferred 1,2-metal insertion, was rationalized by the small metal size of yttrium relative to lanthanum, thereby increasing the steric interaction between substrate and catalyst during alkyne insertion into the monomeric, alkynyl species. To investigate the substrate effects on the rate and selectivity of a precatalyst Cp*₂LnCH(SiMe₃)₂ that favors head-to-tail dimerization due to steric control, reactions of 5A with representative substrates were performed.

Catalytic reactions

Even though ¹H NMR spectroscopy indicated rapid and quantitative formation of CH₂(SiMe₃)₂, no catalytic reactivity was observed with excess amounts of 2-ethynyltoluene and 2-ethynylanisole (50-200 equiv.). The reaction of 5A with 2-ethynylthiophene (54 equiv.) was significantly slower than the analogous reaction with phenylacetylene (by a factor of 11) and full substrate conversion was observed after 2 days at room temperature. The rate of reaction was first-order in substrate for at least 3 half-lives (kₛ = 0.391(4) M⁻¹·min⁻¹, t₁/₂ = 201(2) min), suggesting either rate-limiting alkyne insertion or protonolysis. The product mixture after substrate conversion consisted of the trans-head-to-head dimer 12d and two higher oligomers of unknown structure.

The reaction of 5A with excess 2-ethynylpyridine (55 equiv.) was reminiscent of the analogous reaction catalyzed by 5D (Section 5.3.5). Three kinetic regions were observed during substrate conversion, but the rate of reaction was lower and significant catalyst deactivation took place at a lower degree of substrate conversion. The first 53 min (27% substrate conversion) correspond to a region of approximately first-order rate dependence in substrate (R² = 0.9811, kₛ = 170(7) min⁻¹, kₘ = 0.46(2) M⁻¹·min⁻¹) which is followed successively by a region of intermediate kinetic behavior and a region of approximately zero-order rate-dependence in substrate (R² = 0.9649, kₛ = 1.34(5) × 10⁻⁴ min⁻¹) after 198 min (56% conversion). After monitoring the reaction for three days, a substrate conversion of 74% was found. Quite surprisingly, only the trans-head-to-head dimer (12d) was formed. No evidence for other reaction products than those expected from trans-head-to-head dimerization was obtained with GC/GC-MS analysis after quenching the reaction mixture with D₂O.

The reaction of 5A with 1-methyl-2-ethynlypyrrole (55 equiv.) was more rapid than the analogous reaction with phenylacetylene. Complete substrate conversion was observed after 50 min at room temperature.

| Table 5-5. The substrate effects of the 5A-catalyzed 1-alkyne oligomerization.a |
|---|---|---|---|---|---|---|
| Entry | Substrate | Conv. (%) | kₛ(M⁻¹·min⁻¹) | t₁/₂(min) |
| 1 | a | 93.7 | 5.2 | 0.4 | 0.7 | 100 (2 h) | 4.5(1) |
| 2 | d | 0.0 | 51.2 | 0.0 | 0.0 | 100 (44 h) | 0.391(4) |
| 3 | f | 0.0 | 100.0 | 0.0 | 0.0 | 74 (72 h) | 0.46(2) |
| 4 | g | 20.6 | 69.9 | 6.4 | 3.2 | 100 (0.83 h) | 9.1(1) |

a Reaction conditions: [5A] = 8.8-8.9 mM, substrate (54-55 equiv.), benzene-d₆ and 25 °C. Yields are determined by normalized in situ ¹H NMR spectroscopy and represent average values of two or more runs. The experimental error was found to be ±0.2. b Conversion as determined determined by in situ ¹H NMR. c The observed second-order reaction constant kₛ, obtained from linear regression analysis (see text for details).
The rate of reaction was first-order in substrate for at least 5 half-lives ($k_{\text{obs}} = 9.1(1) \text{ M}^{-1} \cdot \text{min}^{-1}$, $t_{1/2} = 8.5(1) \text{ min}$). The reaction products were identified as $8f$:$9f$:$11f$:$12f$ in a 20.6:69.9:6.4:3.2 molar ratio, respectively.

**Substrate effects**

It seems that the tolerance of Cp*$_2$YCH(SiMe$_3$)$_2$ ($5A$) towards sterically hindered substrates is low. Indeed, no catalytic activity for the reaction of $5A$ with 1-ethynyltoluene ($2b$) and 2-ethynylanisole ($2c$) was observed, despite rapid and quantitative protonolysis of $5A$ by 1-alkyne forming CH$_2$(SiMe$_3$)$_2$. This observation implies that ortho-substituted phenylacetylenes are sterically too crowded for alkyne insertion into the metal-carbon bond of the monomeric alkynyl species Cp*$_2$YCCR ($R = \text{C}_6\text{H}_4$-$2$-$\text{CH}_3$, $\text{C}_6\text{H}_4$-$2$-$\text{OCH}_3$).

Another observation is the relative importance of steric and electronic effects in the observed regioselectivity of the 1-alkyne reactions catalyzed by Cp*$_2$YCH(SiMe$_3$)$_2$ ($5A$). For the reactions of $5A$ with 2-ethynylthiophene ($2d$), 2-ethynylpyridine ($2f$) and 1-methyl-2-ethynylpyrrole ($2g$), major products originating from 2,1-insertion are observed. These results may plausibly be rationalized by a combination of steric and electronic effects in the case of $2d$ and $2g$ (Section 5.5.3), while exclusive trans-head-to-head dimerization of $2f$ seems to be the result of both electronic effects and an interaction between heteroatom and metal center, resulting in a heteroatom-directed reaction (Section 5.5.3).

These results provide also additional evidence that the extent of oligomerization is determined by the steric properties of the substrate, as larger relative amounts of oligomers higher than dimers are observed for $2d$ and $2g$ as compared to phenylacetylene. The influence of the steric size of the 1-alkyne substituent on the relative rates of 1-alkyne dimerization and trimerization was proposed before for the reactions of Cp*$_2$LaCH(SiMe$_3$)$_2$ ($5D$) with 2-ethynyltoluene and 2-ethynylanisole relative to that with phenylacetylene (Section 5.3.3).

The higher reactivity of $2g$ relative to phenylacetylene may be explained by its higher (kinetic) acidity, thereby suggesting that protonolysis of a butenyl yttrocene derivative is rate-limiting in the present catalytic dimerization reactions mediated by $5A$. The lower reactivities of $2d$ and $2f$ are most likely the result of catalyst inhibition, due to reversible, nonproductive metal heteroatom interactions.

**Figure 5-9.** Plot of the substrate concentration versus time for the $5A$-catalyzed oligomerization of $2a$, $2d$ and $2f$. The curves connecting the data points of $2a$, $2d$ and $2g$ represent fitted first-order exponentials, while the curve connecting the data points of the reaction with $2f$ is drawn as a guide for the eye (see text for details).

The rate of reaction was first-order in substrate for at least 5 half-lives ($k_{\text{obs}} = 9.1(1) \text{ M}^{-1} \cdot \text{min}^{-1}$, $t_{1/2} = 8.5(1) \text{ min}$). The reaction products were identified as $8f$:$9f$:$11f$:$12f$ in a 20.6:69.9:6.4:3.2 molar ratio, respectively.
5.4. Stoichiometric reactions of (hetero)aromatic 1-alkynes

5.4.1. The reactivity of alkyl and hydride derivatives

Introduction

In an effort to understand the substrate effects in the present catalytic 1-alkyne oligomerization reactions, mediated by Cp*₂LaCH(SiMe₃)₂ (5D), stoichiometric reactions with representative substrates were performed. Stoichiometric reactions of 5D with phenylacetylene revealed that the reaction between 5D and the substrate, producing the monomeric alkynyl derivative Cp*₂LaCCPh and CH₂(SiMe₃), is slower than that of Cp*₂LaCCPh with substrate, giving rise to two regioisomeric insertion products. The monomeric alkynyl species was not observed, as it readily rearranged into a butatrienediyl derivative via a dimeric alkynyl species. This dimeric alkynyl species was observed at low temperature by means of in situ ¹H NMR spectroscopy. The butatrienediyl derivative was formed selectively from the reaction of [Cp*₂La(µ-H)]₂ with phenylacetylene (2 equiv.) at room temperature.

Reactions with 2-ethynylthiophene

The reaction of 5D with 2-ethynylthiophene (2d) was rapid in non-coordinating solvents, such as toluene and hexane, at room temperature, as evidenced by an instantaneous color change from colorless to dark red. ¹H NMR experiments in benzene-d₆ indicated the formation of a product mixture consisting of the butatrienediyl derivative [(Cp*₂La)₂[µ-(C₆H₃S-2)C₆(C₆H₃S-2)]] (22d), the but-1-en-3-yn-1-yl derivative Cp*₂LaC(2-C₆H₃S)=CHCC(2-C₆H₃S) (24d) and the organic compounds, (E)-1,4-di(2-thienyl)but-1-en-3-yne (12d) and 2,4-di(2-thienyl)but-1-en-3-yne (11d) (eq. 5.1). The reaction of the hydride derivative [Cp*₂La(µ-H)]₂ (25D) with a stoichiometric amount of 2d in benzene-d₆ was very clean at room temperature, affording 22d as the only observable product.

The identity of 22d was determined unequivocally by single-crystal X-ray diffraction (details are discussed in Section 5.4.6), while NMR analysis in combination with quenching experiments with H₂O and D₂O.
provided evidence for the identity of 24d. In accordance with Cp* 2LaC(Ph)=C(H)CCPh (24a) discussed previously (Chapter 4), the thienyl derivative 24d exhibited two singlets in the 1H NMR spectrum at δ 1.98 and 7.35 ppm in a 30:1 ratio, assigned to the Cp* and the =CH group, respectively.

When 2-ethynylthiophene (2d) was condensed onto a solution of a stoichiometric amount of 5D in toluene at -78 ºC, the colorless solution changed into a suspension containing a bright yellow solid. Upon slowly warming at room temperature the bright yellow color of the suspension changed into dark red. Isolation of the isolated dark red crystalline material led to its identification as the butatrienediyl derivative {(Cp* 2La)2[µ-η2:η2-(2-C4H3S)C4-(2-C4H3S)]} (22d). Analogous low temperature 1H NMR experiments in toluene-d8 revealed the presence of two new organometallic species at -60 °C, as indicated by two Cp* 1H NMR resonance at δ 2.22 and 2.00 ppm. The major species exhibiting a Cp* 1H NMR resonance at δ 2.22 ppm, was identified as the dimeric alkynyl derivative {Cp* 2La[(µ-CC(2-C4H3S)])2} (21d), while the minor species exhibiting a Cp* 1H NMR resonance at δ 2.00 ppm, was identified as the butenynyl derivative Cp*2LaC(2-C4H3S)=CHCC(2-C4H3S) (24d).

Upon standing at -60 ºC, 21d converted gradually into the butatrienediyl derivative 22d, exhibiting a Cp* 1H NMR resonance at δ 2.11 ppm at -60 ºC (eq. 5.2). The conversion of 21d into 22d was also observed for the phenyl-substituted analogue, albeit less rapidly (Chapter 4). When the reaction mixture was allowed to warm up to room temperature, the Cp* 1H NMR resonances of 22d and 24d shifted upfield (Figure 5-10). These shifts were found to be reversible, as previously observed for the phenyl-substituted analogues 22a and 24a (Chapter 4). Similar to reactions with phenylacetylene, reactions of 24D and [Cp*2La(µ-H)]2 (25D) with a small excess of 2-ethynylthiophene (1-2 equiv.) at low temperatures resulted in the concomitant formation of a small amount of an unidentified organometallic by-product (~2-5% relative to starting material), tentatively assigned to an oligomeric alkynyl derivative.

Concluding remarks

These results indicate that the rate of 1-alkyne insertion into the metal-carbon bond of the monomeric, alkynyl derivative relative to protonolysis of 5D by 1-alkyne is more rapid for reactions of 5D with 2-ethynylthiophene (2d) than for reactions of 5D with phenylacetylene (2a). In fact, quantitative conversion of 5D was observed with stoichiometric amounts of phenylacetylene in conjunction with vigorous stirring, while amounts of unreacted 5D were present in the reaction mixtures of 5D with 2d under identical reaction conditions and after addition of small excesses of 2d. It is believed that this difference in behavior can plausibly be ascribed to the smaller size of the thiényl ring versus the phenyl ring, the higher (kinetic) acidity of the acetylenic proton in 2d versus 2a and precoordination of the heteroatom to the metal in the reaction of 5D with 2d (Section 5.5.3).

5.4.2. The reactivity of the dimeric alkynyl derivatives

Introduction

Another substrate effect was observed for the rate of conversion of the dimeric, alkynyl derivative into the corresponding butatrienediyl derivative. Whereas [Cp*2La(µ-CCPh)]2 (21a) was found to be stable for several hours at -50 ºC (Chapter 4), [Cp*2La(µ-CC(2-C4H3S))]2 (21d) underwent quantitative C-C coupling
The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metallocenes

into the corresponding butatrienediyl derivative within 1 hour at -50 °C (eq. 5.2). This difference in behavior may arguably be attributed to a combination of steric (the ring size of the alkyne substituent) and electronic (viz. the inductive/field effect of the alkyne substituent) effects. In an attempt to determine the relative importance of these effects, a kinetic study was performed using 1H NMR spectroscopy at low temperature to establish the rate of C-C coupling for [Cp*₂La(µ-CCR)]₂ [R = Ph (21a), 2-C₄H₃S (21d), 3-C₄H₃S (21e)] complexes, prepared in situ from Cp*₂LaCH(SiMe₃)₂ (5D) and the appropriate 1-alkyne. The 3-thienyl derivative was included, as the 3-thienyl group represents an alkyne substituent having steric properties similar to those of the 2-thienyl group and electronic properties similar to those of the phenyl group (Section 5.5.1).

**Kinetic study of C-C coupling**

As noted before, an accurate kinetic analysis was impeded by the low solubility of the dimeric, alkyne derivative 21 and overlapping ¹H NMR resonances of the butatrienediyl derivative with the residual protio resonances of toluene-d₈. Nonetheless, the time-dependent conversion of 21 into 22 could be determined by monitoring the decrease of the normalized, Cp* 1H NMR intensity of 21 formed in situ from Cp*₂LaCH(SiMe₃)₂ (5D) and 1-alkyne. Reasonable kinetic data was obtained by normalization against CH₂(SiMe₃)₂ formed in situ from rapid and quantitative protonolysis of 5D by the 1-alkyne. In all cases, the rate of C-C coupling was found to be first-order in 21, consistent with previous results (Chapter 4). Kinetic analysis indicated that the 2-thienyl derivative (21d, R² = 0.9988, t₁/₂ = 8.63(12) min) undergoes C-C coupling ~5 times more rapid than the 3-thienyl derivative (21e, R² = 0.9967, t₁/₂ = 40.6(4) min), while the 3-thienyl derivative reacts ~3 times more rapid than the phenyl derivative (21a, R² = 0.9937, t₁/₂ = 132(2) min). These findings reveal therefore that the rate of C-C coupling in the dimeric alkyne complexes is dominated by the steric effects of the alkyne substituent rather than the electronic effects.

5.4.3. **The reactivity of amide derivative towards phenylacetylene**

In the absence of Lewis bases

In marked contrast to the observed reactivity of the alkyl 5D and hydride 25D derivatives towards phenylacetylene, the amide derivative Cp*₅La(N(SiMe₃)) (26D) displayed no significant reactivity towards stoichiometric amounts of phenylacetylene at ambient temperatures. Increasing the reaction temperature led to complete substrate conversion into (E)- (12a) and (Z)-1,4-diphenylbut-1-en-3-yne (13a), 1,3,6-triphenylhexa-1,5-diyne (15a) and 1,3,6-triphenylhexa-1,2-diene-5-yne (16a), accompanied by 4% conversion of 26D.

Clearly, metalation is rate-limiting in the catalytic conversion of substrate. It seems natural to ascribe the low reactivity of the La-N bond in Cp*₅LaN(SiMe₃) (26D) versus the La-C bond in Cp*₅LaCH(SiMe₃) (1D) towards phenylacetylene to the donation of electron density from the nitrogen lone pair into empty metal...
orbitals, thereby accounting for the higher thermodynamic stability of amide ligands relative to alkyl ligands in rare-earth metal chemistry. An alternative view involves the lower basicity \([\text{N(SiMe}_3\text{)}_2]\) as compared to \([\text{CH(SiMe}_3\text{)}_2]\).^{24}

**Relative strength of Lewis base coordination**

In order to assess the relative strengths of the Lewis base coordination to the metal center of \(\text{Cp}^*\text{LaCCPh} (20a)\), reactions of \(\text{Cp}^*\text{LaN(SiMe}_3\text{)}_2 (26D)\) with phenylacetylene (1 equiv.) were performed in benzene-\(d_6\) at 80 °C in the presence of a small excesses (5 equiv.) of thiophene, THF and pyridine. The reactions were monitored after appropriate intervals with \(^1\text{H NMR spectroscopy. When \(\text{Cp}^*\text{LaN(SiMe}_3\text{)}_2 (26D)\) was heated to 80° in the presence of phenylacetylene (1 equiv.) and pyridine (5 equiv.), complete conversion of phenylacetylene was observed within three days, accompanied by 78% conversion of 26D (eq. 5.3). The reaction mixture consisted of dimers of phenylacetylene, i.e. (\(\text{E}\))-1,4-diphenylbut-1-en-3-yne (13a), and one new lanthanum species, identified as the Lewis base adduct \(\text{Cp}^*\text{LaCCPh:N}=\text{C}=\text{N:C}_5\text{H}_5 (20a·NC}_5\text{H}_5)\) on the basis of its independent synthesis from the reaction of \(\text{Cp}^*\text{LaCCPh:THF} (20a·THF)\) and pyridine (vide infra, eq. 5.7).

\[
\begin{align*}
\text{Cp}^*\text{LaN(SiMe}_3\text{)}_2 & + \text{Ph} \quad \text{80 °C} \quad \text{C}_6\text{D}_6

\text{Cp}^*\text{LaN(SiMe}_3\text{)}_2 & + \text{phenylacetylene dimers} \quad \text{78%}
\end{align*}
\]

In the presence of THF, complete conversion of phenylacetylene was also observed within three days. In this case, the reaction mixture consisted not only of small amounts of dimers, (\(\text{Z}\)- and (\(\text{E}\))-1,4-diphenylbut-1-en-3-yne, but trimers, 1,3,6-triphenylhexa-1,5-diyne (15a) and 1,3,6-triphenylhexa-1,2-diene-5-yne (16a), as well. Concomitantly, 62% of 26D was converted into several species of which the major components were identified as \(\text{Cp}^*\text{LaCCPh:THF} (20a·THF, 9%)\) and [(\(\text{Cp}^*\text{La})_2(\mu-\eta^3\text{-PhC}_4\text{Ph})] (22a, 12%). The presence of significant amounts of \(\text{Cp}^*\text{H} (18\%)\) suggested that the formed species are thermally not stable at 80 °C. In fact, similar \(\text{Cp}^*\text{H} \text{NMR resonances were observed upon heating a benzene-\(d_6\) solution of 20a·THF to 80 °C and it seems therefore reasonable to ascribe the observed reactivity, including the formation of 22a, to thermolysis of the initially formed 20a·THF (eq. 5.4). The analogous reaction of \(\text{Cp}^*\text{LaN(SiMe}_3\text{)}_2 (26D)\) with phenylacetylene (1 equiv.) in the presence of thiophene (5 equiv.) was identical to the reaction of 26D with phenylacetylene (1 equiv.) at 80 °C. Complete conversion of phenylacetylene into 12a, 13a, 15a and 16a was achieved within 1 day at 80 °C, accompanied by 4% conversion of 26D.

\[
\begin{align*}
\text{Cp}^*\text{LaN(SiMe}_3\text{)}_2 & \quad \text{80 °C} \quad \text{C}_6\text{D}_6

\text{Cp}^*\text{LaN(SiMe}_3\text{)}_2 & \quad \text{phenylacetylene oligomers} \quad \text{62%} \quad \text{decomposition products}
\end{align*}
\]

In the presence of THF, complete conversion of phenylacetylene was also observed within three days. In this case, the reaction mixture consisted not only of small amounts of dimers, (\(\text{Z}\)- and (\(\text{E}\))-1,4-diphenylbut-1-en-3-yne, but trimers, 1,3,6-triphenylhexa-1,5-diyne (15a) and 1,3,6-triphenylhexa-1,2-diene-5-yne (16a), as well. Concomitantly, 62% of 26D was converted into several species of which the major components were identified as \(\text{Cp}^*\text{LaCCPh:THF} (20a·THF, 9%)\) and [(\(\text{Cp}^*\text{La})_2(\mu-\eta^3\text{-PhC}_4\text{Ph})] (22a, 12%). The presence of significant amounts of \(\text{Cp}^*\text{H} (18\%)\) suggested that the formed species are thermally not stable at 80 °C. In fact, similar \(\text{Cp}^*\text{H} \text{NMR resonances were observed upon heating a benzene-\(d_6\) solution of 20a·THF to 80 °C and it seems therefore reasonable to ascribe the observed reactivity, including the formation of 22a, to thermolysis of the initially formed 20a·THF (eq. 5.4). The analogous reaction of \(\text{Cp}^*\text{LaN(SiMe}_3\text{)}_2 (26D)\) with phenylacetylene (1 equiv.) in the presence of thiophene (5 equiv.) was identical to the reaction of 26D with phenylacetylene (1 equiv.) at 80 °C. Complete conversion of phenylacetylene into 12a, 13a, 15a and 16a was achieved within 1 day at 80 °C, accompanied by 4% conversion of 26D.
The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metallocenes

The weak interaction between Cp*$_2$LaCCPh and thiophene was furthermore demonstrated by the reaction of [Cp*$_2$La(µ-2-C$_4$H$_3$S)]$_2$ with phenylacetylene (1 equiv.) and the reaction of Cp*$_2$LaCCPh(THF) (20a·THF) with thiophene. In the former reaction, [(Cp*$_2$La)$_2$(µ-η$_2$-η$_2$-PhC$_4$Ph)] (22a) and thiophene were produced cleanly (eq. 5.5), whereas no reactivity was observed between 20a·THF and an excess of thiophene at room temperature (eq. 5.6). Thus, thiophene fails to protect the monomeric alkynyl derivative Cp*$_2$LaCCPh from dimerization and subsequent C-C coupling.

