Catalytic Oligomerization of Terminal Alkynes by Lanthanide Carbyls \( \eta^5-C_5Me_5 \) \( \text{Ln} \) \( \text{CH(SiMe}_3 \text{)_2} \) \( \text{Ln} = \text{Y, La, Ce} \)

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Lanthanide and group 3 carbyls \( \text{Cp}^* \) \( \text{Ln} \) \( \text{CH(SiMe}_3 \text{)_2} \) \( \text{Ln} = \text{Y, La, Ce} \) are active catalyst precursors for the oligomerization of terminal alkynes \( \text{HCC} \equiv \text{CR} \) \( \text{R} = \text{alkyl, aryl, SiMe}_3 \). The regioselectivity and the extent of oligomerization depend strongly on the lanthanide applied as well as on the alkylene substituent \( \text{R} \). For yttrium, alkyl-substituted alkynes are dimerized selectively to \( 2,4 \)-disubstituted \( 1 \)-buten-3 ynies whereas mixtures of two enyne isomers, i.e. \( 2,4 \)-disubstituted \( 1 \)-buten-3 ynies and \( 1,4 \)-disubstituted \( 1 \)-buten-3 ynies, are found for phenylacetylene and \( \text{trimethylsilyl} \)acetylene. The reactions with lanthanum and cerium produce, besides dimers, higher oligomers (trimers, tetramers) of various sorts (allenes and dinones). NMR studies indicate that lanthanide acetylides \( \text{Cp}^* \text{LnC} \equiv \text{CR} \), formed by \( \sigma \)-bond metathesis between the carbyl and the acetylene \( \text{CH} \) bond, are the active species in the catalytic cycle. Two oligomeric cerium acetylides \( \text{Cp}^* \text{CeC} \equiv \text{CR} \), \( \text{R} = \text{t-Bu} \); \( \text{R} = \text{Me} \) have been synthesized on a preparative scale. Spectroscopic data for these compounds suggest a significant contribution of the \( \text{CC} \) triple bond in the bonding of the acetylide unit.

Introduction

Linear and cyclooligomerization of terminal alkynes by various transition metals has been studied extensively. However, only a few catalyst systems, mainly based on Pd, Rh, Ru, Cu, or Cr, are known for the dimerization of terminal alkynes. The coupling reactions are not very selective, and in general, mixtures of various dimers are produced: \( 1,4 \)-disubstituted butatrienes, \( 2,4 \)-disubstituted enynes, or \( 1,4 \)-disubstituted enynes (Figure 1).

The first step in the catalytic cycle is believed to be an alkylene \( \text{CH} \) bond activation, which produces the active metal acetylide, \( \text{L} \equiv \text{MC} \equiv \text{CR} \). However, detailed mecha-
natic studies have not been reported yet and the factors that govern regio- and stereoselectivity are not fully understood.

Extensive research in our group\(^4\) on titanium(II) carbyls, Cp\(^*\)TiR, and by Japanese colleagues\(^5\) on less well-defined systems, Cp\(^*\)TiCl\(_2\)/RMgX have shown that these catalyze the dimerization of terminal alkynes. The reactions are remarkably selective and give exclusively linear head-to-tail dimers, 2,4-disubstituted 1-butene-3-ynes. The coupling reactions appear to be rather sensitive to the size of the alkyn substituent R, and bulky alkynes such as tert-butylacetylene could not be dimerized. Recently, it was demonstrated that group 3 alkyls Cp\(^*\)Sc\(^R\) and Cp\(^*\)YR\(^2\) also catalyze the head-to-tail dimerization of propyne to 2-methyl-1-penten-3-yn.

With bent sandwich carbyls Cp\(^*\)LnCH(SiMe\(_3\))\(_2\) of the early lanthanides lanthanum and cerium available,\(^6\) we thought that it would be interesting to investigate the behavior of these complexes to terminal alkynes. Lanthanum and cerium are much larger than titanium, scansium, and yttrium,\(^7\) and this allows the study of the influence of increased space around the metal on the selectivity and activity as well as on the scope of the oligomerization.