The facile displacement of coordinated THF by pyridine in the reaction of Cp*$_2$LaCCPh (20a·THF) with pyridine (1 equiv.) clearly established the preference for pyridine coordination over THF coordination and the kinetic lability of the base adduct (Eq. 5.7). The thermal stability of Cp*$_2$LaCCPh(NC$_5$H$_5$) (20a·NC$_5$H$_5$) relative to the analogous THF adduct 20a·THF provides evidence for a strong interaction between pyridine and the lanthanum metal center. This feature is also apparent from the increased tendency to block catalytic activity relative to THF for the reactions of Cp*$_2$LaN(SiMe$_3$)$_2$ (26D) and phenylacetylene in the presence of small excess of Lewis base.

These results clearly indicate that pyridine coordinates stronger to Cp*$_2$LaCCPh than THF and that the interaction between thiophene and Cp*$_2$LaCCPh is relatively weak. Considerable literature precedent exists for this relative order of the coordinating ability of nitrogen-, oxygen-, and sulfur-containing compounds towards electrophilic, hard metal centers. 27 More specifically, pyridine is well-known to displace coordinated ether ligands, such as THF and diethyl ether, in rare-earth metal chemistry 28 and the interaction of yttrocene metal centers with the soft sulfur atom of thiophene has been shown to be weaker than those with the relatively hard oxygen and nitrogen atoms.29,30

5.4.4. The reactivity of amide derivatives towards other 1-alkynes

In the absence of exogenous bases

The low reactivity of 26D towards 1-alkynes versus alkyl and hydride derivatives allows for the evaluation of substrate effects on the rate of substrate conversion in the absence of large substrate-to-catalyst ratios. In analogy to phenylacetylene, no reactivity was observed for reaction mixtures in benzene-$d_6$ containing Cp*$_2$LaN(SiMe$_3$)$_2$ (26D) and stoichiometric amounts of 2-ethynyltoluene (2b) after several days at room temperature. The analogous reactions of 26D with the heteroaromatic 1-alkynes were considerably more rapid. For example, complete substrate conversion of 2-ethynylpyridine (2f) and 2-ethynylthiophene (2d) were completely consumed within 3 and 2 days, respectively. In all cases, ~1% of 26D was consumed.

The reaction of 26D with 2-ethynylpyridine (2f) was found to be even more rapid, as 79% substrate conversion was achieved after 70 min. Monitoring the decrease of substrate with in situ $^1$H NMR spectroscopy revealed that the rate of substrate conversion was zero-order dependent on substrate concentration during the first 53 min ($k_{obs} = 13.4(6)$ M$^{-1}$min$^{-1}$, R$^2 = 0.9909$), corresponding to 69% substrate conversion. In spite of a
dramatic rate decrease after 70 min, complete substrate conversion was apparent within 20 h, accompanied by 1% conversion of 26D and the formation of a multitude of Cp* 1H NMR resonances. This kinetic behavior is analogous to that described above for reactions of Cp* 2LnCH(SiMe3)2 (Ln = Y, La) and 2-ethynlypyridine (2f) and was rationalized in terms of product inhibition (Section 5.3.5).

Although metalation may arguably be rate-limiting in the catalytic conversion of 1-alkyne mediated by 26D, the large differences of the substrate conversion rates cannot be rationalized by considering the differences in (kinetic) acidity alone. In fact, the (kinetic) acidity of the acetylenic proton of 2-ethynlythiophene is higher than that of 2-ethynlypyridine, while that of 2-ethynylanisole is similar to that of phenylacetylene (Section 5.5.1). Because neither steric nor electronic effects of the 1-alkyne substituent account for the observed differences, it seems that the rate of substrate conversion is dominated by interactions between metal center and substrate instead. In the case of phenylacetylene, substrate reactivity most likely involves an initial (relatively weak) interaction between the metal center and the carbon-carbon triple bond and/or the phenyl moiety.21,22 2-Ethynlythiophene and -pyridine, on the other hand, possess a heteroatom, which is capable of interacting stronger with the metal center of the catalyst. It is interesting to note that metal heteroatom interactions seem to promote catalytic substrate conversion in the oligomerization reactions mediated by 26D, whereas catalytic rate depression was observed in the oligomerization reactions of (hetero)aromatic 1-alkynes mediated by Cp*2LaCH(SiMe3)2 (5D) where protonolysis of the catalyst precursor is not rate-limiting.

Substrate coordination

The high observed reactivity of 2-ethynlypyridine (7f) towards Cp*2LaN(SiMe3)2 (26D) relative to other (hetero)aromatic 1-alkynes is remarkable (vide supra) and was rationalized in terms of metal-heteroatom interactions. Evidence for the coordination of 2-ethynlypyridine to the metal center in 26D in benzene-d8 solution is provided by the upfield shifts of the proton NMR resonances of 2f in the presence of 26D relative to

![Figure 5-12. Integrated rate plot of the concentration of 26D versus time for the reaction of 26D with a 5-fold molar excess of 2a, 2d and 2e in THF-d8 at 80 °C, as monitored by in situ 1H NMR spectroscopy. Lines connecting the data points represent fitted linear plots (see text for details).](image-url)
The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metallocenes

Scheme 5-5. The proposed beneficial effect of heteroatom precoordination in the metatation reaction of 2-ethynylthiophene by Cp*₂LaN(SiMe₃)₂ (26D) as compared to the analogous reaction with 3-ethynylthiophene.

Metatation reactions

Because the reaction of Cp*₂LaN(SiMe₃)₂ (26D) with phenylacetylene in THF afforded Cp*₂LaCCPh(THF), quantitatively, after 5 h at 80 °C, it was decided to study the effect of some representative substrates on the metatation rate under comparable reaction conditions. Monitoring the conversion of 26D in the presence of a 5-fold molar excess of substrate in THF-d₈ at 80 °C by normalized, in situ ¹H NMR spectroscopy revealed that the rate of metatation was first-order in 26D for the reaction with phenylacetylene (2a, R² = 0.9969, kₘₚ = 0.405(4) M⁻¹·min⁻¹, t₁/₂ = 25.4(4) min), 2-ethynylthiophene (2d, R² = 0.9948, kₘₚ = 0.55(1) M⁻¹·min⁻¹, t₁/₂ = 19.5(4) min) and 3-ethynylthiophene (2e, R² = 0.9972, kₘₚ = 0.288(3) M⁻¹·min⁻¹, t₁/₂ = 35.3(4) min). Hence, the metatation rate was found to increase in the following order: 2-ethynylthiophene (1.0) < phenylacetylene (1.4) < 3-ethynylthiophene (1.8). The analogous reaction with 2-ethynylpyridine (2f) in THF took place rapidly at room temperature and was not clean. Complete conversion of a 5-fold molar excess of 2f (relative to 26D) was observed into the corresponding trans-head-to-head dimer after 1 h at room temperature, accompanied by 71% conversion of 26D. Smaller excesses of 2f led to lower degrees of conversion for 26D.

In contrast to reactions in noncoordinating solvent at room temperature (i.e. benzene, vide supra), the differences in metatation rates for different acetylenic substrates revealed that the effects of substrate-metal interaction and the (kinetic) acidity are relatively modest in THF at 80 °C. Even though 2-ethynylthiophene (2d) possesses an acetylenic proton of considerably higher (kinetic) acidity than that of phenylacetylene (Appendix), metatation of 2d by 26D takes place only ~1.3 times more rapid than that of phenylacetylene. The rate of metatation of 3-ethynylthiophene by 26D is ~1.4 times slower than that of phenylacetylene, but the (kinetic)
acidity of these 1-alkynes are comparable (Appendix). As a consequence, the relative order of metalation rate cannot be rationalized in terms of (kinetic) acidity alone.

It seems natural to explain the high reactivity of 2-ethynylpyridine ($2f$) and 2-ethynylthiophene ($2d$) relative to phenylacetylene to heteroatom metal interactions. The interaction of the metal center with the nitrogen or sulfur atom is stronger than that with the phenyl group or the carbon-carbon triple bond and is likely to compete more efficiently with THF for coordination to the metal center. The close proximity of the ethynyl group to the coordinating heteroatom of $2d$ and $2f$ may plausibly accelerate the rate of metalation as well (Scheme 5-5). Literature precedent for precomplexation of the metal center to the heteroatom exists for metalation reactions of heterocycles by rare-earth metallocene derivatives. In addition, the heteroatom-directed metalation of (hetero)aromatics by lithium and aluminum compounds is well-established and also believed to involve precomplexation of the metal center to the heteroatom. The unfavorable position of the ethynyl group relative to the coordinating sulfur atom in 3-ethynylthiophene may account for the lower reactivity of 3-ethynylthiophene ($2e$) relative to phenylacetylene, as sulfur coordination may arguably compete with metalation (proceeding with or without initial coordination to the ethynyl group). Further discussion of this aspect termed heteroatom-assisted reactivity is deferred to a later section (Section 5.5.3).

The reactivity of Lewis base adducts of monomeric alkynyl derivatives

Introduction

Analogous to Cp*$_2$LaCCPh(THF) ($20a$·THF), the THF adducts Cp*$_2$LaCCR(THF) ($20$·THF) of most of the studied 1-alkynes (except for $R = NC_5H_4-2$, vide infra) were accessible through the reactions of Cp*$_2$LaCH(SiMe$_3$)$_2$ ($5D$) or Cp*$_2$LaN(SiMe$_3$)$_2$ ($26D$) with the corresponding 1-alkynes HCCR ($2$) in the presence of excess THF. The interaction between thiophene and lanthanum was found to be too weak to stabilize the metal center electronically in the Cp*$_2$LaCCPh derivative (Section 5.4.3). As a consequence, no thiophene base adducts $20a$·SC$_4$H$_4$ could be prepared. The high preference for pyridine coordination relative to THF coordination allowed for the preparation of pyridine adducts Cp*$_2$LaCCR(NC$_5$H$_5$) ($20$·NC$_5$H$_5$) from reactions of $20$·THF and pyridine, but these compounds were also accessible through reactions of $5D$ or $26D$ with the corresponding 1-alkynes RCCH in the presence of a small molar excess of pyridine.

The kinetic lability of the present lanthanocene derivatives, typical of rare-earth metal complexes, in combination with the high preference for pyridine coordination and the high reactivity of 2-ethynylpyridine ($2f$), thwarted all attempts to prepare base adducts of Cp*$_2$LaCC(2-NC$_5$H$_5$) ($20f$) from Cp*$_2$LaN(SiMe$_3$)$_2$ ($26D$) or Cp*$_2$LaCCPh·NC$_5$H$_5$ ($20a$·NC$_5$H$_5$). For example, reactions of $26D$ with equimolar amounts of $2f$ in THF afforded product mixtures, containing considerable amounts of the trans-head-to-head dimer of $2f$ and unreacted $26D$ (10-30% conversion). Also the presence of pyridine (10-50 equiv.) in these reactions did not inhibit catalytic substrate conversion.

The synthesis of THF adducts

In this study, the THF adducts Cp*$_2$LaCCPh·THF ($20a$·THF), Cp*$_2$LaCC(2-C$_4$H$_3$S)·THF ($20d$·THF) and Cp*$_2$LaCC(3-C$_4$H$_3$S)·THF ($20e$·THF) were prepared from Cp*$_2$LaN(SiMe$_3$)$_2$ and the appropriate 1-alkyne (1 equiv.) in THF after heating for 1 day to 80 °C under reflux (Scheme 5-6). The adducts were characterized by multinuclear 1D and 2D NMR spectroscopy, but the relatively large nuclear spin and quadrupole moment of $^{139}$La (I = 7/2, 99.91%) did not allow for the observation of the acetylenic carbon NMR resonances. In all cases,
The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metallocenes

off-white solids were obtained in virtually quantitative yield after in vacuo removal of volatiles. They were soluble in aromatic solvents and THF, but highly insoluble in aliphatic solvents. Attempts to obtain single-crystals suitable for X-ray analysis have not been successful. Upon standing at room temperature in the solid state, these compounds rearranged within several days into the corresponding butatrienediyl derivatives.

The reactivity of THF adducts

When the above adducts 20a·THF, 20d·THF and 20e·THF were allowed to react with an excess of the corresponding 1-alkyne (50 equiv.) at ambient temperatures, no significant reactivity was observed after several hours. However, small amounts of oligomerization products formed upon increasing the reaction temperature, as observed with 1H NMR spectroscopy. The rate of catalytic substrate conversion was found to decrease in the order: 20d·THF > 20a·THF > 20e·THF and seems related to the effects of heteroatom metal interactions, as discussed for the metalation reactions of the corresponding 1-alkynes by Cp*2LaN(SiMe3)2 (26D) (Section 5.4.4).

Even though catalytic 1-alkyne conversion was relatively slow for Cp*2LaCCPh·THF (20a·THF) in non-coordinating solvents, transmetalation was found to take place rapidly at ambient temperatures. The addition of HCCR (2) to a benzene-d6 solution of 20a·THF yielded equilibrium mixtures of 20·THF, phenylacetylene (2a), Cp*2LaCCR·THF (20a·THF) and 2. No change in composition was observed ~10 min after addition of 2, as seen with 1H NMR spectroscopy. Gratifyingly, 1H NMR spectroscopy could be used to determine the relative amount of species present in the equilibrium after reaction of 20a·THF with a stoichiometric amount of 2-ethynylthiophene (2d) and 3-ethynylthiophene (2e). The integral data provided a value for the equilibrium K which is likely to represent the difference in (equilibrium) acid strength of the particular 1-alkyne versus phenylacetylene towards the active catalyst of the present 1-alkyne oligomerization reaction (eqs. 5.9-5.10). Because the relationship between equilibrium acidity and kinetic acidity is commonly not linear in nonpolar solvents, the relative equilibrium acidities can not be used to estimate the kinetic acidities of the 1-alkynes in the present study (Appendix).

\[
\text{Cp}^*2\text{La} + \text{S} + \text{Cp}^*2\text{La} \quad \xrightleftharpoons[K=0.08(5)]{} \quad \text{Cp}^*2\text{La} + \text{S} \\
\text{Cp}^*2\text{La} + \text{S} + \text{Cp}^*2\text{La} \quad \xrightleftharpoons[K=0.80(4)]{} \quad \text{Cp}^*2\text{La} + \text{S}
\]

5.4.6. The molecular structures of butatrienediyl derivatives

In analogy to [(Cp*2La)(µ-PhC₆H₄)] (22a) (Chapter 4), representative (hetero)aromatic analogues [(Cp*2La)(µ-ArC₆H₄)] (C₆H₄Me-2 (22b) and 2-C₆H₃S (22d)) were prepared conveniently in high isolated yields (80-90%) from reactions of [Cp*2La(µ-H)]₂ and stoichiometric amounts of the appropriate 1-alkyne in hexane at room temperature. Crystallization at low temperature afforded dark red crystalline solids for the reaction with phenylacetylene (2a), 2-ethynyltoluene (2b) and 2-ethynylthiophene (2d). The red color seems to be typical of these compounds and independent of both metal and alkyne substituent.

To investigate the substrate effects on the molecular structure of the butatrienediyl derivatives 22 both in solution and in the solid state, these complexes were characterized by NMR spectroscopy and single-crystal X-ray crystallography. The 1H and 13C NMR spectral parameters of the lanthanocene butatrienediyldiyl
derivatives \([\text{Cp}^*\text{La}_2(\mu-\text{RC}_4\text{R})]\) \(\text{R} = \text{Ph}\) (22a), \(\text{C}_8\text{H}_8\text{Me}-2\) (22b) and 2-\(\text{C}_8\text{H}_6\text{S}\) (22d) are shown in Table 5-6. The complexes 22a, 22b and 22d exhibit equivalent Cp* resonances in the \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectrum and the \(^{13}\text{C}\) NMR resonances of the butatrienediyl ligand are in the same range as previously observed for \([\text{Cp}^*\text{La}_2(\mu-\text{RC}_4\text{R})]\) \(\text{R} = \text{Me}, \text{Bu}\). No evidence for fluxional behavior was obtained with \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy for the compounds 22a and 22d in the temperature range from -80 °C to 100 °C, in both aliphatic (i.e. methycyclohexane-\(d_1\)) and aromatic (i.e. benzene-\(d_6\), toluene-\(d_8\)) solvents.

The complex 22b exhibited no fluxional behavior in toluene-\(d_8\) in the temperature range form -80 °C to 100 °C, but displayed broad \(^1\text{H}\) NMR resonances at room temperature at \(\delta 6.70\) and \(2.21\) ppm in methycyclohexane-\(d_8\) solution, assigned to the \(\alpha-\text{CH}\) and the \(\text{CH}_2\) protons of the \(\text{ortho}-\text{tolyl}\) substituent, respectively. When the temperature was increased to 85 °C, the \(^1\text{H}\) NMR resonances coalesced, forming a doublet and singlet at \(\delta 6.70\) and \(2.23\) ppm, respectively. This behavior can reasonably be ascribed to hindered rotation of the \(\text{ortho}-\text{tolyl}\) group.

Single crystals of \([\text{Cp}^*\text{La}_2(\mu-\text{Ph}_2\text{C}_4\text{H}_4\text{C}_6\text{H}_4\text{Me}-2)_2]\) (22a), \([\text{Cp}^*\text{La}_2(\mu-\text{Ph}_2\text{C}_4\text{H}_4\text{Me}-2)_2]\) (22b) and \([\text{Cp}^*\text{La}_2(\mu-\text{Me}_2\text{C}_4\text{H}_4\text{Me}-2)_2]\) (22d) were obtained by cooling saturated toluene solutions of the corresponding compounds to \(-40\) °C. In all cases, toluene solvates were obtained. Although the molecular structure of 22a-2C\(_8\)H\(_8\) was already published, the X-ray structure determination in this study allowed for a more accurate determination of bond distances and angles corresponding to the butatrienediyl moiety. In addition, a different space group was found as well. It is believed that these arguments justify the use of the present data for comparison with other butatrienediyl derivatives.

Complexes 22a-2C\(_8\)H\(_8\), 22b-2C\(_8\)H\(_8\) and 22d-2C\(_8\)H\(_8\) crystallize in the monoclinic space groups \(P2_1/m\) \((Z = 2), C2/m\) \((Z = 2)\) and \(C2\) \((Z = 4)\), respectively. The molecular structures are shown in Figures 5-13, 5-14 and 5-15 and relevant bond lengths and angles are given in Table 5-7. The solid state molecular structures of complexes 22a, 22b and 22d are analogous to those of other butatrienediyl permethylanthanidocenes \((\text{Cp}^*\text{Sm})_2(\mu-\text{η}^2-\text{η}^2-\text{RC}_4\text{R})_2\) \(\text{R} = \text{Ph}^{22}\) \(22\text{Ea}\), \(\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2\text{Ph}^{22}\) \(22\text{Ej}\)), \((\text{Cp}^*\text{Ce})_2(\mu-\text{η}^2-\text{η}^2-\text{RC}_4\text{R})_2\) \(\text{R} = \text{Me}\) \(22\text{Ci}\), \(\text{Bu}\) \(22\text{Ch}\), and \((\text{Cp}^*\text{La})_2(\mu-\text{η}^2-\text{η}^2-\text{BuC}_6\text{H}_4\text{Bu})_2\) \(22\text{d}\)). Most La-C bond distances are larger and reflect the differences in \(\text{La}^\text{III}\) versus \(\text{Sm}^\text{III}\) \((\Delta \delta = 0.081 \text{ Å})\) and \(\text{Ce}^\text{III}\) versus \(\text{La}^\text{III}\) \((\Delta \delta = 0.017 \text{ Å})\) for eight-coordination ionic radii. The La-C bonds corresponding to the butatrienediyl fragment are not longer, however, probably as a result of the more open La\(^{III}\) coordination sphere which allows closer approach. Even though complexes 22a and 22d\(^{2d}\) exhibit rotational disorder in the conformation of the Cp* rings, the Cp* rings were found to be eclipsed for almost all conformations. The Cp* ligands in 22b are in a perfectly eclipsed conformation with a twist angle of 0.0(5) °. It

### Table 5-6. NMR spectral parameters of the \([\text{Cp}^*\text{La}_2(\mu-\text{RC}_4\text{R})]\) \(\text{R} = \text{Ph}\) (22a), \(\text{C}_8\text{H}_8\text{Me}-2\) (22b) and 2-\(\text{C}_8\text{H}_6\text{S}\) (22d) complexes.*

<table>
<thead>
<tr>
<th>Complex</th>
<th>1H NMR</th>
<th>13C NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph (22a)</td>
<td>C(_6)Me(_3)</td>
<td>2.06 C(_6)Me(_3)</td>
</tr>
<tr>
<td></td>
<td>6.79 o-CH</td>
<td>6.82 o-CH</td>
</tr>
<tr>
<td></td>
<td>7.02 p-CH</td>
<td>7.07 p-CH</td>
</tr>
<tr>
<td></td>
<td>7.25 m-CH</td>
<td>7.21 m-CH</td>
</tr>
<tr>
<td></td>
<td>11.51 C(_6)Me(_3)</td>
<td>11.23 C(_6)Me(_3)</td>
</tr>
<tr>
<td></td>
<td>120.84 C(_6)Me(_3)</td>
<td>120.28 C(_6)Me(_3)</td>
</tr>
<tr>
<td></td>
<td>126.30 CH</td>
<td>123.63 CH</td>
</tr>
<tr>
<td></td>
<td>126.90 CH</td>
<td>129.00 γ-CH</td>
</tr>
<tr>
<td></td>
<td>134.13 i-C</td>
<td>137.67 i-C</td>
</tr>
<tr>
<td></td>
<td>150.07 LaCC</td>
<td>153.78 LaCC</td>
</tr>
<tr>
<td></td>
<td>217.31 LaCC</td>
<td>214.24 LaCC</td>
</tr>
</tbody>
</table>

* Chemical shifts in ppm and spectra measured in C\(_6\)D\(_6\) at 25 °C. Assignments based on \(^1\text{H}^\text{-}\text{H}\) and \(^{13}\text{C}^\text{-}\text{C}\) coupling and 2D NMR experiments (for details, see Experimental Section).
The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metalloccenes

Figure 5-13. An ORTEP representation of 22a·2C7H8 with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms and solvate toluene molecules are omitted for clarity. The conformation shown is one of the four conformations found.40

Figure 5-14. ORTEP plot of 22b·2C7H8 with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms and solvate toluene molecules are omitted for clarity.
Figure 5-15. ORTEP plot of 22\textsubscript{d}·2C\textsubscript{7}H\textsubscript{8} with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms and solvate toluene molecules are omitted for clarity.

Figure 5-16. ORTEP plot of 28D·C\textsubscript{7}H\textsubscript{8} with thermal ellipsoids drawn at the 50% probability level. The hydrogen atoms and solvate toluene molecules are omitted for clarity.
The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metallocenes has been suggested that the presence of eclipsed Cp* ligands is the result of steric crowding, but examples of X-ray structures with eclipsed rings in which steric crowding is not evident have been reported as well.

The overall geometry of \((\text{Cp}^* \text{La})_2 \left[ \mu- \eta^3: \eta^2-(2-\text{C}_4\text{H}_3\text{S})_2\text{C}_4 \right] \) \((22d)\) is similar to that of \((22a)\), but differences are found in the butatrienediyl ligand. The \(\eta^3\)-bonding of the lanthanum atom in \((22a)\) (i.e., La1-C30/La2-C29 = 2.578(2) Å, La1-C29/La2-C28 = 2.810(2) Å and La1-C28/La2-C29 = 2.920(2) Å) is shifted to \(\eta^2\) in \((22d)\) (i.e., La-C25 = 2.78(6); 2.80(7) Å). The butatrienediyl fragment is also more linear and symmetrical in \((22d)\) than in \((22a)\) and the carbon-carbon bond distances therein are shorter in \((22d)\) than in \((22a)\). It may be argued that the linearity in the butatrienediyl moiety and the shift from \(\eta^3\) to \(\eta^2\) coordination is brought about by coordination of the sulfur atom in the thienyl group towards the metal center, but the La-S bond length of 3.6267(11) Å seems too large for a significant interaction. La-S bond distances in lanthanocenes are lacking in literature, but reported La-S bond distances in non-metallocene lanthanum complexes range from 2.89 to 3.24 Å. To discriminate between an interaction between metal center and sulfur atom in \((\text{Cp}^* \text{La})_2 \left[ \mu- \eta^2: \eta^1-(\text{C}_6\text{H}_4\text{Me}-2)\right] \) \((22d)\) and a substituent effect, involving the electronic and/or steric properties of the 2-thienyl substituent, an X-ray structure determination of \([\text{Cp}^* \text{La}(\mu-2-\text{C}_4\text{H}_3\text{S})] \) \((28d)\) was undertaken. The dimeric, 2-thienyl derivative \((28d)\) was prepared from the reaction of \([\text{Cp}^* \text{La}(\mu-\text{H})]_2\) and thiophene (2 equiv.), as described previously, and suitable single crystals were obtained by allowing a warm toluene solution of \((28d)\) to cool slowly to room temperature. The complex \((28d)\) crystallized as a toluene solvate \((28d) \cdot \text{C}_7\text{H}_8\) in the monoclinic space group \(C2/c\) with \(Z = 4\). The molecular structure of \((28d) \cdot \text{C}_7\text{H}_8\) is shown in Figure 5-16. The observed La-S distance of 3.1134(7) Å confirms the above hypothesis that the La-S distance of 3.6267(11) Å in \((22d)\) is too large for a significant interaction.

The molecular solid state structure of \((\text{Cp}^* \text{La})_2 \left[ \mu- \eta^3: \eta^2-(\text{C}_6\text{H}_4\text{Me}-2)\right] \) \((22b)\) is similar to those of \((22a)\) and \((22b)\). Although the Ct-La-Ct angle of 120.43(8)° is considerably smaller than the values previously observed for \((\text{Cp}^* \text{La})(\mu-X)(\mu-Y)\) complexes \((129.6-140.8°)\), the other metrical parameters of the \(\text{Cp}^*\)-La fragment of \((22b)\) are normal. Similar to \((22d)\), a change from trihapto bonding of the metal center in \((22a)\) (i.e., La1-C30/La2-

### Table 5-7. Selected bond lengths (Å) and angles (°) of the \((\text{Cp}^* \text{La})_2 \left[ \mu- \eta^2: \eta^2-(\text{C}_6\text{H}_4\text{Me}-2)\right] \) complexes.

<table>
<thead>
<tr>
<th></th>
<th>Ph ((22a))</th>
<th>(\text{C}_6\text{H}_4\text{Me}-2) ((22b))</th>
<th>2-(\text{C}_4\text{H}_3\text{S}) ((22d))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bond lengths</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La1-C27</td>
<td>2.566(1)</td>
<td>La-C18</td>
<td>2.548(4)</td>
</tr>
<tr>
<td>La2-C30</td>
<td>2.707(1)</td>
<td></td>
<td>2.598(3)</td>
</tr>
<tr>
<td>La1-C28</td>
<td>2.801(1)</td>
<td>La1-C19</td>
<td>2.820(4)</td>
</tr>
<tr>
<td>La2-C29</td>
<td>2.819(1)</td>
<td>La-C26</td>
<td>2.790(3)</td>
</tr>
<tr>
<td>La1-C29</td>
<td>2.912(1)</td>
<td>La1-C19a</td>
<td>2.996(4)</td>
</tr>
<tr>
<td>La2-C28</td>
<td>2.928(1)</td>
<td>La-C26a</td>
<td>2.993(3)</td>
</tr>
<tr>
<td>La1-Cp</td>
<td>2.84(1)</td>
<td>La-Cp</td>
<td>2.834(9)</td>
</tr>
<tr>
<td>La2-Cp</td>
<td>2.84(3)</td>
<td></td>
<td>2.78(6); 2.80(7)</td>
</tr>
<tr>
<td>La1-Ct</td>
<td>2.06(2)</td>
<td>La-Ct</td>
<td>2.075(2)</td>
</tr>
<tr>
<td>La2-Ct</td>
<td>2.06(3)</td>
<td></td>
<td>2.00(1); 2.04(1)</td>
</tr>
<tr>
<td>La2-C17</td>
<td>1.338(2)</td>
<td>C18-C19</td>
<td>1.312(7)</td>
</tr>
<tr>
<td>La2-C18</td>
<td>1.327(2)</td>
<td>C25-C26</td>
<td>1.319(4)</td>
</tr>
<tr>
<td>C28-C29</td>
<td>1.332(1)</td>
<td>C19-C19a</td>
<td>1.349(7)</td>
</tr>
<tr>
<td>C29-C30</td>
<td>1.464(2)</td>
<td>C18-C17</td>
<td>1.471(7)</td>
</tr>
<tr>
<td>C29-C31</td>
<td>1.464(1)</td>
<td></td>
<td>1.464(4)</td>
</tr>
<tr>
<td><strong>Bond angles</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ct-La1-Ct</td>
<td>146.2(1)</td>
<td>Ct-La-Ct</td>
<td>120.4(1)</td>
</tr>
<tr>
<td>Ct-La2-Ct</td>
<td>137.3(3)</td>
<td></td>
<td>127.1(2); 128.8(3)</td>
</tr>
<tr>
<td>C28-C29-C30</td>
<td>147.2(1)</td>
<td>C18-C19-C19a</td>
<td>148.5(4)</td>
</tr>
<tr>
<td>C29-C30-C31</td>
<td>148.3(1)</td>
<td></td>
<td>153.5(3)</td>
</tr>
<tr>
<td>C21-C27</td>
<td>122.7(1)</td>
<td>C19-C18-C17</td>
<td>132.8(4)</td>
</tr>
<tr>
<td>C21-C28</td>
<td>127.0(1)</td>
<td></td>
<td>122.8(3)</td>
</tr>
</tbody>
</table>

* The average distance between the centroid of the cyclopentadienyl ligand and the metal is denoted by Ct, while the average distance of the metal to the cyclopentadienyl carbons is denoted by La-Cp (see text for details).
Scheme 5-7. Selected bond angles (°) and distances (Å) of the lanthanum butatrienediyl derivatives 22 as a function of the alkyne substituent R.

<table>
<thead>
<tr>
<th>R</th>
<th>(22a)</th>
<th>(22b)</th>
<th>(22d)</th>
<th>(22h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La-C1</td>
<td>2.587(2)</td>
<td>2.548(4)</td>
<td>2.598(3)</td>
<td>2.642(3)</td>
</tr>
<tr>
<td>La-C2</td>
<td>2.810(2)</td>
<td>2.820(4)</td>
<td>2.790(3)</td>
<td>2.761(3)</td>
</tr>
<tr>
<td>La-C3</td>
<td>2.920(2)</td>
<td>2.9968(2)</td>
<td>2.993(3)</td>
<td>2.912(3)</td>
</tr>
<tr>
<td>a</td>
<td>148.3(1)</td>
<td>148.5(4)</td>
<td>153.5(3)</td>
<td>153.7(3)</td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.333(2)</td>
<td>1.312(7)</td>
<td>1.319(4)</td>
<td>1.310(4)</td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.332(1)</td>
<td>1.349(7)</td>
<td>1.313(4)</td>
<td>1.338(4)</td>
</tr>
</tbody>
</table>

For sake of simplicity average values are given (see Table 5-7). *Values taken from Ref. 16d.

C29 = 2.578(2) Å, La1-C29/La2-C28 = 2.810(2) Å and La1-C28/La2-C29 = 2.920(2) Å to dihapto bonding in 22d (i.e. La-C18 = 2.548(4) Å, La-C19 = 2.820(4) Å and La-C26a = 2.9968(2) Å) is observed relative to the parent compound 22a, accompanied by a transition towards a more linear and symmetrical butatrienediyl ligand (i.e. C19-C18-C17 = 132.8(4) º in 22b relative to C29-C30-C31/C21-C27-C28 = 124.8(1)º in 22a). However, contrary to 22d, the carbon-carbon bond distances in the butatrienediyl ligand are not shorter in 22d as compared to 22a. More specifically, the carbon-carbon bond distance of the former acetylenic carbon-carbon triple bond is considerably longer in 22b (i.e. C17-C18 = 1.471(7) Å) than in 22a (i.e. C27-C28/C29-C30 = 1.333(2) Å), while the distances of the central carbon-carbon bond in the butatrienediyl ligand are comparable in both complexes.

In view of the observed hindered rotation of the ortho-tolyl substituent in solution and the anticipated mild electronic effects upon ortho-methyl substitution (Appendix), it seems natural to ascribe the differences between the molecular structures of 22a and 22b mainly to the increased steric interactions, due to the presence of the ortho-methyl group. In fact, the distance of the carbon atom of the ortho-methyl group to the metal (i.e. La-C11a = 3.189(7) Å) and the closest methyl carbon atoms of the Cp* ligand (i.e. C11-C7 = 3.573(8) Å, C11-C6 = 3.938(7) Å) and the butatrienediyl ligand (i.e. C11-C19 = 3.024(8) Å) fall in the range of 3.0-3.9 Å and seem too large for significant interactions. Even so, the notion of relatively large steric interactions within the complex is supported by the eclipsed conformation of the Cp* ligands and the exceptionally large C1-La-C1 angle.

The metric parameters of 22d as compared to 22a suggest that butatrienediyl derivatives with a small, σ-electron-withdrawing alkyne substituent exhibit characteristics associated with a more advanced stage of C-C coupling towards a 1,4-dimetalated butatriene structure, i.e. relatively short C2-C3 and La1-C1 bond distances and a relatively large La1-C3 bond distance and α angle (Scheme 5-7). A similar analysis of the molecular structures corresponding to the other structurally analyzed butatrienediyl derivatives, i.e. [(Cp*La)2µ-RC4R] (R = Ph 22a, 2-MeC6H4 22b, and 'Bu 22h), is less clear-cut, however.

5.5. Discussion of substrate effects

5.5.1. Introduction

Before discussing the substrate effects on the rate and selectivity of the present oligomerization reaction, the properties of the studied 1-alkynes have to be considered first. The oligomerization reactions involve both insertion and protonolysis reactions of 1-alkynes and the intrinsic rate of these reaction sequences is governed by the electronic and steric properties of the 1-alkyne. Several studies have demonstrated that the kinetic acidity of 1-alkynes is (mainly) determined by the inductive/field effects of the substituent and the
The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metallocenes

following order of kinetic acidity has presently been inferred from NMR spectroscopy for the 1-alkynes used in this study: 2-ethynylthiophene (2d) > 2-ethylypyridine (2f) ≈ 1-methyl-2-ethynylpyrrole (2g) > 3-ethynylthiophene (2b) ≈ phenylacetylene (2a) ≈ 2-ethynyltoluene (Appendix).

In Section 5.5.2, it is argued that a combination of both steric and electronic substituent effects determine the kinetics of the reaction of dimeric, bridged alkynyl derivatives [Cp’₂Ln(μ-CCR)]₂ into butatrienediyl derivatives [(Cp’₂Ln)₂(μ-RC₄R)]. The present study did not provide evidence that the butatrienediyl derivatives play a role in the catalytic oligomerization reactions, however. The catalytic rate and selectivity in the oligomerization reactions were found to be governed by an interplay of steric and electronic 1-alkyne substituent effects, substrate and product inhibition and catalyst deactivation. The relative importance of these effects depends on the specific properties of the substrate and is discussed in Section 5.5.3.

5.5.2. Substrate effects in the reactivity of the dimeric alkynyl derivatives

Introduction

The experimental data reported so far indicate that the rearrangement of dimeric alkynyl lanthanidocene derivatives [Cp’₂Ln(μ-C≡CR)]₂ (21) into the corresponding butatrienediyl derivatives [(Cp’₂Ln)₂(μ-RC₄R)] (22) is determined predominantly by the steric properties of the Cp’ ligand, the metal Ln and the alkynyl substituent R.48 No rearrangements into butatrienediyls have been reported for rare-earth metalocene alkynes having sterically less demanding cyclopentadienyl groups, such as the unsubstituted or monoalkyl-substituted cyclopentadienyl ligands.48 In marked contrast, rearrangements of dimeric alkyynes into butatrienediyls are commonly observed for pentamethylcyclopentadienyl complexes. These observations have led to the common belief that the bridged alkynyl dimers of pentamethylcyclopentadienyl complexes are sterically too crowded to be stable and that C-C coupling of the alkynyl ligand takes place in order to relieve steric congestion. The decreased steric interaction between the Cp’ ligands of the two Cp’₂Ln moieties in the butatrienediyl complexes relative to the dimeric alkynyl complexes is shown in Scheme 5-8. When steric crowding is minimal, stable bridged dimeric alkynyl structures form and rearrangement into butatrienediyl derivatives does not take place.

Scheme 5-8. Steric interactions between Cp’₂Ln moieties in the dimeric alkynyl [Cp’₂Ln(μ-CCR)] (21) and butatrienediyl complexes [(Cp’₂Ln)₂(μ-η³-RC₄R)] (22).

Alkyne substituent effects on the rate of C-C coupling

The present study provides evidence that the alkyne substituent plays also an important role in determining the rate of C-C coupling in rare-earth metalocene alkynyl derivatives. The following observations have been made within a series of lanthanum derivatives [Cp*₂La(μ-C≡CR)]₂ (21a) as a function of the alkyne substituent: (i) the methyl analogue [Cp*₂La(μ-C≡CMe)]₂ (22i) rearranged at room temperature (t₁/₂ = 3.2 h, 25 °C) to produce an equilibrium mixture of 21a and [(Cp*₂La)(μ-MeC₄Me)] (22i); (ii) the tert-butyl analogue [Cp*₂La(μ-C≡C(tBu)]₂ (22h) rearranged much slower (t₁/₂ = 2.2 h, 50 °C), but irreversibly, into 22h and has been isolated at 0 °C; (iii) the phenyl analogue [Cp*₂La(μ-C≡CPh)] (21a) could only be observed at low temperatures and rearranged both quantitatively and irreversibly into 22a within 13 h at -50 °C (t₁/₂ = 2.2 h, -50 °C) (Chapter 4), (iv) the 3-thienyl analogue [Cp*₂La(μ-C≡C(C₄H₃S-3))]₂ (21e) rearranged completely and irreversibly into 22e within 3.8 h at -50 °C (t₁/₂ = 0.7 h, -50 °C) (Section 5.4.4), and (v) the 2-thienyl analogue [Cp*₂La(μ-C≡C(C₄H₃S-2))]₂ (21d) rearranged completely and irreversibly into 22d within 52 min at -50 °C (t₁/₂ = 8.6 min, -50 °C) (Section 5.4.4). Because the electronic properties of the 3-thienyl and phenyl substituent are similar (Appendix), the rate of rearrangement in 21 seems to be determined by both the steric and electronic properties of the alkyne substituent.
Scheme 5-9. The proposed transition state of the C-C coupling reaction of a dimeric alkynyl lanthanidocene (21) into a butatrienediyld lanthanidocene (22).