Exploratory (NMR tube) experiments revealed that the early lanthanide carbyls are indeed very active catalysts for the oligomerization of terminal alkynes. The process appeared not to stop at the dimer level but to proceed to further oligomers. The oligomerization was accompanied by the quan-

RESULTS AND DISCUSSION

NMR Tube Experiments. The reactions of the yttrium and cerium carbyls, Cp\(^*\)LnCH(SiMe\(_3\))\(_2\) (1, Ln = Y; 3, Ln = Ce) with an excess of alkynes HC≡CR (R = Ph, SiMe\(_3\), and t-Bu) were initially carried out in sealed NMR tubes with benzene-d\(_6\) solutions of 1 and 3. The acetylides [Cp\(^*\)LnC≡CSiMe\(_3\)]\(_n\) (5, \(n = Y\); 6, \(n = Ce\)) were formed quantitatively (eq 2).

\[
\text{Cp}^*\text{LnCH(SiMe}_3\text{)}_2 + \text{HC}≡\text{CPh} \rightarrow \left(\frac{1}{n}\right)[\text{Cp}^*\text{LnC≡CSiMe}_3]_n + \text{CH}_2(\text{SiMe}_3)_2
\]

The reaction of the cerium derivative with phenylacetylene produced a mixture of starting carbyl 3, small amounts of CH\(_2\)(SiMe\(_3\))\(_2\), and several alkyn oligomers. However, in this case clear assignment of resonances arising from [Cp\(^*\)CeC≡CPh]\(_n\) proved not possible.

Excess of (trimethylsilyl)acetylene was slowly converted (ca. 4 h) to a mixture of alkyn oligomers by solutions of 1 and 3. The acetylides [Cp\(^*\)LnC≡CSiMe\(_3\)]\(_n\) (5, \(n = Y\); 6, \(n = Ce\)) were formed quantitatively (eq 2).

\[
\text{Cp}^*\text{LnCH(SiMe}_3\text{)}_2 + \text{HC}≡\text{CSiMe}_3 \rightarrow \text{Ln} = (\text{Y} (1), \text{Ce} (3)) \left(\frac{1}{n}\right)[\text{Cp}^*\text{LnC≡CSiMe}_3]_n + \text{CH}_2(\text{SiMe}_3)_2
\]

The yttrium acetylide is stable under these conditions. However, the cerium derivative was slowly converted to a mixture of yet unidentified cerium compounds. It is likely that these originate from consecutive reactions of 6 with alkyn oligomers (vide infra).

Catalytic activity depends on the solvent applied. For instance, tert-butylacetylene was quickly oligomerized in benzene-d\(_6\) solutions of 3. Like the reaction with phenylacetylene, a mixture of the starting carbyl 3 and [Cp\(^*\)CeC≡C-t-Bu]\(_n\) (7) (ca. 1:1 ratio) were formed together with free CH\(_2\)(SiMe\(_3\))\(_2\). However, the reaction of 3 with tert-butylacetylene in a coordinating solvent such as THF-d\(_4\) only resulted in a stoichiometric reaction and the formation of Cp\(^*\)CeC≡C-t-Bu·THF-d\(_8\) (8-d\(_9\)) together with CH\(_2\)(SiMe\(_3\))\(_2\) (eq 3).

\[
\text{Cp}^*\text{CeC≡C-t-Bu·THF-d}_8 \rightarrow \text{Cp}^*\text{CeC≡C-t-Bu·THF-d}_8 + \text{CH}_2(\text{SiMe}_3)_2
\]

was not observed and even after several weeks at room temperature, the remainder of the tert-butylacetylene was unchanged.

Preparative Catalytic Oligomerization. The standard reaction procedure for preparative alkyn oligomerization involved addition of a large excess of alkyn (>45 mmol of alkyn/mmol of Ln) to hexane or toluene solutions of 1–3. After stirring for 2–2.5 h at room temperature, the reactions were quenched by exposing the mixtures to air and the alkyn oligomers were analyzed by GC, GC/MS, and NMR spectroscopy.