The electronic effects of the methyl and tert-butyl substituent do not differ significantly, as they both are electron-donating via a resonance and an inductive/field mechanism (Appendix).\(^{50}\) The difference in behavior between \(\text{Cp}^*\text{La}([\mu-C-\text{C}_{\text{Me}}])\); \((22\text{h})\) and \(\text{Cp}^*\text{La}([\mu-\text{C}_{\text{S}}-\text{S}_{-2}])\); \((22\text{i})\) can thus plausibly be ascribed to the larger steric requirements of the tert-butyl group relative to the methyl group. The larger size of the methyl group versus the tert-butyl group seems evident and this reasonable assumption is indeed supported by several quantitative scales of steric substituent effects. In spite of extensive research efforts on the steric effects of substituents, a reliable and general method to quantify steric effects is lacking.\(^{52}\) Among the scales proposed, the steric substituent constants \(E_a\) and \(\alpha\) are the most widely used and listings of constants are readily available. Taft defined \(E_a\) as \(E_a = \log(k/k_0)\) on the basis of acid-catalyzed hydrolysis of aliphatic esters with \(k_0\) for a methyl substituent,\(^{53}\) while Charton calculated the steric parameter \(\nu\) from bond lengths and volumes, as defined by Van der Waals radii.\(^{54}\)

It seems therefore that sterically hindered groups, such as the tert-butyl group (\(\nu = 1.24\)), retard the rate of rearrangement in dimeric alkynyls \((21)\) as compared to sterically less hindered groups, such as the methyl group (\(\nu = 0.52\)). The steric requirements of the planar phenyl group are difficult to compare with those of the non-planar tert-butyl group in the present molecular environment.\(^{55}\) Attempts to rationalize the observed higher reactivity of \(\text{Cp}^*\text{La}([\mu-C_{-\text{C}_{\text{Me}}})]; \) \((21\alpha)\) relative to \(\text{Cp}^*\text{La}([\mu-C_{-\text{S}}-\text{S}_{-2})]; \) \((21\beta)\) in terms of electronic substituents depend on the relative importance of inductive/field and resonance effects on the rate of C-C coupling in the dimeric alkynyl derivatives. When only field and inductive effects are considered, the phenyl group has a relative strong \(\sigma\)-electron-withdrawing effect (\(F = 0.12\)), \(\alpha\) = 0.12, whereas the tert-butyl group is mildly \(\sigma\)-electron-donating (\(F = -0.02\)), \(\sigma = -0.01\)). The phenyl group (\(R = -0.13\)) is, on the other hand, less electron-donating via resonance effects than the tert-butyl group (\(R = -0.18\)).

Insight into the relative importance of inductive/field and resonance effects on the rate of C-C coupling in the dimeric alkynyl derivatives \(\text{[Cp}^*\text{La}([\mu-C_{-\text{S}}-\text{S}_{-2})]; \) \((21)\) can be obtained by taking the 2- and 3-thienyl derivatives into account. The 2-thienyl and 3-thienyl substituent have comparable steric sizes and resonance effects, but they differ in their inductive/field effects (Appendix). The high reactivity of \(\text{[Cp}^*\text{La}([\mu-C_{-\text{C}_{\text{Me}}})]; \) \((21\alpha)\) as compared to \(\text{[Cp}^*\text{La}([\mu-C_{-\text{C}_{\text{S}}-\text{S}_{-2})]; \) \((21\beta)\) can thus plausibly be ascribed to the stronger inductive/field effect of the 2-thienyl substituent, thereby revealing that inductive/field effects dominate the electronic substituent effects on the rate of C-C coupling in the dimeric alkynyl derivatives \(\text{[Cp}^*\text{La}([\mu-C_{-\text{C}_{\text{S}}-\text{S}_{-2})]; \) \((21)\). The higher reactivity of \((21\beta)\) relative to \((21\alpha)\) can be attributed to both a smaller and more \(\sigma\)-electron withdrawing alkyl substituent.\(^{56}\)

The view that small, \(\sigma\)-electron-withdrawing alkyl substituents accelerate the rate of C-C coupling in \(\text{[Cp}^*\text{La}([\mu-C_{-\text{S}}-\text{S}_{-2})]; \) \((21)\) also supported by reported data on decaethylsamarocene derivatives. The following order of decreasing stability of \(\text{[Cp}^*\text{Sm}([\mu-C_{-\text{C}_{\text{S}}-\text{S}_{-2})]; \) was obtained as a function of the alkyl substituent:\(^{50}\) \text{Bu} > \text{Pr} > \text{CH}_{3}\text{CH}_{3}\text{Ph} > \text{CH}_{3}\text{CH}_{2}\text{Pr} > \text{Ph}.\(^{57}\) In addition, the metric parameters of \((22d)\) as compared to \((22a)\) exhibit characteristics associated with a more advanced stage of C-C coupling towards a 1,4-dimetalated butatriene structure, i.e. relatively short C2-C3 and La1-C1 bond distances and a relatively large La1-C3 bond distance and \(\alpha\) angle (Scheme 5-7). Although mechanistically different,\(^{58}\) evidence has been presented that electron-withdrawing alkyl substituents also accelerate the oxidative C-C coupling of alkynyl ligands in group 4 metal alkynyl derivatives.\(^{59}\)

A simple model can be devised which rationalizes the structures of the bridged alkynyls \((21)\) and butatrienediyld \((22)\) in terms of an interaction between the lanthanide metal and the carbon atoms of the alkynyl ligand (Scheme 5-9). The monomeric alkynyl species is unstable and gains electron density by forming a two-electron, three-atom bond with the \(\alpha\)-carbon of an alkynyl ligand of another monomeric alkynyl derivative. The
The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metallocenes

**Scheme 5-10.** The general mechanistic scenario proposed for the rare-earth metalloocene-catalyzed oligomerization of 1-alkynes.

Asymmetrically bridging, σ-bonded acetylide dimers thus formed seem to represent a compromise between a symmetric bridge (no π interaction) and a σ,π-bonded structure. In the case of permethyllanthanidocenes, the electrophilic lanthanide metal center finds additional stabilization by interacting with the electron-density of the C≡C bond and/or the β-carbon of the alkynide ligand. If this Ln-Cβ interaction is strong enough and not impeded by steric constraints, C-C coupling occurs and 22 forms. Although the electronic effects of the insertion reaction in lanthanide complexes have not been addressed directly, there exists ample indirect evidence that electron-withdrawing substituents at the β-position of the concerted, four-center transition state accelerate the insertion process. These considerations support the above notion that σ-electron withdrawing substituent at Cβ promote C-C coupling of the alkynyl ligands in dinuclear, bridged alkynyl complexes to form butatrienediyl complexes. The available experimental data does not warrant detailed speculation concerning the transition state (concerted or stepwise) or the effect of the resonance electronic effects induced by the alkyne substituent.

### 5.5.3. Substrate effects in the catalytic 1-alkyne oligomerization reactions

**Introduction**

A general mechanistic scenario for the rare-earth metalloocene-catalyzed oligomerization of 1-alkynes has been proposed and is shown in Scheme 5-10 (Chapter 4). It is believed that the substrate effects in the present oligomerization reactions of (hetero)aromatic 1-alkynes can be explained in terms of steric substituent effects, electronic substituent effects, substrate and product inhibition and heteroatom-assisted C-C bond formation. The relative importance of these effects varies with the properties of the 1-alkyne, thereby altering the relative rates of the catalytic reaction sequences in a specific manner.

**Steric substituent effects**

The importance of steric effects in both the regioselectivity of dimerization and the degree of oligomerization (i.e. dimerization versus trimerization) of the rare-earth metalloocene-catalyzed oligomerization has previously been discussed for reactions of different precatalyst with phenylacetylene (Chapter 4). The dependence of the regioselectivity of dimerization on the metal coordination space was rationalized by a balance...
The results obtained with the sterically more hindered ortho-substituted phenylacetylenes, 2-ethynyltoluene (2b) and 2-ethylnylanisole (2c), are in accord with the above view. Reactions of Cp*-LaH(SiMe3)2 (5D) with these substrates afforded less trimer and more head-to-tail dimer as compared to analogous reactions with phenylacetylene (Table 5-1). The reaction of 2c yielded less trimer and more head-to-tail dimer than that of 2b, most likely due to the larger steric size of 2c. In both cases, the rate of reaction was found to be first-order in substrate. The Cp*-H NMR resonances during the catalytic conversion of 2b were obscured by product resonances, but only two Cp*-H NMR resonances at δ 1.98 and 1.87 ppm were observed in the catalytic conversion of 2c, tentatively assigned to the regioisomeric but-1-en-3-yn-1-yl derivatives Cp*-La(R)=C(R)CCR and Cp*-LaH(C(R)=C(R)CCR (R = 2-MeOC6H4). Thus, both the kinetic behavior and the observed reaction intermediates suggest that the oligomerization reactions of 2b and 2c resembles more that of the reaction of Cp*-YCH(SiMe3)2 (5A) with phenylacetylene than that of 5D with phenylacetylene. This finding implies the presence of ortho-substituents affects the relative rates of the catalytic reaction sequences in such a manner, that the intermolecular protonolysis reaction of the butenynyl derivatives with substrate becomes rate-limiting.

### Electronic substituent effects

Electronic effects can be transmitted either through the σ framework (inductive and field effects) or the π system (resonance effects). In principle, electronic 1-alkyne substituent effects may play a role in determining both the rate and selectivity of the present oligomerization reaction. Evidence has been presented that the kinetic acidity of the present 1-alkynes increases with the σ-electron-withdrawing character of the alkyne substituent. It can thus be anticipated that the rate of protonolysis reaction sequences by the 1-alkyne is accelerated by the presence of more σ-electron-withdrawing alkynyl substituents. However, the kinetic acidity of the 1-alkyne is only expected to influence the oligomerization reaction rate, when protonolysis by 1-alkyne is rate-limiting. Rate-limiting protonolysis was implicated for the reactions of 2-ethynyltoluene and 2-ethynylanisole. Both substrates have comparable kinetic acidities and do not provide evidence for the above hypothesis, since the slower reaction rate of 2-ethynylanisole relative to 2-ethynyltoluene can arguably be attributed to metal-oxygen interactions, resulting in product and/or substrate inhibition (Section 5.3.6).

Because the extent of oligomerization (i.e. dimerization versus trimerization) is determined by the relative rate of protonolysis by 1-alkyne versus 1-alkyne insertion (Scheme 5-10), dimerization may be promoted relative to trimerization by a more σ-electron-withdrawing 1-alkyne substituent. The observed behavior of 2-ethynylthiophene and 2-ethynylpyridine in the present catalytic reactions supports this view, as they both undergo less trimerization than other substrates of similar or larger steric requirements and lower kinetic acidity (e.g. phenylacetylene, 2-ethynyltoluene and 2-ethylnylanisole). Conversely, 3-ethynylthiophene undergoes more trimerization than the more acidic 2-ethynylthiophene, in spite of the comparable steric requirements of their substituents.

Because the electronic demands of the transition state for 1-alkyne insertion into the alkynyl derivative favor an electron-withdrawing group at the α-position, the regioselectivity of dimerization may, in principle, also be affected by the σ-electron withdrawing character of the 1-alkyne substituent (Scheme 5-11). An unambiguous correlation between the regioselectivity of dimerization and the σ-electron-withdrawing character of the alkyne substituent is difficult to discern, as other effects, such as heteroatom-assisted C-C bond formation (vide infra), may also influence the observed regioselectivity. Another consequence of a relatively
The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metallocenes

177 high substrate acidity concerns catalyst deactivation via Cp*H abstraction and this aspect is discussed in a following section.

Substrate and product inhibition

The presence of heteroatoms is well-known to decrease catalytic turnover in rare-earth metallocene catalyzed reactions, most likely due to competition for vacant Cp’2LnR coordination sites. In the present reactions, both intra- and intermolecular heteroatom metal interactions can be envisaged. The catalytic consequences of intermolecular metal heteroatom coordination are believed to be twofold. Firstly, catalyst inhibition by substrate and product is expected, when intermolecular metal heteroatom coordination is competitive with 1-alkyne coordination and/or protonolysis by 1-alkyne. Secondly, heteroatom-assisted C-C bond formation may take place, when the coordination of a properly placed heteroatom with the metal center preceds substrate reactivity (vide infra).

Evidence for catalyst inhibition by substrate and product coordination was provided by the reactions of Cp*2LaCH(SiMe3)2 (5D) with 2-ethynylthiophene (2d) and 2-ethynlypyridine (2f) in the presence of thiophene and pyridine, respectively (Sections 5.3.4 and 5.3.5). In both cases, catalytic rate depression was observed, accompanied by a lower attainable degree of substrate conversion. Kinetic analysis of these reactions revealed also a deviation from first-order rate dependence on substrate concentration at lower degrees of substrate conversion than observed for analogous reactions in the absence of thiophene and pyridine. Deviation from first-order rate dependence on substrate concentration at lower degrees of substrate conversion, accompanied by a lower degree of catalytic substrate conversion, was also observed for reactions of 5D with 3-ethynylthiophene (2e) (Sections 5.3.3), 2-ethynlypyridine (2f) (Section 5.3.5) and 2-ethynylanisole (2e) (Section 5.3.6) upon increasing the absolute substrate concentration. Clearly, nonproductive product and substrate coordination to the catalyst compete more effectively with catalytic reaction sequences upon increasing the absolute substrate concentration, thereby lowering both the catalytic rate and the attainable degree of substrate conversion (Scheme 5-5).

The extent of catalyst inhibition via metal heteroatom coordination depends also on the relative strength of these noncovalent interactions. Deviation from first-order behavior was observed after 1.2 half-lives (57% substrate conversion) for 2f, after 1.9 half-lives (72% substrate conversion) for 2c and after 5.6 half-lives (97% substrate conversion) for 2e under similar reaction conditions. This order agrees with the well-known coordinating ability of the nitrogen-, oxygen-, and sulfur-containing substrates and products towards the electrophilic metal center, as unambiguously demonstrated by the reactions of Cp*2La(N(SiMe3))2 (26D) with phenylacetylene in the presence of thiophene, THF and pyridine (Section 5.4.4).

Substrate and product inhibition was also suggested by the presence of a multitude of Cp*1H NMR resonances during substrate conversion in the reaction of Cp*2LaCH(SiMe3)2 (5D) with 3-ethynylthiophene (2e) (Sections 5.3.2) and 2-ethynlypyridine (2f) (Section 5.3.6). The absence of products other than expected for the present oligomerization reactions argues for the formation of various Lewis base adducts of the reaction intermediates (Scheme 5-5). This view is supported by the fact that the number of Cp*1H NMR resonances increased at higher degrees of substrate conversion, when the low substrate concentration can compete less effectively with base adduct formation of the reaction intermediates. In marked contrast, no multitude of Cp*1H NMR resonances was observed during and after substrate conversion in the 5D-catalyzed reactions of 2-ethynylthiophene (2d) and 1-methyl-2-ethynlypyrrole (2g). The former observation can arguably be explained by...
interactions of the metal center and the proximal sulfur atom in compared to phenylacetylene. It seems therefore not unreasonable to ascribe the relative stability of formed but-1-en-3-yn-1-yl species ortho by the observed shift towards an coordination in a pent-1-en-4-yn-1-yl (Chapter 3) and an ynyl-enolate derivative of yttrocene are known as well.62 This intramolecular coordination results in an increased steric hindrance around the metal center and a competition for a vacant coordination site between the intramolecular carbon triple bond and the incoming substrate. As a consequence, protonolysis by 1-alkyne is favored over 1-alkyne insertion in these derivatives for both steric and electronic reasons.63 The influence of the alkyl substituent on the intramolecular coordination of the carbon-carbon triple bond interaction of the but-1-en-3-yn-1-yl derivatives is ambiguous at present.64

Several types of intramolecular interactions can be envisaged in the but-1-en-3-yn-1-yl derivatives formed from insertion into the alkynyl species (Scheme 5-10). The first type of intramolecular metal interaction in the but-1-en-3-yn-1-yl intermediate involves interaction of the metal with the C=C bond. Analogous interactions in d0 metal complexes have been reported, such as intramolecular alkyne coordination65b (30) and insertion in but-1-en-3-yn-1-yl metalloenes of catonic group 4 metal66c-e (29). Intramolecular alkyne coordination in a pent-1-en-4-yn-1-yl (Chapter 3) and an ynyl-enolate derivative of yttrocene are known as well.67 This intramolecular coordination results in an increased steric hindrance around the metal center and a competition for a vacant coordination site between the intramolecular carbon triple bond and the incoming substrate. As a consequence, protonolysis by 1-alkyne is favored over 1-alkyne insertion in these derivatives for both steric and electronic reasons.63 The influence of the alkyl substituent on the intramolecular coordination of the carbon-carbon triple bond interaction of the but-1-en-3-yn-1-yl derivatives is ambiguous at present.64

The second type of intramolecular metal interaction in the but-1-en-3-yn-1-yl intermediate is associated with the proximal (hetero)aromatic moiety of the alkynyl species. In the case of phenylacetylene, the formed but-1-en-3-yn-1-yl species 24a is likely to be stabilized by an interaction with the α-phenyl ring in analogy with α-phenylvinyl zirconocene cations66a and α-arylethyl rare-earth metal complexes (M) described in literature.66c The lower reactivity of the α1-benzyls (M, the 2,1-insertion product) relative to β-arylethyl species (N, the 1,2-insertion product) has been explained in terms of a sterically unfavored insertion (Scheme 5-13).67 The stability of these α-arylethyl species has been reported to be influenced by both steric and electronic effects.66a Ortho-substitution has, for example, been shown to result in a destabilization of α-arylethyl species, as indicated by the observed shift towards an α1-benzyl in the case of yttrium half-sandwich complexes66d and an increased reactivity (via β-H elimination) in the case of a permethylanthanocene system.66e The rate of styrene hydrostilblylation (in which PhSH2 protonolysis of the α-arylethyl species is rate-determining) is, furthermore, decreased by p-F and increased by p- and o-MeO substitution of styrene.66f

Attempts to prepare and isolate the but-1-en-3-yn-1-yl derivatives present as catalytic intermediates in the reaction of 5D and the studied (hetero)aromatic 1-alkynes have not been successful. The above considerations are therefore deemed plausible, but tentative at present. Supporting evidence is, however, provided by Cp*LaC(2-C4H3S)=C(H)CC(2-C4H3S) (24d) as the only observable organometallic species during and after substrate conversion in the reaction of 5D with excess 2-ethynylthiophene (2d) (Sections 5.3.3). The relative stability of the but-1-en-3-yn-1-yl derivative 24d is surprising, considering the relatively high kinetic acidity of 2d in combination with its smaller size and its arguably stronger interaction with the catalyst as compared to phenylacetylene. It seems therefore not unreasonable to ascribe the relative stability of 24d to an interaction of the metal center and the proximal sulfur atom in 24d.

The relative importance of the above intramolecular interactions in the but-1-en-3-yn-1-yl intermediates on the observed reactivity is difficult to establish. Even when the but-1-en-3-yn-1-yl derivatives represent the resting state of the catalyst, it is difficult to determine whether this relative stability is due to the above interactions or due to different effects on the relative stability in other catalytic intermediates. Even so, the reactivity of the but-1-en-3-yn-1-yl derivative has been found to be rate-limiting in the catalytic reactions of Cp*LaCH(SiMe3)2 with 2-ethynyltoluene (2b), 2-ethynylanisole (2d) and 2-ethynylthiophene (2d), all reactions where the above intramolecular interactions in the but-1-en-3-yn-1-yl intermediate can be expected.
The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metallocenes

Heteroatom-directed C-C bond formation

The position of the sulfur atom relative to that of the ethynyl group appears to be pivotal in the observed selectivity and activity in the catalytic reactions of Cp*₂LaCH(SiMe₃)₂ (5D) with 2-ethynylthiophene (2d) and 3-ethynylthiophene (2e). Whereas 2d is consumed relatively rapidly and selectively (98% for the trans-head-to-head dimer 12), 2e is converted 6 times slower and less selectively (88% for 12) (Sections 5.3.3). The origin of this behavior is presently believed to be twofold. Firstly, the 3-thienyl group is less electron-withdrawing than the 2-thienyl group (Appendix), thereby accounting for a possibly lower tendency to undergo trans-head-to-head dimerization relative to head-to-tail dimerization and trimerization (vide supra). And secondly, heteroatom precoordination in the reaction of 2d may have beneficial effects on both the rate and selectivity of catalytic trans-head-to-head dimerization.

Under the reasonable assumption that alkyne insertion into the active catalyst is preceded by coordination to the ethynyl group, precoordination of the catalyst to the sulfur atom of the substrate is likely to favor trans-head-to-head dimerization in the catalytic conversion of 2-ethynylthiophene, due to stabilization of the transition state leading to coordination of the proximal ethynyl group and stabilization of the transition state leading to 2,1-insertion (Scheme 5-15). When precoordination of the active catalyst to the sulfur atom of the substrate takes place in the oligomerization reaction of 3-ethynylthiophene, however, coordination of the distant ethynyl group has to compete with coordination to the sulfur atom and the transition state leading to 2,1-metal insertion will not be stabilized by a heteroatom metal interaction. Literature precedent for precomplexation of the metal center to the heteroatom exists for metalation reactions of heterocycles by rare-earth metallocene derivatives and metalation reactions of aromatics by lithium and aluminum compounds. In fact, the high selectivity for α-metalation was proposed to be the result of the stabilization of the corresponding transition state by a heteroatom metal interaction.

Precoordination to the sulfur atom in the 5D-catalyzed reactions of 2d and 2e is supported by the observation of several base adducts during and after substrate conversion in the 5D-catalyzed reaction of 2e, whereas only one lanthanocene derivative was observed in the analogous reaction with 2d. Other observations supporting heteroatom-assisted C-C bond formation are (i) the slower metalation of 2e by Cp*₂La(N(SiMe₃))₂ (26D) relative to the metalation of phenylacetylene by 26D, in spite of a comparable (kinetic) acidity (Appendix), and (ii) the higher preference for trans-head-to-head dimerization in the reactions of 2-ethynylpyridine (2f) mediated by Cp*₂LaCH(SiMe₃)₂ (5D) and Cp*₂YCH(SiMe₃)₂ (5A), as compared to the analogous reactions with phenylacetylene (Table 5-2). Most significantly, exclusive trans-head-to-head dimerization was observed for the reaction of 5A with 2f (Sections 5.3.7), whereas selective head-to-tail dimerization was observed for the analogous reaction with phenylacetylene (11a: 12a: 15a: 16a = 93.7:5.2:0.4:0.7).

Catalyst deactivation

Catalyst deactivation leading to the observed formation of Cp*H in the present 1-alkyne oligomerization reactions has been proposed to involve the formation of a dialkynyl species Cp*La(C≡CR)₂ from the reaction of Cp*₂LaCCPh and 1-alkyne, possibly followed by ligand rearrangement of Cp*₂La(C≡CR)₂ into Cp*₂La(C≡CR) and La(C≡CR) (Chapter 4). The observed substrate effects on the formation of Cp*H support the view that catalyst deactivation via Cp* abstraction is promoted by increasing acidity of the acetylenic proton of the substrate (Table 5-1).
Concluding remarks

The present results indicate that the catalytic reactions of Cp*₂LaCH(SiMe₃)₂ (5D) with phenylacetylene (2a) and 1-methyl-2-ethynylpyrrole (2g) involve a rate-limiting pre-equilibrium of a monomeric, alkynyl derivative Cp*₂LaCCR (20) with its Lewis base adduct Cp*₂LaCCR·RCCH (20·2). As a consequence, the rate of 1-alkyne oligomerization exhibits saturation kinetics. In both cases, high substrate-to-catalyst molar ratios increase the degree of catalyst deactivation via Cp*H abstraction and the rate of 1-alkyne trimerization relative to that of 1-alkyne dimerization. The higher selectivity for trans-head-to-head dimerization of 2g relative to 2a is attributed to the increased σ-electron-withdrawing character of the 1-methyl-2-pyrrolyl group relative to the phenyl group.

The catalytic reactions of Cp*₂LaCH(SiMe₃)₂ (5D) with 2-ethynyltoluene (2b), 2-ethynylanisole (2c) and 2-ethynylthiophene (2d) proceed via rate-limiting protonolysis of the but-1-en-3-yn-1-yl derivative(s). The rate of these oligomerization reactions is first-order in substrate. Catalyst inhibition via heteroatom metal interactions determine the observed substrate reactivity of 2c and 2d, but the catalytic consequences, such as catalytic rate depression at relatively high substrate-to-catalyst molar ratios, deviation from first-order kinetic behavior at relatively high substrate conversion and a low degree of catalytic substrate conversion at relatively
The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metallocenes

high substrate-to-catalyst molar ratios, are more pronounced in the former. The higher selectivity for trans-head-to-head dimerization of 2d relative to phenylacetylene is attributed to the increased σ-electron-withdrawing character of the 2-thienyl group relative to the phenyl group. Steric effects dominate the activity and selectivity of the catalytic reactions with 2b and 2c. Hence, a lowered catalytic turnover, accompanied by a lower selectivity for trans-head-to-head dimerization and trimerization, is observed as compared to the analogous reactions with phenylacetylene. The absence of C-O cleavage products in the reactions of 5D with 2e reveal that catalyst reactivity towards the methoxy group cannot compete with the catalytic reaction sequences.68

The 5D-catalyzed reactions of 3-ethynylthiophene (2e) are dominated by substrate and product inhibition. Even though the rate of reaction is initially first-order in substrate, Lewis base adducts of the catalytic intermediates are observed throughout the course of reaction and increasingly so at relatively high substrate conversion. The catalytic consequences of substrate and product inhibition (i.e. catalytic rate depression, deviation from first-order kinetic behavior at higher substrate conversion and a lower degree of catalytic substrate conversion) become increasingly important at higher substrate-to-catalyst molar ratios. The lower selectivity for trans-head-to-head dimerization and the higher selectivity for trimerization relative to the analogous reactions with 2-ethynylthiophene and phenylacetylene are attributed to the lower σ-electron-withdrawing character of the 3-thienyl group relative to the 2-thienyl and phenyl group.

The catalytic reactions of Cp*2LaCH(SiMe3)2 (5D) with 2-ethynylpyridine (2g) are characterized by a competition between highly selective trans-head-to-head dimerization and catalyst inhibition via metal-nitrogen interactions. The catalytic consequences of substrate and product inhibition are more pronounced than observed for other heteroaromatic 1-alkynes, due to the well-recognized strong coordination of nitrogen Lewis bases to rare-earth metals. The absence of products other than those expected from trans-head-to-head dimerization argues that the relatively facile ortho-metalation of pyridyl moieties, typical for rare-earth metallocene derivatives,68 cannot compete with the catalytic reaction sequences. In spite of a pronounced catalyst inhibition by substrate and product, catalytic dimerization of 2g is of considerable practical value at relatively low substrate-to-catalyst molar ratios. For example, exclusive trans-head-to-head dimerization and 95% substrate conversion is achieved within 30 min, when a 50-fold molar excess of 2f relative to 5D is used. This finding is deemed quite remarkable, considering the reported failure to prepare an alkynyl decamethylsamarocene derivative of 2-ethynylpyridine69 and the lack of catalytic reactivity of 4-vinylpyridine in the lanthanidocene-catalyzed intermolecular hydroamination reaction.18e

5.7. Experimental section

General considerations. For general remarks and physical and analytical measurements, see Sections 2.7 and 3.5. The compounds Cp*2LaN(SiMe3)2,70 and [Cp*2La(µ-2-C4H3S)]2,26 Pd(PPh3)2Cl2,71 and
2-iodo-1-methylpyrrole\textsuperscript{10,72} were prepared according to literature procedures. Thiophene (distilled over Na) and pyridine (distilled over KOH) were dried as recommended.\textsuperscript{75}

**General purification procedure for 1-alkynes.** The colored oils or liquids obtained after synthesis or received after purchase were brought in a flask containing freshly ground CaH\textsubscript{2} and stirred at room temperature for at least 24 h.\textsuperscript{73} Subsequent vacuum transfer and passage through a plug of neutral alumina afforded colorless oils which were stored immediately under nitrogen, in the dark and at -30 °C.

**Preparation of substituted (hetero)aromatic 1-alkynes. (a) General procedure.** The following procedure is a modification of a general method.\textsuperscript{10} A 1-L, three-neck, round-bottom flask, equipped with a magnetic stir bar, cooler, and drop funnel was charged with 2-methyl-3-butyn-2-ol (15.0 ml, 155 mmol) and piperidine (100 mL). The mixture was degassed in vacuo. After Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (0.379 g, 0.540 mmol) and PPh\textsubscript{3} (0.278 g, 1.06 mmol) were added the suspension was stirred for 0.5 h at 60 °C. Successive addition of a suspension containing CuI (0.278 g, 1.06 mmol) was followed by heating and stirring the reaction mixture was heated and stirred overnight under reflux. Vacuum filtration, rotatory evaporation and flash column chromatography (neutral alumina, petroleum ether/diethyl ether) afforded dark-colored oils. Residual piperidine and 2-methyl-3-butyn-2-ol were removed from the product by vacuum distillation using a 20-cm Vigreux column. Subsequent Kügelrohr distillation provided 2-methyl-4-(2-aryl)but-3-yn-2-ol as oils. A flash column chromatography (neutral alumina, petroleum ether/diethyl ether) was followed by crystallization from petroleum ether at low temperature affording white needles in most cases.

The 2-methyl-4-(2-aryl)but-3-yn-2-ol (4) was deprotected according to a modified general procedure.\textsuperscript{10} A 100-mL round-bottom flask was equipped with a magnetic stir bar and connected to a 30-cm Vigreux column, condenser and a single receiver which was cooled with liquid nitrogen. The flask was charged with butynol (7.3 g), freshly powdered KOH (2.3 g) and paraffin oil (20 mL). Gradual heating to 200 °C under vacuum and stirring yielded a colorless oil as distillate. Acetone was removed from the distillate by vacuum distillation (40 °C/60 mmHg), followed by flash column chromatography (neutral activated alumina, petroleum ether, affording a colorless oil.

**b) 2-Ethynyltoluene (2b).** Crystallization from petroleum ether at -40 °C provided 2-methyl-4-(2-methylphenyl)but-3-yn-2-ol (4b) as white needles. Yield: 25.4 g (93%). Flash column chromatography (neutral activated alumina, petroleum ether) afforded 2-ethynyltoluene (2b) as a colorless oil. Yield: 4.62 g (95%).

**2-Methyl-4-(2-methylphenyl)but-3-yn-2-ol (4b):** 1H NMR (400 MHz, CDCl\textsubscript{3}, 25 °C): \(\delta 1.62\) (s, CH\textsubscript{3}, 6 H), 2.15 (s, OCH, 3 H), 2.40 (s, CH\textsubscript{3}, 3 H), 7.10 (dt, \(J_{HH} = 7.7\) Hz, \(J_{HM} = 2.3\) Hz, CH, 1 H), 7.18 (dd, \(J_{HM} = 6.3\) Hz, \(J_{NN} = 1.5\) Hz, CH, 1 H), 7.19 (dt, \(J_{HM} = 6.3\) Hz, \(J_{NN} = 1.5\) Hz, CH, 1 H), 7.36 (dt, \(J_{HM} = 7.7\) Hz, \(J_{NN} = 1.5\) Hz, CH, 1 H). \(13C\{}\{1H\} NMR (100 MHz, CDCl\textsubscript{3}, 25 °C): \(\delta 20.56\) (CH\textsubscript{3}), 31.57 (CH\textsubscript{3}), 65.71 (CMe), 80.98 (C\textsubscript{3}), 97.83 (C\textsubscript{3}), 122.38 (C\textsubscript{C}), 125.45 (CH), 128.24, 129.33, 131.78, 140.10 (CCH). GC-MS, m/z (relative intensity): 174 (M\textsuperscript{+}; 24), 160 (14), 159 (M\textsuperscript{-} - CH\textsubscript{3}; 100), 115 (32), 43 (44). IR (KBr, [cm\textsuperscript{-1}]): 3245 (br s), 3061 (m), 2950 (w), 2862 (m), 2735 (w), 2103 (m), 1747 (m), 1598 (m), 1460 (m), 1380 (s), 1159 (s), 1093 (m), 1042 (m), 730 (m), 672 (w), 578 (m), 512 (m), 396 (m), 326 (m), 3061 (m), 3202 (m), 2948 (m), 2920 (m), 2862 (m), 2735 (w), 2103 (m), 1919 (w), 1806 (w), 1666 (w), 1595 (m), 1482 (s), 1455 (s), 1378 (m), 1264 (m), 1107 (m), 1042 (m), 943 (m).

**c) 2-Ethynylanisole (2c).** Kügelrohr distillation (120-160 °C, ~11 mTorr) provided 2-methyl-4-(2-aryl)but-3-yn-2-ol (4c) as a light-orange oil. Yield: 20.0 g (99%). No suitable crystallization conditions were found. Flash column chromatography (neutral alumina, petroleum ether) afforded 2-ethynylanisole (2c) as a light-orange oil. Yield: 7.33 g (92%).

**2-Methyl-4-(2-methoxyphenyl)but-3-yn-2-ol (4c):** 1H NMR (300 MHz, CDCl\textsubscript{3}, 25 °C): \(\delta 2.42\) (s, CH\textsubscript{3}, 3 H), 3.23 (s, CH\textsubscript{2}, 1 H), 7.1-7.4 (m, CH\textsubscript{3}, 4 H). \(13C\{1H\} NMR (300 MHz, CDCl\textsubscript{3}, 25 °C): \(\delta 2.32\) (s, CH\textsubscript{3}, 3 H), 2.92 (s, CH\textsubscript{2}, 1 H), 6.95-6.80, 7.40-7.48 (m, CH\textsubscript{3}, 4 H). \(13C\{1H\} NMR (125 MHz, CDCl\textsubscript{3}, 25 °C): \(\delta 20.55\) (CH\textsubscript{3}), 80.92 (C\textsubscript{CH\textsubscript{2}}), 82.30 (C\textsubscript{C}), 121.91 (C\textsubscript{CH\textsubscript{2}}), 125.49, 128.69, 129.42, 132.50 (CH\textsubscript{3}), 140.72 (C\textsubscript{C}). \(13C\{1H\} NMR (125 MHz, CDCl\textsubscript{3}, 25 °C): \(\delta 20.60\) (CH\textsubscript{3}), 91.53 (C\textsubscript{C}), 82.79 (C\textsubscript{C}), 121.82 (C\textsubscript{CH\textsubscript{2}}), 125.82, 128.86, 129.69, 132.83 (CH\textsubscript{3}), 140.85 (C\textsubscript{C}). GC-MS, m/z (relative intensity): 116 (M\textsuperscript{+}, 62), 115 (M\textsuperscript{-} - H, 100), 89 (12), 74 (41), 63 (12), 51 (5), 50 (5), 39 (6). IR (neat, [cm\textsuperscript{-1}]): 3296 (s), 3061 (m), 3020 (m), 2948 (m), 2920 (m), 2862 (m), 2735 (w), 2103 (m), 1919 (w), 1806 (w), 1666 (w), 1595 (m), 1482 (s), 1455 (s), 1378 (m), 1264 (m), 1107 (m), 1042 (m), 943 (m).

**Chapter 5**

2-iodo-1-methylpyrrole\textsuperscript{10,72} were prepared according to literature procedures. Thiophene (distilled over Na) and pyridine (distilled over KOH) were dried as recommended.\textsuperscript{75}
1.31 (15), 115 (12), 105 (14), 91 (13), 77 (14), 43 (100). IR (KBr, [cm⁻¹]): 3395 (br s), 2977 (m), 2932 (m), 2822 (m), 2038 (w), 1595 (m), 1574 (m), 1491 (s), 1462 (m), 1433 (m), 1361 (m), 1293 (m), 1268 (s), 1241 (m), 1161 (m), 1114 (m), 1047 (m), 1023 (m), 961 (m), 907 (m).

2-Ethenylnaloside (2e)²: ¹H NMR (500 MHz, CDCl₃, 25 °C): δ 3.35 (s, OCH₃, 3H), 9.60 (s, Me₂, 3H). ¹³C-{¹H} NMR (125 MHz, CDCl₃, 25 °C): δ 51.29 (s, C-α, 3H), 77.25 (C-β, 1H), 69.58 (dd, Jαβ = 5.0 Hz, Jαγ = 1.1 Hz, C-γ, 1H), 110.95 (C-δ, 1H), 110.43 (C-ε, 1H), 119.69 (C-ν, 1H), 121.69 (C-π, 1H), 126.96 (C-ω, 1H). GC-MS, m/z (relative intensity): 170 (M+; 56), 155 (M+ - H; 100), 143 (M+ - H - CO; 21), 119 (M+ - H - CO - CO; 20), 89 (M+ - CO - CO - CO; 49). IR (neat, [cm⁻¹]): 3391 (s), 3067 (m), 2928 (m), 2856 (m), 1720 (s), 1489 (s), 1463 (m), 1363 (m), 1290 (m), 1252 (s), 1178 (m), 1162 (m), 1110 (m), 1046 (m), 937 (m).

2-Ethenylnaphthol (2f): Recrystallization from petroleum ether afforded 2-methyl-4-(3-thienyl)but-3-yn-2-ol (2f) as light-yellow crystals. Yield: 28.53 g (81%). Flash chromatography (neutral alumina, hexanes) yielded 2-ethenylnaphthol (2f) as a light-yellow oil. Yield: 5.94 g (93%).

2-Ethenylpyridine (2i): Crystallization from THF/petroleum ether at room temperature afforded 2-methyl-4-(2-pyridyl)but-3-yn-2-ol (2i) as light-yellow crystals. Yield: 28.53 g (81%). Flash chromatography (neutral alumina, hexanes) yielded 2-ethenylnaphthol (2f) as a light-yellow oil. Yield: 5.94 g (93%).

The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metallocenes

183
Typical NMR-Scale Catalytic 1-Alkyne Oligomerization Reactions Mediated by Cp*₂LaCH(SiMe₃)₂. (a) General procedure. A catalyst stock solution was prepared in benzene-d₆. The amount of (pre)catalyst was weighed, while the volume of the solvent was determined using of volumetric glassware. In cases of relatively high substrate-to-catalyst ratios, a specified amount of cyclooctane was added with a microsyringe to the catalyst solution to serve as an internal standard. The catalyst stock solution was transferred into a vial with screw-cap and stored after use at -40°C in the glovebox. The density for each substrate was determined experimentally and the volume of the 1-alkyne needed was calculated with a microsyringe to the catalyst solution in the NMR tube.

After substrate addition, the sample was inserted within 5 min (at room temperature) into the probe of the spectrometer and the reaction was followed by single-pulse, in situ ¹H NMR spectroscopy, using appropriate long pulse delays (at least 300 s for the acetylenic proton of the substrate) to avoid signal saturation under anaerobic conditions. As soon as the substrate was completely consumed, the reaction mixture was analyzed with quantitative ¹H NMR spectroscopy (appropriate long pulse delays and long experiment times so as to obtain reliable proton intensities and signal-to-noise ratios, respectively). Finally, the reaction mixture was quenched with methanol-d₆, methanol, H₂O or D₂O and the final organic products were identified by ¹H, ¹³C, ¹³C-¹H) and 2D NMR, GC, GC-MS and high-resolution mass spectroscopy. In most cases, the products were characterized in
The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metalloccenes

situ, but in some cases the major product could be isolated by performing several purification steps (i.e. filtration over a plug of neutral alumina using hexanes as eluent to remove inorganic solids, evaporation of volatiles, sublimation of dimers, fractional crystallization, vide infra).

(b) Phenylacetylene (2a). As described above, 100.0 µL (910.5 µmol, 1071 equiv.) of phenylacetylene was converted by Cp*R*LaCH(SiMe₃)₃ (0.85 µmol in 500.0 µL of benzene-d₆) into a mixture of 2,4-diphenylbut-1-en-3-yne (11a), trans-1,4-di(phenylbut-1-en-3-yne (12a), 1,3,6-triphenyl-1,5-hexadiyne (15a) and 1,3,6-triphenylhexa-1,2,5-yne (16a).

(c) 2-Ethynyltoluene (2b). As described above, 121.1 mg (1043 µmol, 519 equiv.) of 2-ethynyltoluene was oligomerized by Cp*R*LaCH(SiMe₃)₃ (2.01 µmol in 500.0 µL of benzene-d₆) into a mixture of 2,4-di(2-methylphenyl)-1-en-3-yne (11b), trans-di(2-methylphenyl)but-1-en-3-yne (12b) and 1,3,6-tri(2-methylphenyl)-1,5-hexadiyne (15b).

2,4-Di(2-methylphenyl)1-en-3-yne (11b): ¹H NMR (400 MHz, C₆D₆, 25 °C): δ (CH signals not assigned), 5.34 (d, JHH = 2.1 Hz, HCC(H)=C-CH₃, 1H), 5.78 (d', JHH = 1.1 Hz, HCC(H)=C-CH₃, 1H). ¹³C{¹H} NMR (75 MHz, C₆D₆, 25 °C): 14.33 (C(CH₃)), 22.68 (CH₃), 151.12 (CH=CH), 189.10 (M+ - 2CH₃ – 2OCH₃). GC-MS, m/z (relative intensity): 232 (M+), 222 (M+ - CH₃), 213 (M+ - CH₃ - 2H), 202 (M+ - 2CH₃), 115 (M+ - CH₃ - C₆H₄(CH=CH), 115 (M+ - CH₃ - C₆H₄(CH=CH) - CH₂C₆H₄CH=CH₂). ²H NMR (400 MHz, C₆D₆, 25 °C): δ (CH signals not assigned), 2.87 (dd, JHH = 2.1 Hz, HCC(H)=C-CH₃, 1H), 5.34 (d', JHH = 1.1 Hz, HCC(H)=C-CH₃, 1H). ¹³C{¹H} NMR (75 MHz, C₆D₆, 25 °C): 14.33 (C(CH₃)), 22.68 (CH₃), 151.12 (CH=CH), 189.10 (M+ - 2CH₃ – 2OCH₃). GC-MS, m/z (relative intensity): 232 (M+), 222 (M+ - CH₃), 213 (M+ - CH₃ - 2H), 202 (M+ - 2CH₃), 115 (M+ - CH₃ - C₆H₄(CH=CH) - CH₂C₆H₄CH=CH₂). HR-MS: C₉H₈O₈ calc.: 232.1250, found: 232.1245.

(d) 2-Ethynylisopropylbenzene (2c). As described above, 137.3 mg (1039 µmol, 517 equiv.) of 2-ethynylisopropylbenzene was dimerized by Cp*R*LaCH(SiMe₃)₃ (2.01 µmol in 500.0 µL of benzene-d₆) to a mixture of 2,4-di(2-methoxyphenyl)-1-en-3-yne (11c) and trans-1,4-di(2-methoxyphenyl)but-1-en-3-yne (12c).

2,4-Di(2-methoxyphenyl)1-en-3-yne (11c): ¹H NMR (400 MHz, C₆D₆, 25 °C): δ 2.45 (s, CH₃), 3.14 (s, OCH₃), 3.26 (s, OCH₃), 3.81 (s, OCH₃), 5.56 (d, JHH = 1.1 Hz, HCC(H)=C, 1H), 5.60 (d', JHH = 1.1 Hz, HCC(H)=C, 1H). ¹³C{¹H} NMR (75 MHz, C₆D₆, 25 °C): 55.00 (OCH₃), 55.22 (OCH₃), 93.36 (C=CH), 110.62, 110.91, 120.52, 129.52 133.50 (Ar), 157.39 (Ar), 160.59 (Ar, COCH₃), 165.87 (Ar, COCH₃), (other signals unidentified). ¹³C{¹H} NMR (75 MHz, C₆D₆, 25 °C): 55.70 (OCH₃), 55.40 (OCH₃), 92.15 (C=CH), 92.59 (C=CH), 110.32, 120.07, 120.63 133.23 (Ar), 156.87 (Ar), 160.03 (Ar, COCH₃), (other signals obscured). GC-MS, m/z (relative intensity): 244 (M+), 100, 249 (M+ - CH₂-CH₂), 234 (M+ - 2CH₃-CH₂), 218 (M+ - 2CH₃-2CH₂-CH), 202 (15), 189 (M+ - 2CH₃-2CH₂-CH), 178 (15), 176 (16), 158 (12), 151 (10), 131 (M+ - CH₃OC₆H₄CH=CH₂), 30, 119 (M+ - CH₃OC₆H₄C=CH₂ - CH₂, 51), 115 (21), 91 (M+ - CH₃OC₆H₄C=CH₂ - CH₂ - CH₃-CH₂, 54%), 76 (12).

Scheme 5-16. Numbering scheme of (E)-1,4-di(o-methoxyphenyl)but-1-en-3-yne (12c).

(Å) - (Å)
(e) 2-Ethynylthiophene (2d). As described above, 112.0 mg (1036 µmol, 515 equiv.) of 2-ethynylthiophene was oligomerized by Cp*²LaCH(SiMe₃)₂ (2.01 µmol in 500.0 µL of benzene-C₇H₈). GC-MS, m/z (relative intensity): 264 (M⁺; 100), 249 (M⁺ - CH₂; 6), 234 (M⁺ - 2CH₂; 12), 231 (10), 218 (M⁺ - 2CH₃; 16), 205 (19), 202 (12), 189 (20), 178 (13), 176 (13), 131 (M⁺ - CH₂OC₆H₄C=CH₂; C₆H₅; 23), 119 (M⁺ - CH₂OC₆H₄C=CH₂ - CH₂; C₆H₅; 38), 91 (M⁺ - CH₂OC₆H₄C=CH₂ - CH₂ - C₆H₅; 39). HR-MS: C₂₆H₂₆O₂.calc.: 264.11502, found: 264.11402.

Scheme 5-17. Numbering scheme of (E)-1,4-di(2-thienyl)but-1-en-3-yne (12d).

1,3,6-Tri(2-thienyl)-1,5-hexadiyne (15d). 1H NMR (300 MHz, CD₂CO, 25 °C): δ 7.22 (dd, J₁₂ = 2.8 Hz, H(CC₆H₄C=CH₂; 1H₂); 2.72 (dd, J₁₂ = 6.6 Hz, H(CC₆H₄C=CH₂; 1H₂) = 2.8 Hz, H(CC₆H₄C=CH₂; 1H₂), 4.11 (t, J₁₂ = 6.6 Hz, H(CC₆H₄C=CH₂; 1H₂), GC-MS, m/z (relative intensity): 324 (M⁺; 1), 203 (M⁺ - CH₂OC₆H₄C=CH₂; C₆H₅; 100), 171 (M⁺ - CH₂OC₆H₄C=CH₂ - C₆H₅; 5), 158 (M⁺ - CH₂OC₆H₄C=CH₂ - C₆H₅ - 2CH₃; 3), 121 (CH₂OC₆H₄C=CH₂; C₆H₅; 7).
(E)-1,4-Di(3-thienyl)but-1-en-3-yne (12e): ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 8.42 (dd, J₁H₂ = 4.9 Hz, J₃H₂ = 1.8 Hz, J₁H₃ = 1.0 Hz, 1-H, 1H), 8.35 (dddd, J₂H₂ = 4.7 Hz, J₂H₃ = 1.9 Hz, J₂H₄ = 1.0 Hz, 14-H, J₁H₄ = 0.4 Hz, 14-H, 1H), 7.33 (dddd, J₂H₂ = 15.8 Hz, J₁H₂ = 0.8 Hz, J₂H₃ = 0.6 Hz, 9-H, 1H), 7.14 (ddd, J₁H₃ = 7.8 Hz, J₄H₃ = 1.1 Hz, J₂H₄ = 1.0 Hz, 4-H, 1H), 6.99 (dddd, J₂H₂ = 15.8 Hz, J₂H₃ = 0.6 Hz, J₂H₄ = 0.4 Hz, 8-H, 1H), 6.94, 6.92 (ddd, J₃H₂ = 7.7 Hz, J₃H₃ = 7.7 Hz, J₃H₄ = 1.2 Hz, 3/12-H, 1H), 6.60 (ddd, J₃H₂ = 7.7 Hz, J₃H₃ = 1.0 Hz, J₃H₄ = 1.2 Hz, 11-H, 1H), 6.54, 6.53 (ddd, J₂H₂ = 4.9 Hz, J₂H₃ = 7.7 Hz, J₂H₄ = 1.2 Hz, 2/13-H, 1H). ¹³C{¹H} NMR (125 MHz, C₆D₆, 25 °C): δ 88.77 (6-C), 93.93 (7-C), 112.14 (8-C), 122.55, 122.74, 123.00, 127.29, 135.55, 136.14, 136.14, 142.16 (py, CH), 144.20 (10-C), 150.03 (py, CH), 150.47 (9-C), 154.08 (5-C). GC-MS, m/z (relative intensity): 206 (M⁺, 56), 205 (M⁺ - H, 100), 178 (M⁺ - H - CHN; 12), 152 (5), 128 (10), 103 (4), 89 (6), 78 (11), 63 (3), 56 (2), 51 (7). HR-MS: C₁₇H₁₄N₂S calc.: 266.08439, found: 266.08342.

(i) 1-Methyl-2-ethylpyridine (2g). As described above, 108.3 mg (1030 µmol, 1200 equiv.) of 1-methyl-2-ethylpyridine was dimerized by Cp*LaCH(SiMe₃) (0.85 µmol in 500.0 µL of benzene-d₆) into 2,4,4-di(1-methyl-2-pyrydyl)but-1-en-3-yne (11g), trans-1,4-di(1-methyl-2-pyrydyl)but-1-en-3-yne
(12g), 1,3,6-tri(1-methyl-2-pyryrol)1,5-hexa-diyne (15g) and 1,3,6-(1-methyl-2-pyryrol)hexa-1,2-diene-5-yne (16g).

2,4-Di(1-methyl-2-pyryrol)but-1-en-3-yne (11g): 1H NMR (400 MHz, C6D6, 25 °C): δ 5.65 (s, HCH=C, 1H), 5.62 (s, HCH=C, 1H), 1.62 (s, HCH=C, 1H). GC-MS, m/z (relative intensity): 210 (M+; 100), 209 (M+ - H; 39), 194 (M+ - H - CH2; 17), 193 (M+ - 2H - CH2; 18), 168 (M+ - CN - CH3 - H or - CH3 - HCN; 32), 167 (M+ - 2H - CH3 - CN or - H - CH3 - HCN; 31).

(E)-1,4-Di(1-methyl-2-pyryrol)but-1-en-3-yne (12g): 1H NMR (400 MHz, C6D6, 25 °C): δ 2.67 (s, A), 3.15 (s, JH = 3H), 6.14 (dd, JHM = 3.8 Hz, JHH = 2.7 Hz, JHH = 0.7 Hz, C), 5.64 (d, JHM = 3.8 Hz, JHH = 2.7 Hz, H), 6.18 (d, JHH = 15.8 Hz, F), 6.18 (dd, JHM = 2.7 Hz, JHH = 1.6 Hz, B), 6.27 (ddd, JHM = 3.8 Hz, JHH = 1.6 Hz, JHH = 0.7 Hz, D), 6.70 (dd, JHM = 3.8 Hz, JHH = 1.6 Hz, G), 6.77 (ddd, JHH = 15.8 Hz, JHH = 0.7 Hz, JHH = 0.7 Hz, E). 13C{1H} NMR (100 MHz, C6D6, 25 °C): δ 33.16 (1), 34.02 (14), 83.69 (8), 94.11 (9), 103.97 (7), 108.32 (4), 108.79 (3), 109.06 (12), 115.27 (11), 116.92 (10), 123.65 (13), 124.57 (2), 128.54 (6), 131.30 (5), 131.98 (1), 134.01 (4), 134.54 (8), 143.83 (15), 145.67 (12), 146.41 (2), 146.63 (8), 149.41 (11), 154.87 (1), 155.52 (2), 156.72 (5). GC-MS, m/z (relative intensity): 210 (M+; 100), 209 (M+ - H; 40), 194 (M+ - H - CH2; 16), 193 (M+ - 2H - CH2; 16), 168 (M+ - CN - CH3 - H or - CH3 - HCN; 24), 167 (M+ - 2H - CH3 - CN or - H - CH3 - HCN; 22). HR-MS: C14H14N2, calc.: 210.11569, found: 210.11574.

Scheme 5-20. Numbering scheme of (E)-1,4-di(1-methyl-2-pyryrol)but-1-en-3-yne (12g).
(c) 2-Ethynylpyridine. As described above, 53.0 mg (514 µmol, 55 equiv.) of phenylacetylene was dimerized by Cp*2YCH(SiMe3)2 (9.32 µmol in 500.0 µL of benzene-d6) into trans-1,4-di(2-pyridyl)but-1-en-3-yne (12f).

Kinetic Studies of 1-Alkyne Oligomerization Reactions. A catalyst stock solution was prepared by weighing the amount of precatalyst and dissolving the solid in a specified volume of benzene-d6, as determined by volumetric glassware. After preparation, the catalyst solution was transferred into a pre-weighted vial with screw-cap and weighted. For experiments with relatively high molar substrate-to-catalyst ratios, a specified amount of internal standard (cyclooctane) was also added with a microsyringe. After use, the catalyst stock solution was stored at -40 ºC 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 using a 500.0-µL microsyringe. The volume of substrate needed for the kinetic experiment was calculated from the density which was determined experimentally and this amount was added with a microsyringe to the catalyst solution. The time period between substrate addition and the start of an arrayed NMR experiment was measured for each experiment and found to be usually in the range of 6-10 min. The time needed to transfer the sample tube from the glove box into the probe of the Inova-500 or Unity-400 spectrometer was ~5 min after substrate addition. Prior to sample insertion, the probe had been set to the appropriate temperature (T ± 0.2 ºC; checked with a methanol temperature standard).

Data were acquired using one scan per time interval. Long time intervals (at least 300 s) were used to avoid signal saturation under anaerobic conditions. In most cases, the reaction kinetics were monitored from the intensity changes in the substrate resonance (the acetylenic proton) and in the product resonances over 3 or more half-lives on the basis of acetylene consumption. For experiments involving relatively low substrate-to-catalyst ratios, the substrate concentration was measured from the normalized integral of the acetylenic proton relative to that of CH2(SiMe3)2. The CH2(SiMe3)2 is present as a result of rapid and quantitative protonolytic ligand cleavage during catalyst generation. For experiments involving relatively high substrate-to-catalyst ratios, hydride or butatrienediyl catalyst precursors, the substrate concentration was measured from normalization of the acetylenic substrate signal against that of cyclooctane. The reproducibility of kinetic data, using different batches of substrate and catalyst stock solutions, was within 5%.

Typical NMR tube reaction of Cp*2LaNH(SiMe3)2 (26D) with phenylacetylene. Phenylacetylene (2.89 µL, 26.3 µmol) was added with a microsyringe to an NMR tube containing Cp*2LaNH(SiMe3)2 (15.0 mg, 26.3 µmol) in benzene-d6. The solution was followed by 1H NMR spectroscopy. No reaction was observed after 10 days at room temperature. When the reaction temperature was increased to 80 ºC, 1H NMR spectroscopy indicated that phenylacetylene was completely converted within 12 h into trans-1,4-diphenylbut-1-en-3-yne (12a), cis-1,4-diphenylbut-1-en-3-yne (13a) 1,3,6-tri phenyl-1,5-hexadiyne (15a) and 1,3,6-tri phenylhexa-1,2,5-yne (16a). Concomitantly, Cp*2LaNH(SiMe3)2 was converted for 4% into HNSi(SiMe3)2 and unidentified organometallic species. After quenching with H2O, the presence of 12a, 13a, 15a, 16a, Cp*H and HNSi(SiMe3)2 was indicated by GC/GC-MS.

Preparative-scale 1-alkyne oligomerization reactions catalyzed by Cp*2LaCH(SiMe3)2. (a) General procedure. Substrates (0.88-1.76 mmol, molar substrate-to-catalyst ratios of 50-100) were weighed and/or added with a microsyringe to a stirred solution of Cp*2LaCH(SiMe3)2 (10.0 mg, 17.6 µmol) in hexane (5.0 mL) in a Schlenk vessel. After stirring for 2 h at room temperature, the reactions were quenched by exposing the reaction mixtures to air. The crude product mixtures were filtered through a plug of neutral alumina (hexanes as eluent) to remove inorganic residues. After solvent removal by rotatory evaporation, the trans-head-to-head dimers were conveniently isolated by vacuum sublimation or fractional crystallization.

(b) 2-Ethynylisobenzofuran. Substrate (1.86 g, 14.1 mmol, 800 equiv.) was added to a hexane solution of Cp*2LaCH(SiMe3)2 and stirred for 1 day at room temperature. After above work-up, trans-1,4-di-(2-methoxyphenyl)but-1-en-3-yne (12e) was isolated as light-yellow crystals from a methanol/benzene solution at low temperature. Yield: 781.3 mg (42%).

(c) 2-Ethynylindene. Substrate (158.0 mg, 1.46 mmol, 83 equiv.) was added to a hexane solution of Cp*2LaCH(SiMe3)2. After above work-up, trans-1,4-di(2-thienyl)but-1-en-3-yne (12d) was isolated as off-white solid by vacuum sublimation (80 ºC, 1 mmHg). Yield: 115.3 mg (73%).

(d) 3-Ethynylindene. Substrate (100.5 mg, 929 µmol, 53 equiv.) was added to a hexane solution of Cp*2LaCH(SiMe3)2. After above work-up, trans-1,4-di(3-thienyl)but-1-en-3-yne (12e) was isolated as colorless crystals by slow evaporation of methanol onto a benzene solution at room temperature. Yield: 55.4 mg (55%).
NMR tube reaction of [(Cp*₂La)(η₆-η₃-η₃-η₃-PhC₆H₅)] (22a) with THF. THF (0.50 µL, 6.2 µmol) was added with a microsyringe to an NMR tube containing [(Cp*₂La)(η₆-η₃-η₃-η₃-PhC₆H₅)] (6.2 mg, 6.1 µmol) in benzene-d₈. The reaction was followed for 16 h at room temperature, but no change was observed. Similarly, the addition of excess THF (4.5 µL, 56 µmol) did not result in a change in the reaction mixture as observed with ¹H NMR spectroscopy after 1 day at room temperature. When the reaction mixture was increased to 80 °C, a color change from dark-red to light-yellow was observed after 1 h. After 11 h, ¹H NMR spectroscopy indicated the presence of Cp*²LaCCPh(THF) (by comparison with an authentic sample, vide infra) and unidentified Cp*⁻¹H NMR resonances. D₂O was added to reaction mixture and GC/GC-MS analysis indicated the presence of phenylacetylene-δ, Cp*D and small amounts of unidentified compounds (e.g. m/z = 107 and 205).

Thermolysis of Cp*₂LaCCPh(THF). A solution of Cp*₂LaCCPh(THF) (22.6 mg, 38.3 µmol) in benzene-d₈ was heated to 100 °C and the reaction was followed in situ with ¹H NMR spectroscopy. After 8 min Cp*₂LaCCPh(THF) was converted for 56% into [(Cp*₂La)(η₆-η₃-η₃-PhC₆H₅)] and for 64% after 138 min. Further heating to 100 °C did not lead to a significant change, but additional unidentified Cp*⁻¹H NMR resonances were observed after 6 h at 100 °C. After 12 h the mixture was allowed to cool to room temperature and red crystal formed upon standing at room temperature. Decantation and NMR analysis in benzene-d₈ led to the identification of the red crystals as [(Cp*₂La)(η₆-η₃-η₃-PhC₆H₅)]. D₂O was added to remaining part of the reaction mixture and GC/GC-MS analysis indicated the presence of phenylacetylene-δ, Cp*D and small amounts of unidentified compounds (e.g. m/z = 107 and 205) similar to those observed in the reaction of [(Cp*₂La)(η₆-η₃-η₃-PhC₆H₅)] with excess THF at 80 °C (vide supra).

Kinetics of the C-C coupling reaction in [Cp*₂La(µ-CCR)]₂ complexes. A stock solution was prepared by dissolving Cp*₂LaCH(SiMe₃)₂ (80.0 mg, 141 µmol) in toluene-d₈ (4.00 mL). The solution was transferred into a pre-weighted vial with screw-cap and weighted. In a typical experiment, an NMR tube was charged with 500.0 µL of the stock solution using a 500.0-µL microsyringe. The NMR tube was connected to the high-vacuum line and a specified volume of substrate was condensed onto the solution at -196 °C. After substrate addition, the tube was sealed off in vacuo and kept at -30 °C after use. A Teflon-capped NMR tube was charged with 500.0 µL of the stock solution using a 500.0-µL microsyringe. The prerequisite amount of 1-alkyne was added with a microsyringe to the solution of Cp*₂LaCCPh(THF). The resulting mixture was analyzed with NMR spectroscopy and the relative amount of species present could be determined by quantitative ¹H NMR spectroscopy (pulse delays of 30 s to avoid signal saturation under anaerobic conditions and long experiment times in order to obtain good signal-to-noise ratios) using hexamethyldisiloxane as an internal standard. The progress of reaction was followed in situ with ¹H NMR spectroscopy for several hours, but no changes in the relative amounts of the species present were observed after 8 min at room temperature. The reaction was performed at least two times and the integral data thus obtained provided average values and the experimental error.

Transmetalation reactions of Cp*₂LaCCPh(THF) with 2- and 3-ethylthiophene. (a) General procedure. A stock solution was prepared by dissolving Cp*₂LaCCPh(THF) (151.8 mg, 262.4 µmol) and hexamethyldisiloxane (85.0 µL, 400 µmol) in benzene-d₈ (3.00 mL). The solution was transferred into a vial with screw-cap and stored at -30 °C after use. A Teflon-capped NMR tube was charged with 500.0 µL of stock solution using a 500.0-µL microsyringe. The prerequisite amount of 1-alkyne was added with a microsyringe to the solution of Cp*₂LaCCPh(THF). The resulting mixture was analyzed with NMR spectroscopy and the relative amount of species present could be determined by quantitative ¹H NMR spectroscopy (pulse delays of 30 s to avoid signal saturation under anaerobic conditions and long experiment times in order to obtain good signal-to-noise ratios) using hexamethyldisiloxane as an internal standard. The progress of reaction was followed in situ with ¹H NMR spectroscopy for several hours, but no changes in the relative amounts of the species present were observed after 8 min at room temperature. The reaction was performed at least two times and the integral data thus obtained provided average values and the experimental error.

(b) 2-Ethynylthiophene. 2-Ethynylthiophene (4.51 µL, 42.5 µmol) was added with a microsyringe to an NMR tube containing 500.0 µL of the prepared stock solution of Cp*₂LaCCPh(THF) (42.5 µmol). ¹H NMR spectroscopy indicated the presence of Cp*₂LaCCPh(THF), Cp*₂LaCC(2-C₆H₅S) (by comparison with an
authentic sample, vide infra), phenylacetylene and 2-ethynylthiophene in a 0.065:0.31:0.275:0.100 ratio, respectively.

3-Ethynylthiophene: 3-Ethynylthiophene (4.26 µL, 42.5 µmol) was added with a microsyringe to an NMR tube containing 500.0 µL of the prepared stock solution of Cp*3LaCCPh(THF) (42.5 µmol). 1H NMR spectroscopy indicated the presence of Cp*3LaCCPh(THF), Cp*3LaCC(3-C4H3S)·THF (by comparison with an authentic sample, vide infra), phenylacetylene and 3-ethynylthiophene in a 0.54:0.71:0.69:0.71 ratio, respectively.

NMR tube reaction of Cp*3LaCCPh(THF) with pyridine. Pyridine (3.5 µL, 43 µmol) was added with a microsyringe to a solution of Cp*3LaCCPh(THF) (24.6 µg, 42.5 µmol) in benzene-δ. The clean formation of Cp*3LaCCPh(NC5H5) and free THF was observed. The reaction was followed for several hours with 1H NMR spectroscopy, but no change was observed after 8 min at room temperature. The addition of excess THF (42.5 µL, 425 µmol, 10 equiv.) did not result in shifted proton NMR resonances for THF and pyridine. Evaporation to dryness and dissolution in benzene-δ allowed for its characterization.

Cp*3LaCCPh(NC5H5): 1H NMR (500 MHz, C6D6, 25 °C): δ 2.10 (s, C5Me5, 30 H), 6.48 (ddd, JCH = 7.7 Hz, Jαβ = 4.6 Hz, Jαi = 1.4 Hz, p-CH, 2 H), 6.76 (t, JCH = 7.7 Hz, Jαβ = 1.7 Hz, p-CH, 1 H), 7.00 (dt, JCH = 7.4 Hz, Jαβ = 1.5 Hz, p-CH, 1 H), 7.12 (dt, Jαβ = 7.7 Hz, Jαi = 1.6 Hz, m-CH, 2 H), 7.73 (dt, Jαβ = 7.7 Hz, Jαi = 1.6 Hz, o-CH, 2 H), 8.54 (dt, Jαβ = 5.5 Hz, Jαi = 1.5 Hz, o-CH, 2 H). 13C NMR (125.7 MHz, C6D6, 25 °C): δ 11.26 (q, JCH = 125.0 Hz, C5Me5), 106.08 (s, C5Me5), 124.68 (dd, JCH = 166.6 Hz, Jαβ = 6.8 Hz, β-CH), 125.77 (dd, JCH = 160.6 Hz, Jαβ = 7.8 Hz, p-CH), 128.35 (dd, JCH = 158.6 Hz, Jαβ = 9.2 Hz, m-CH), 131.93 (dt, JCH = 160.2 Hz, Jαβ = 7.1 Hz, o-CH), 138.69 (dd, JCH = 163.8 Hz, Jαβ = 6.18 Hz, γ-CH), 148.25 (d, JCH = 180.1 Hz, α-CH). 1H-13C gHSQC (500-125.7 MHz, C6D6, 25 °C): δ 2.09 → 11.26, 6.46 → 124.5, 6.74 → 138.7, 6.99 → 125.8, 7.12 → 128.3, 7.71 → 131.7, 8.48 → 148.26. 1H-13C gHMBC (500-125.7 MHz, C6D6, 25 °C): δ 6.29 → 119.22, 7.12 → 131.94-128.37, 7.73 → 131.94-128.75-106.09.

Synthesis of [Cp*3La(μ-η’-q2-(2-MeC5H5)2C(2-MeC5H5))2] (22b). An aliquot of 2-ethynyltoluene (17.0 mg, 146 µmol) was added with a microsyringe to a stirred suspension of [Cp*3La(μ-H)] (60 mg, 73 µmol) in hexane (10 mL). The pale yellow suspension turned dark immediately. After being stirred for 1 h at room temperature, the resulting dark red solution was concentrated in vacuo and low-temperature crystallization afforded dark-red crystals. Yield: 56 mg (73%).

1H NMR (500 MHz, C6D6, 25 °C): δ 1.97 (s, C5Me5, 30 H), 2.33 (s, C7H3, 3 H), 6.82 (d, Jαβ = 7.4 Hz, o-CH, 1 H), 7.07 (t, Jαβ = 7.4 Hz, CH, 1 H), 7.21 (t, Jαβ = 7.6 Hz, CH, 1 H), 7.24 (t, Jαβ = 7.5 Hz, m’-CH, 1 H). 13C{1H} NMR (125.7 MHz, C6D6, 25 °C): δ 11.23 (C5Me5), 21.76 (CH), 120.28 (CMe5), 126.63 (CH), 126.90 (CH), 131.22 (CH), 131.59 (CH), 137.67 (α-C), 140.18 (CMe5), 153.78 (LaC), 214.24 (LaC). 1H NMR (500 MHz, C6D6, 25 °C): δ 1.80 (s, C5Me5, 30 H), 2.21 (s, CH3, 3 H), 6.70 (br, s, o-CH, 1 H), 7.04 (t, Jαβ = 7.1 Hz, m-CH, 1 H), 7.15 (t, Jαβ = 7.1 Hz, p-CH, 1 H), 7.25 (d, Jαβ = 7.3 Hz, m-CH, 1 H). The broad 1H NMR resonance at δ 6.70 ppm became sharper at higher temperatures. At 85 °C a doublet was observed (see text for more details). 1H{1H} NMR (125.7 MHz, C6D6, 25 °C): δ 11.10 (C5Me5), 179.82 (CMe5), 126.50 (m-CH), 126.63 (p-CH), 130.09 (m-CH), 139.70 (CMe5). Neither the 1H{1H} NMR resonances of the i-C and o-CH groups were observed, nor was the LaCCC resonance. The 13C NMR resonance of the CH2 group overlaps with that of the residual proto-solvent, as seen with a 1H-13C correlation experiment. 1H-13C gHSQC (500-125.7 MHz, C6D6, 25 °C): 1.80 → 11.08, 2.22 → 21.39, 7.04 → 126.63, 7.15 → 126.50, 7.25 → 130.09. 1H-13C gHMBC (500-125.7 MHz, C6D6, 25 °C): 1.80 → 119.78, 2.21 → 139.70-130.09, 7.15 → 139.70-130.09, 7.25 → 139.70-126.50. Anal. Calcd. for C48H16La2S2: (808.82): C, 56.43%; H, 9.22%. Found: C, 56.23%; H, 9.09%.

Synthesis of [Cp*3La(μ-η’-q2-(2-C5H5S)2C(2-C5H5S))] (22d). An aliquot of 2-ethynylthiophene (18.5 mg, 171 µmol) was added with a microsyringe to a stirred suspension of [Cp*3La(μ-H)] (70 mg, 85 µmol) in hexane (15 mL). The pale yellow suspension turned dark red immediately. After being stirred for 1 h at room temperature, the resulting dark red solution was concentrated in vacuo and low-temperature crystallization afforded dark-red crystals. Yield: 71 mg (81%).
Synthesis of Cp*LaCCPh-THF (20a-THF). An aliquot of phenylacetylene (9.0 mg, 88 µmol) was added with a microsyringe to a solution of Cp*La(NiSiMe3)2 (50 mg, 88 µmol) in THF (2 mL). After stirring for 12 h at 80 °C, the resulting solution was evaporated to dryness and an off-white solid was obtained. Yield: 48.6 mg (93%).

1H NMR (500 MHz, C6D6, 25 °C): δ 2.02 (s, C5Me5, 30 H), 7.04 (dd, 3JCH = 6.6 Hz, 2JCH = 1.1 Hz, 3JCH = 1.2 Hz, p-CH, 1 H), 7.13 (t, 2JCH = 7.6 Hz, 3JCH = 1.7 Hz, m-CH, 2 H), 7.27 (dt, 1JCH = 8.0 Hz, 2JCH = 1.1 Hz, o-CH, 2 H). 13C{1H} NMR (125.7 MHz, C6D6, 25 °C): δ 11.42 (C5Me5), 105.51 (i-C), 119.23 (C5Me5), 125.93 (CH), 126.80 (CH). The 13C NMR resonances of the LaCC fragment were not observed.

1H NMR (500 MHz, C6D6, 25 °C): δ 1.20 (m, β-THF, 4 H), 2.13 (s, C5Me5, 30 H), 3.57 (m, α-THF, 4 H), 6.98 (tt, 1JCH = 7.4 Hz, 2JCH = 1.5 Hz, p-CH, 1 H), 7.10 (t, 2JCH = 7.7 Hz, 3JCH = 1.7 Hz, m-CH, 2 H), 7.67 (dt, 1JCH = 7.2 Hz, 2JCH = 1.5 Hz, o-CH, 2 H). 13C{1H} NMR (125.7 MHz, C6D6, 25 °C): δ 11.25 (q, 3JCH = 125.0 Hz, C5Me5), 24.25 (t, 1JCH = 133.5 Hz, β-THF), 68.71 (t, 148.6 Hz, α-THF), 105.52 (s, i-C), 119.23 (s, C5Me5), 125.71 (dt, 3JCH = 160.9 Hz, 2JCH = 7.4 Hz, β-CH), 128.33 (dd, 1JCH = 158.9 Hz, 1JCH = 7.7 Hz, m-CH), 131.86 (dd, 1JCH = 158.4 Hz, 2JCH = 7.0 Hz, o-CH). The 13C NMR resonances of the LaCC fragment were not observed. 1H-13C gHSQC (500-125.7 MHz, C6D6, 25 °C): δ 2.13 ↔ 11.25, 6.97 ↔ 125.86, 7.10 ↔ 128.41, 7.66 ↔ 131.80. 1H-13C gHMBC (500-125.7 MHz, C6D6, 25 °C): δ 2.13 ↔ 119.24, 6.98 ↔ 132.2, 7.10 ↔ 132.2-125.9, 7.68 ↔ 132.2-125.9-105.3.

Synthesis of Cp*LaCC(2-C3H5)-THF (20d-THF). An aliquot of 2-ethylcyclohexi nene (9.5 mg, 88 µmol) was added with a microsyringe to a solution of Cp*La(NiSiMe3)2 (50 mg, 88 µmol) in THF (2 mL). After stirring for 12 h at 80 °C, the resulting solution was evaporated to dryness and an off-white solid was obtained. Yield: 48.0 mg (93%).

1H NMR (500 MHz, C6D6, 25 °C): δ 2.00 (s, C5Me5, 30 H), 6.79 (dd, 2JCH = 5.1 Hz, 1JCH = 3.5 Hz, β-CH), 6.83 (dd, 3JCH = 3.5 Hz, 2JCH = 1.2 Hz, γ-CH), 6.98 (dd, 1JCH = 5.1 Hz, 2JCH = 1.2 Hz, α-CH). 13C{1H} NMR (125.7 MHz, C6D6, 25 °C): δ 11.40 (C5Me5), 97.98 (i-C), 119.72 (C5Me5), 123.78 (CH), 127.13 (CH), 126.86 (CH). The 13C NMR resonances of the LaCC fragment were not observed. 1H NMR (500 MHz, C6D6, 25 °C): δ 1.20 (m, β-THF, 4 H), 2.10 (s, C5Me5), 3.57 (m, α-THF, 4 H), 6.64 (m, ν-CH), 6.64 (m, α-CH), 7.14 (m, γ-CH).

13C{1H} NMR (125.7 MHz, C6D6, 25 °C): δ 11.27 (q, 1JCH = 125.0 Hz, C5Me5), 24.21 (t, 1JCH = 133.2 Hz, β-THF), 68.65 (t, 148.3 Hz, α-THF), 98.00 (s, i-C), 119.37 (s, C5Me5), 123.43 (dd, 3JCH = 185.3 Hz, 2JCH = 10.7 Hz, 1JCH = 7.4 Hz, ν-CH), 126.84 (dd, 1JCH = 166.3 Hz, 3JCH = 6.0 Hz, 2JCH = 3.7 Hz, β-CH), 128.65 (dd, 1JCH = 165.8 Hz, 2JCH = 6.6 Hz, 3JCH = 8.0 Hz, γ-CH). The 13C NMR resonances of the LaCC fragment were not observed. 1H-13C gHSQC (500-125.7 MHz, C6D6, 25 °C): δ 2.10 ↔ 11.23, 6.64 ↔ 123.47-128.69, 7.14 ↔ 128.65. 1H-13C gHMBC (500-125.7 MHz, C6D6, 25 °C): δ 2.10 ↔ 119.37, 6.64 ↔ 128.65, 7.14 ↔ 128.65.

Synthesis of Cp*LaCC(3-C3H5)-THF (20e-THF). An aliquot of 3-ethylcyclohexi nene (9.5 mg, 88 µmol) was added with a microsyringe to a solution of Cp*La(NiSiMe3)2 (50 mg, 88 µmol) in THF (2 mL). After stirring for 12 h at 80 °C, the resulting solution was evaporated to dryness and an off-white solid was obtained. Yield: 44.5 mg (93%).

1H NMR (500 MHz, C6D6, 25 °C): δ 2.01 (s, C5Me5), 6.93 (dd, 3JCH = 4.9 Hz, 2JCH = 1.2 Hz, β-CH), 7.07 (dd, 1JCH = 3.0 Hz, 3JCH = 1.2 Hz, α-CH), 7.11 (dd, 2JCH = 4.9 Hz, 3JCH = 3.0 Hz, α-CH). 13C{1H} NMR (125.7 MHz, C6D6, 25 °C): δ 11.38 (C5Me5), 24.24 (t, C5Me5, 30 H), 3.57 (m, α-CH), 6.77 (dd, 1JCH = 5.0 Hz, 2JCH = 3.1 Hz, α-CH), 7.19 (dd, 3JCH = 5.0 Hz, 1JCH = 1.1 Hz, β-CH), 7.11 (dd, 1JCH = 3.1 Hz, 2JCH = 1.1 Hz, γ-CH). 13C{1H} NMR (125.7 MHz, C6D6, 25 °C): δ 11.27 (q, 3JCH = 125.0 Hz, C5Me5), 24.32 (t, 1JCH = 133.4 Hz, β-THF), 69.07 (t, 148.7 Hz, α-THF), 99.76 (s, i-C), 119.24 (s, C5Me5), 124.23 (dd, 3JCH = 185.4 Hz, 2JCH = 7.7 Hz, 1JCH = 5.9 Hz, α-CH), 128.38 (dd, 1JCH = 186.1 Hz, 3JCH = 8.6 Hz, 2JCH = 4.3 Hz, γ-CH), 131.03 (dd, 1JCH = 168.4 Hz, 3JCH = 4.6 Hz, 2JCH = 8.7 Hz, β-CH). The 13C NMR resonances of the LaCC fragment were not observed. 1H-13C gHSQC (500-125.7 MHz, C6D6, 25 °C): δ 2.13 ↔ 11.27, 6.77 ↔ 124.28, 7.19 ↔ 131.07, 7.20 ↔ 124.94. 1H-13C gHMBC (500-125.7 MHz, C6D6, 25 °C): δ 2.12 ↔ 119.24, 7.19 ↔ 124.2.
Appendix. The acidity of the studied 1-alkynes

Introduction

The term acidity or acid strength comprises both a thermodynamic and kinetic aspect. Kinetic acidity is related to the rate of proton transfer, while thermodynamic acidity refers to the position of equilibria between acids and their conjugate bases. The rates of proton transfer have been measured for many oxygen and nitrogen acids (termed normal acids) and found to be diffusion-controlled in aqueous solution. Proton transfers tend to be much slower in non-aqueous solvents than in water, especially in non-protic media. In general, carbon acids (termed pseudo acids) undergo proton transfer reactions at a much lower rate than oxygen and nitrogen acids. It is commonly believed that the intrinsically slow rate of proton transfer in carbon acids is the result of the delocalized nature of the proton-accepting electron pairs in the carbon bases, whereas the proton-accepting electron pairs in oxygen and nitrogen acids are localized on single atoms. The proton transfer rates of 1-alkynes have been found to be diffusion-controlled in aqueous solution, on the basis of unit-slope Brønsted relationships (vide infra). These findings suggested that the carbanionic electron pair of the acetylide ion resides in a localized sp hybrid orbital and that 1-alkynes behave as normal acids rather than pseudo acids. More recently, doubt was cast on this common belief by the observation of primary kinetic isotope effects in proton-transfer reactions of certain 1-alkynes, indicating rate-limiting proton transfer.56

Kinetic acidity and inductive/field effects

The acidities of most of the 1-alkynes employed in this study are not known in literature, but it is believed that the relative order of acidity can be approximated by reported empirical relationships. The kinetic acidity of a number of 1-alkynes have been determined experimentally by measuring the rate of base-catalyzed hydrogen-isotope exchange. Even though many of the early investigations in this field have dealt with the effect
Chapter 5

of the substituent on the rate of isotopic exchange and empirical relationships between substituent parameters and the rate of exchange were found, the number and structural diversity of the 1-alkynes considered in each study has often been somewhat limited.87 A study of 17 substituted phenylacetylenes of which the rate of detritiation were measured in aqueous buffer solution at 25 °C revealed a linear correlation for meta- and para-substituents and their corresponding Hammett σ constants (vide infra).87e Interestingly, the relative rates of ortho-methyl and ortho-methoxy substituted phenylacetylenes were identical and both 0.78-fold lower than that of phenylacetylene. The absence of significant steric effects in this system was demonstrated by the observed rate of mesitylacetylene which differed only 14% from that calculated by assuming additivity of the effects of three methyl groups.

A more recent study in this field, based on the rate of base-catalyzed hydrogen exchange of 13 substituted 1-alkynes in aqueous buffer solution, revealed a good linear correlation between the rate of hydrogen-exchange and inductive or field substituent constants σI (vide infra).87j The observation that the addition of resonance substituent constants did not improve the correlation implied that resonance interactions of the 1-alkyne substituent are of minor importance in determining the kinetic acidity and that the kinetic acidity of 1-alkynes can be estimated from the inductive or field constants σI alone. Even though this conclusion was in contradiction with some early studies in this field, it did support the common belief that the carbanionic electron pair of the acetylide ion resides in an sp hybrid orbital which is orthogonal to the acetylenic π-system. Because delocalization of this electron pair by conjugation with the π-system is not possible, the electrons are localized on a single atom and 1-alkynes behave as normal acids (vide supra). Other more recent studies also confirmed the notion that the substituent effect in 1-alkynes is mainly a field/inductive effect.88

A number of important relationships between substituent groups and chemical properties have been developed over the last decades.89 In many cases, such relationships can be expressed quantitatively and are valuable for the interpretation of reaction mechanisms and for the prediction of reaction rates and equilibria. The most widely used of these relationships is the Hammett equation, which referred originally to the acidity of m- and p-substituted benzoic acids. On the basis of linear free energy relationships, substituent constants σ were derived that can be used as a measure of the substituent’s electronic effect at the reaction site. The recognition that substituent effects are transmitted either through the σ framework (induction and field effects) or a

<table>
<thead>
<tr>
<th>R</th>
<th>σI</th>
<th>σR</th>
<th>F</th>
<th>JCH</th>
<th>JCH</th>
<th>JCH</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.12</td>
<td>-0.13</td>
<td>0.12</td>
<td>-0.13</td>
<td>77.83</td>
<td>83.89</td>
</tr>
<tr>
<td>b</td>
<td>0.10</td>
<td>-0.13</td>
<td>0.12</td>
<td>-0.15</td>
<td>81.53</td>
<td>82.78</td>
</tr>
<tr>
<td>c</td>
<td>0.11</td>
<td>-0.19</td>
<td>0.13</td>
<td>-0.21</td>
<td>81.83</td>
<td>80.52</td>
</tr>
<tr>
<td>d</td>
<td>0.19</td>
<td>-0.14</td>
<td>0.13</td>
<td>-0.08</td>
<td>81.88</td>
<td>77.22</td>
</tr>
<tr>
<td>e</td>
<td>0.10</td>
<td>-0.12</td>
<td>0.08</td>
<td>-0.10</td>
<td>77.54</td>
<td>79.10</td>
</tr>
<tr>
<td>f</td>
<td>0.17</td>
<td>0.20</td>
<td>0.50</td>
<td>-0.13</td>
<td>81.51</td>
<td>76.38</td>
</tr>
<tr>
<td>g</td>
<td>0.20</td>
<td>-0.03</td>
<td>0.40</td>
<td>-0.23</td>
<td>77.33</td>
<td>83.56</td>
</tr>
</tbody>
</table>

The values for σR were calculated from the relationship σR = σp – σI. The values for σI, σp, F and R were obtained from Ref. 51a. The values for 2b, 2c and 2f were approximated with those of C6H4Me-p, C6H4OMe-p and 2-pyrryl, respectively. NMR experiments were conducted in C6D6 under nitrogen at 25 °C. Chemical shifts are reported in ppm relative to TMS and JCH coupling constant (in brackets) are reported in Hz. Repeated experiments suggested that 13C chemical shifts were accurate to ± 0.02 ppm, 1H chemical shifts to ± 0.01 ppm and JCH coupling constants to ± 0.2 Hz.
delocalized π system (resonance) led to a number of methods to split σ values into inductive and resonance contributions. Among these dual-parameter correlations, the substituent constants σ_I and σ_R, on the one hand, and, F and R, on the other hand, represent the most widely used indicators for the ability of a substituent to interact via an inductive/field and resonance mechanism, respectively.

Kinetic acidity and NMR spectroscopy

A second method to estimate 1-alkyne acidity makes use of 13C NMR spectroscopy. NMR shielding in alkynes is presently not well understood and studies have been performed on simple models only. Even so, linear free energy relationships are routinely used to correlate NMR data with Hammett constants in order to determine the transmission of inductive and resonance electronic effects in conjugated systems. This approach is based on the assumption that substituent-induced chemical shifts in NMR spectra primarily depend on the electronic density of the probe nucleus. Substituent effects on the chemical shifts of alkylene carbon atoms have received considerably less attention than analogous effects in other aromatic systems.

Nonetheless, a study of 18 para-substituted phenylacetylenes revealed that the substituent-induced changes in carbon and proton chemical shifts correlate well with Hammett substituent constants, when NMR experiments are conducted under certain conditions (i.e. measurements in an inert solvent, such as in cyclohexane-d12, and under an inert atmosphere, the use of a relatively large number of analogues and the extrapolation of the NMR parameters to infinite dilution). It was concluded that both inductive/field and resonance effects are important in determining the electronic distribution in phenylacetylenes. The authors argued that the observed correlations provided evidence that substituent-induced changes in the proton and carbon chemical shifts in phenylacetylene reflect intramolecular electronic effects with insignificant contributions from solvent and magnetic anisotropy effects. In accord with this view, similar, but poorer correlations were found in a recent study of 13 para- and meta-substituted phenylacetylenes that were measured in chloroform-d1 in air.

The 1-alkynes used in this study were measured in benzene-d6 under a nitrogen atmosphere at relatively low concentrations (0.5-1 mol%) and the NMR parameters acquired are shown in Table 5-9. The fair correlation between the measured carbon chemical shifts and the carbon chemical shifts calculated from the empirically established relationships with F and R provided assurance that the present NMR data represent intramolecular electronic effects to a reasonable degree (Figure 5-19). The discrepancies are most likely due to the magnetic anisotropy effects arising from ortho-substituents, such as in 2-ethynylanisole (2e) and 1-methyl-2-ethynylpyrrole (2g). The fair correlation suggest, in addition, that Hammett substituent constants can be used to investigate the electronic effects of the present (hetero)aromatic 1-alkyne substituents. Other reported
correlations of the proton chemical shift (CC\textsubscript{H}) with either the terminal carbon chemical shift (CC\textsubscript{C}) or its first-order carbon hydrogen coupling constant (\textit{J}\textsubscript{CH}) were not found, most likely due to the larger solvent effects in the \textit{^1}H NMR spectral parameters.

Many studies reported in literature have demonstrated the validity of the well-known linear relationship between the rate of proton transfer from a carbon acid and the first-order carbon-hydrogen coupling constant of the corresponding carbon (\textit{J}\textsubscript{CH}).\textsuperscript{98} The rationale for this behavior is found in the relative amount of s-character of the hybrid orbital on the carbon atom. As the s-character increases, the hybrid orbital is more tightly bound to the carbon atom and the C-H bond becomes more polar, thereby increasing the acidity of the hydrogen atom. By the same reasoning, the formed anion is the most stable in the orbital with the highest s-character. In hydrocarbons, the most important factor affecting couplings is the hybridization of the carbon atom. The effects of polar substituents on \textit{J}\textsubscript{CH} are, however, much larger. Because polar groups affect the electrons of the carbon nucleus via their inductive effects without significantly altering the hybridization of the carbon nucleus, the relationship between \textit{J}\textsubscript{CH} and s-character is generally not suitable for estimating the hybridization of the carbon bonding orbital in heteroatom-substituted compounds.

A plot of the coupling constant \textit{J}\textsubscript{CH} of the terminal carbon in the present 1-alkynes against the inductive/field substituent constant \(\sigma\textsubscript{I}\) of the corresponding 1-alkyne substituent (Table 5-9). The line drawn represents a fitted linear plot (see text for details).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5-18.png}
\caption{Plot of the measured coupling constant (\textit{J}\textsubscript{CH}) of the terminal carbon in the present 1-alkynes versus the inductive/field constant \(\sigma\textsubscript{I}\) of the corresponding 1-alkyne substituent (Table 5-9). The line drawn represents a fitted linear plot (see text for details).}
\end{figure}

relationships between kinetic and equilibrium acidity

Transmetalation equilibria have widely been used to determine the relative acidities of hydrocarbons.\textsuperscript{59} Conversely, kinetic acidities have been measured to determine proton-transfer equilibria. The validity of these methods is based on the commonly observed unit-slope Bronsted relationships. The Bronsted relationship relates the kinetic acidity with equilibrium acidity and, generally, they vary in parallel with each other. Linear relationships between equilibrium and kinetic acidity are frequently found for oxygen and nitrogen acids that display diffusion-controlled proton transfer rates. In contrast, Bronsted plots for proton transfer at
carbon acids and bases are more complex, due to the need for rehybridization and changes in the geometry of the acid or base upon proton transfer.

Unit-slope Brønsted plots have been reported for proton transfer reactions of a number of 1-alkynes in aqueous solution. However, the reactions in this study were performed in non-polar, aprotic solvents, such as benzene and THF. Because proton transfers are well-known to decrease with decreasing solvent polarity and deviations from unit-slope Brønsted plots are well-known to occur, when proton transfers take place at less than diffusion-controlled rates, it seems not unreasonable to assume that Brønsted plots will not be linear for 1-alkynes in non-polar, aprotic solvents. Moreover, equilibrium constants in nonpolar media do not generally reflect the free ion acidity, but rather refer to ion pairs. In media of low polarity extensive ion-pairing and formation of aggregates between ions and neutral molecules takes place and the extent of ion-pairing depends on the solvent, the size of the ions, and the charge distribution in ions.

The transmetalation reaction of \( \text{Cp}^*\text{LaCCPh}(\text{THF}) \) with 2-ethynylpyridine (2d) and 3-ethynylthiophene (2e) afforded equilibrium constants of \( K = 0.08(5) \) and \( K = 0.80(4) \), respectively (Section 5.4.5). These values suggest that 2d and 2e are 1.10 and 0.10 pK\(_a\) units, respectively, more acidic than phenylacetylene, thereby contradicting the relative order of kinetic acidities, based on substituent constants (vide supra). In particular, the 3-thienyl group is less electron-donating than the phenyl group, both \( \text{via} \) a field/inductive and a resonance mechanism, according to the well-established substituent constants \( \sigma \), \( \sigma^+ \), \( \pi \), \( R \) and \( F \). The reason for this discrepancy is not known, but this observation seems to support the above assumption that the kinetic acidity of the present 1-alkynes do not vary linearly with the corresponding equilibrium acidity in benzene. Estimating the acidities of the present 1-alkynes by measuring the equilibrium concentrations of the species present in the transmetalation reaction of \( \text{Cp}^*\text{LaCCPh}(\text{THF}) \) with 1-alkynes is therefore considered to be inappropriate.

Concluding remarks

It is believed that the agreement between two independent empirical relationships, i.e. the relationship between the kinetic acidity of 1-alkynes with \( \sigma \) and the relationship between the rate of proton transfer of carbon acids with \( \Delta \sigma^I \), provides reasonable assurance that the order of kinetic acidity for the present 1-alkynes can be estimated on the basis of \( \Delta \sigma^I \) or \( \sigma \) values. In view of the smaller experimental errors in the \( \Delta \sigma^I \) values relative to those in the calculated detritiation rates, the former approach is presently favored. As a consequence, the following relative order of decreasing kinetic acidity based on measured \( \Delta \sigma^I \) values is obtained for the present 1-alkynes: 2-ethynylthiophene (2d) > 2-ethynylpyridine (2f) \( \approx \) 1-methyl-2-ethynylpyrrole (2g) > 3-ethynylthiophene (2b) \( \approx \) phenylacetylene (2a) \( \approx \) 2-ethynylanisole (2e) \( \approx \) 2-ethyltoluene.

5.8. References and notes

6 The reaction of \( \text{Cp}^*\text{LnCH(SiMe}_3\text{)}_2 \) (\( \text{Ln} = \text{La, Ce} \)) with 2,6-di-tert-butyl-4-methylphenol forming the corresponding aryloxide has been reported, see: (a) Heeres, H. J. Ph. D. Thesis, University of Groningen, 1990; Chapter 3. (b) Heeres, H. J.; Teuben, J. H. Recr. Trav. Chim. Pays-Bas 1990, 109, 226.


The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metallocenes


In a simple Henri-Michaelis-Menten description (Eqs. 5.10 and 5.11; E = enzyme, S = substrate, P = product), the Michaelis constant $K_M = (k_1 + k_p)k_0$ refers to the overall effectiveness of substrate capture summed over all catalyst species ([ET] = [E] + [ES]) and $V_{max} = k_p[ET]$ refers to the maximum reaction rate. In the present situation, substrate capture is rapid relative to the substrate-binding step (i.e. $k_0 > k_1$) and the reaction rate is first-order with respect to [S] ($K_M > [S]$). When the effects of reversible, nonproductive substrate and product coordination to the catalyst are included (Eqs. 5.12-5.13), standard rapid equilibrium analysis yields a modified Henri-Michielis-Menten equation which reproduces the observed kinetic behavior (Eq. 5.14).

$$\begin{align*}
(5.10) & \quad E + S \xrightleftharpoons[k_1]{k_p} ES \xrightarrow{k_0} E + P \\
(5.11) & \quad \frac{d[S]}{dt} = \frac{k_0[E_1][S]}{K_M + [S]} = \frac{V_{max} [S]}{K_M + [S]} \\
(5.12) & \quad E + S \xrightleftharpoons[K_S]{K_P} ES \\
(5.13) & \quad E + P \xrightarrow[K_P]{K_P} EP \\
(5.14) & \quad \frac{d[S]}{dt} = \frac{k_p[E_1][S]}{K_M \left(1 + \frac{[S]}{K_M} + \frac{[P]}{K_P}\right)} = \frac{k_p[E_1][S]}{K_M \left(1 + \frac{(K_S + K_M)[S]}{K_M K_S} + \frac{[P]}{K_P}\right)}
\end{align*}$$

Determination of initial rates may shed more light on the possibility of substrate self-inhibition, but the rapid rate of substrate conversion, the occurrence of catalyst deactivation at very low precatalyst concentration (due to traces of O2 and H2O) and the long relaxation times of the acetylenic proton do...

For examples where the $\pi$-donating ability of amide (L-n-NR$_2$) or azomethine (L-n-N=CR$_2$) ligands has been implicated by the observed reactivity or structure in rare-earth metal chemistry, see: (a) Bercaw, J. E.; Davies, D. L.; Wolczenski, P. T. *Organometallics* 1986, **5**, 443. (b) Heeres, H. J.; Meetsma, A.; Teuben, J. H. *Angew. Chem.* 1990, **102**, 449. (c) Knight, L. K.; Piers, W. E.; Lessard-Fleurat, P.; Parvez, M.; McDonald, R. *Organometallics* 2004, **23**, 2087.

For comparison, the pK$_a$ of Ph$_2$NH (24.95) in an aprotic, polar solvent, DMSO, is considerably lower at 25 ºC than that of Ph$_2$CH$_2$ (32.2), see: Bordwell, F. G. *J. Org. Chem.* 1985, **50**, 4492. For a review, see: (d) Ref. 5b.


The oligomerization of (hetero)aromatic 1-alkynes catalyzed by rare-earth metallocenes


The mechanism of ortho-alumination is considered to be more complex than that of the conventional ortho-lithiation, but complex-induced proximity effects are believed to play an important role, see: Uchiyama, M.; Naka, H.; Matsumoto, Y.; Ohwada, T. J. Am. Chem. Soc. 2004, 126, 10526.


Experimental errors were determined by statistical analysis of values obtained from at least two experiments.

The Cp* ligands in each Cp*La moiety are crystallographical equivalent, but the two Cp*La moieties in 22a·2C7H8 are not. Two conformations were found for each Cp* ligand, resulting in two different environments for each lanthanum metal in 22a·2C7H8. The average twist angles are 0.0(7)° for La1 and 0(1)° for La2. In one conformation, La1 is coordinated to both the C1Aa-C5Aa ring (Cp1a) with centroid Ct1a and the C1Aa-C5Aa ring (Cp1a) with centroid Ct1a, while La2 is coordinated to both the C11C-C15C ring (Cp2a) with centroid Ct2a and the C11Ca-C15Ca ring (Cp2a) with centroid Ct2a. In the other conformation, La1 is coordinated to both the C1B-C5B ring (Cp1b) with centroid Ct1b and Cp2b. The distance averages between metal and Ct-La-Ct. The bond averages of centroid-metal-centroid in each conformation are denoted by La1-Ct1a and Ct3-La1-Ct31 is denoted by Ct-La1 -Ct, while the distance average of La2-Ct2 and La2-Ct 4 is denoted by La2-Ct. The bond average of Ct1-La2-Cp2a and Ct1-La2-Cp2a and Ct4-La2-Ct4a is denoted by Ct-La2-Ct.

The two Cp*La moieties are crystallographically equivalent, whereas the Cp* ligands in each Cp*La moiety are not, resulting in four different environments for the metal center in 22d·2C7H8. The Cp* ligands are more eclipsed than staggered, as evidenced by twist angles of 24(2), 12(2), 11.3(3) and 12(2)° in each conformation (compared to 36° for a perfectly staggered arrangement). In the first conformation La is coordinated to both the C1Aa-C5Aa ring (Cp1a) with centroid Ct1a and the C11C-C15C ring (Cp1a) with centroid Ct2a. In the second conformation La is coordinated to both Cp1a and the C11C-C15C ring (Cp1b) with centroid Ct2b. In the third conformation La is coordinated to both Cp1b and Cp2b. The distance averages between metal and Cp in each conformation are denoted by La-Cp. The distance average between metal and centroid in each conformation are denoted by La-Ct. The bond averages of centroid-metal-centroid in each conformation are denoted by Ct-La-Ct.

The twist angle is defined as the average of the five smallest dihedral angles formed between the ten planes which consist of a ring carbon and the two centroids.


Ct is the centroid of the C1-C5 ring (Cp1) and C2 is the centroid of the C1-C5c ring (Cp2). The average distances of the metal to the cyclopentadienyl carbons of each ring are denoted by La-Cp1 and La-Cp2. Selected bond lengths (Å): La-C21, 4.35(13); La-S, 3.1134(7); La-C1, 2.8283(5); La-Cp2, 2.804(5); La-C1, 2.063(1); La-C22, 3.035(1); C21-C22, 1.368(4); C22-C23, 1.4215(9); C23-C24, 1.437(5); C24-S, 1.722(3); C21-S, 1.743(2). Selected bond angles (°): C1-La-C21, 133.91(3), C21-S-C2, 2.804(5); La-C1, 133.9(1), La-C2, 102.7(1); La-S-C21, 124.8(1); S-C21-C22, 105.6(2); C22-C23-C24, 113.1(3); C23-C24-S, 108.8(2).


The υ values are defined by a relationship derived from Van der Waals radii (υX = υX - υM, where υX and υM are the Van der Waals radii of the X group, respectively). Very good correlations have been obtained between these υ values and rates of esterification of substituted carboxylic acids with methanol or ethanol, thereby indicating that the υ values are solely a function of steric effects.

According to the \( E_s \) and \( \nu \) scale, the steric requirements of the phenyl group (\( \nu = 1.66 \), \( E_s = -2.55 \)) are larger than of the tert-butyl group (\( \nu = 1.24 \), \( E_s = -1.54 \)). This discrepancy with other scales has been attributed to the appreciable resonance effect of the phenyl group. More recently, Sung et al. proposed the steric substituent constant \( S_\alpha \) based on isodesmic reactions and \textit{ab initio} calculations of substituted adamantane systems. According to the \( S_\alpha \) scale, the tert-butyl group (\( S_\alpha = -12.45 \)) is considerably larger than the phenyl (\( S_\alpha = -5.10 \)) and the methyl group (\( S_\alpha = -2.02 \)), see: Sung, K.; Chen, F.-L. Organomet. Lett. 2003, 5, 899.

The 2-thienyl group is most likely smaller (\( \nu = 0.51 \), \( \nu = 0.71 \)), more \( \sigma \)-electron-withdrawing (\( F = 0.13 \), \( \sigma = 0.19 \)) and less \( \pi \)-electron-releasing (\( R = -0.08 \)) than the phenyl group (\( \nu = 1.66 \), \( F = 0.12 \), \( \sigma = 0.12 \), \( R = -0.13 \)).

The \( CH_2CH_2Ph \) (\( \nu = 0.70 \), \( F = -0.01 \), \( R = -0.11 \)) and \( CH_2CH_2Pr \) (\( \nu = 0.68 \), \( F(CH_2Pr) = -0.01 \), \( R(CH_2Pr) = -0.11 \)) groups have similar steric and electronic properties. Although the isopropyl group is more \( \sigma \)-electron-withdrawing (\( F = 0.04 \)), its steric bulk is larger (\( \nu = 0.76 \)) and it is more \( \pi \)-electron-releasing (\( R = -0.19 \)) than the \( CH_2CH_2Ph \) and \( CH_2CH_2Pr \) groups.


Although \( \nu \) values indicate that a methyl group (\( \nu = 0.52 \)) is larger than a methoxy group (\( \nu = 0.36 \)), this scale is more suited to aliphatic molecules. To overcome this deficiency, Gallo et al. proposed a scale of \textit{ortho}-steric parameters (\( S^0 \)) based on the kinetics of quaternization by methyl iodide of 33 substituted pyridines in acetonitrile at 33 °C to quantify the sterer size of \textit{ortho}-substituents in (hetero)aromatic compounds. No correlation with electronic substituent effects was found. The \( S^0 \) scale indicates that the \( \alpha \)-methyl group (\( S^0 = -0.73 \)) is smaller than the \( \alpha \)-methoxy group (\( S^0 = -1.28 \)), see: (a) Berg, U.; Gallo, R.; Klatte, G.; Metzger, J. J. Chem. Soc., Perkin Trans.2 1980, 1350. (b) Gallo, R.; Rouse, C.; Berg, U. Adv. Heterocycl. Chem. 1988, 43, 173.

The transition state for alkynyl protonolysis places the aromatic moiety of the incoming alkynyl molecule further away from the metal center. C-H activation seems also to be electronically favored, since it involves a sp carbon and a hydrogen atom orbital which provide more overlap in the four-center transition state than two sp carbon orbitals.

It can be anticipated that the decrease of electron density at the triple bond will weaken the interaction with the electrophilic lanthanide metal. On the other hand, polarization of the triple bond, as to induce
a partial positive charge at the β-position and a partial negative charge at the α-position is well-known to facilitate insertion into electrophilic metal-carbon bonds.66


Both alkyl Cp*2LnR and hydride [Cp*2Ln(µ-H)]2 derivatives undergo facile ortho-metalation of pyridine, possibly followed by C-C coupling reactions. For examples, see: (a) Ringelberg, S. N. Ph. D. Thesis, University of Groningen, 2001; Chapter 4. (b) Ringelberg, S. N. Ph. D. Thesis, University of Groningen, 2001; Chapter 5.
For ¹H NMR data, see: (a) Ref. 10. For ¹3C NMR data, see: (c) Ref. 76c. For infrared data, see: (b) Wentrup, C.; Winter, H.-W. J. Org. Chem. 1983, 105, 5380. (j) Powell, M. F.; Peterson, M. R.; Ciszmadia, I. G. J. Am. Chem. Soc. 1986, 105, 5380. (k) Powell, M. F. J. Org. Chem. 1986, 51, 819. (l) Ref. 80a. (m) Ref. 77l. For MS data, see: (f) Ref. 81b.  (g) Ref. 77l. For infrared data, see: (h) Ref. 77l. (i) Ref. 81a. (j) Ref. 81b. (k) Ref. 77l. (l) Ref. 80a. (m) Ref. 77l. For infrared data, see: (n) Ref. 77c.
Chapter 5

96 Dawson et al. found the following correlations of $^{13}$C chemical shifts in cyclohexane-$d_{12}$ for 4-substituted phenylacetylenes with the $F$ and $R$ values of the corresponding 1-alkyne substituent: (a) $\delta C-1 = \delta^o + 2.86(27) \times F + 5.23(43) \times R$ ($R^2 = 0.988$) and (b) $\delta C-2 = \delta^o + 2.86(27) \times F + 5.23(43) \times R$ ($R^2 = 0.990$), $\delta C-1$ and $\delta C-2$ representing the chemical shift of the terminal and internal carbon, respectively, and $\delta^o$ representing the chemical shift of the corresponding carbon of the unsubstituted phenylacetylene.