Alkynes HC≡CR (R = n-Pr, t-Bu, SiMe\(_3\), Ph) are oligomerized exclusively to dimers by solutions of Cp\(^*\)YCH(SiMe\(_3\))\(_2\) (1). The regioselectivity of the reactions strongly depends on alkyn applied. Alkynes with alkyl substituents (n-Pr, t-Bu) are very selectively coupled to head-to-tail dimers, 2,4-disubstituted 1-butene-3-ynes (eq 4, Table 1).

\[
\text{Cp}^*\text{YCH(SiMe}_3\text{)}_2 + \text{HC}≡\text{CPh} \rightarrow \left(\frac{1}{n}\right)[\text{Cp}^*\text{YCH(SiMe}_3\text{)}_2]_n + \text{CH}_2(\text{SiMe}_3)_2
\]

will be discussed in more detail further on.

Addition of an excess of phenylacetylene to benzene-d\(_6\) solutions of 1 and 3 resulted in a quick catalytic reaction and after ca. 10 min, all alkyn was oligomerized. For yttrium, oligomerization was accompanied by the quantitative formation of [Cp\(^*\)YCH(SiMe\(_3\))\(_2\)]\(_n\) (4) and CH\(_2\)(SiMe\(_3\))\(_2\) (eq 1).
Table I. Product Distributions for the Oligomerization of Terminal Alkynes by Compounds \( \text{Cp}^*\text{LnCH(SiMes)}_2 \) (Ln = Y, La, and Ce)

<table>
<thead>
<tr>
<th>M</th>
<th>R</th>
<th>Dimers</th>
<th>Trimmers</th>
</tr>
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<tbody>
<tr>
<td>Y</td>
<td>n-Pr</td>
<td>100</td>
<td>A  78</td>
</tr>
<tr>
<td></td>
<td>t-Bu</td>
<td>100</td>
<td>B  91</td>
</tr>
<tr>
<td></td>
<td>SiMe(_3)</td>
<td>20</td>
<td>dimer 89</td>
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<tr>
<td></td>
<td>Ph</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>Me(_3)</td>
<td>78</td>
<td>17  9</td>
</tr>
<tr>
<td></td>
<td>n-Pr</td>
<td>91</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>SiMe(_3)</td>
<td>4</td>
<td>45  45</td>
</tr>
<tr>
<td></td>
<td>Ph</td>
<td>86</td>
<td>13  1</td>
</tr>
<tr>
<td>Ce</td>
<td>Me(_3)</td>
<td>74</td>
<td>19  6</td>
</tr>
<tr>
<td></td>
<td>n-Pr</td>
<td>96</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>i-Pr</td>
<td>99</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>i-Bu</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>SiMe(_3)</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ph</td>
<td>82</td>
<td>16  2</td>
</tr>
</tbody>
</table>

\*Type A, \( \text{H}_2\text{C} = \text{CRC} = \text{CR} \); type B, \( \text{R(H)}\text{C} = \text{C(H)}\text{C} = \text{CR} \).

However, in the case of phenylacetylene and (trimethylsilyl)acetylene a dramatic drop in regioselectivity takes place and mixtures of two enyne isomers are formed: 2,4-disubstituted 1-buten-3-ynes and 1,4-disubstituted 1-buten-3-ynes (eq 5, Table I).

\[ \text{HC} = \text{CMe(xs)} \xrightarrow{2,3} \]

\[ \text{HC} = \text{CMe(xs)} \xrightarrow{2,3} \]

The lanthanum- and cerium-catalyzed oligomerizations of phenylacetylene and (trimethylsilyl)acetylene give, in addition to dimers, significant amounts of trimers as well. NMR spectroscopy shows that these are not simply head-to-tail or head-to-head trimers. Phenylacetylene is oligomerized to a mixture of a single dimer, 1,4-diphenyl-1-buten-3-yne (13), and two trimers (eq 8, Table I).

\[ \text{HC} = \text{CPh(xs)} \xrightarrow{2,3} \]

\[ \text{HC} = \text{CPh(xs)} \xrightarrow{2,3} \]

Proposed Catalytic Cycle. A plausible reaction pathway for the dimerization of terminal alkynes by \( \text{Cp}^*\text{SnR} \) and \( \text{Cp}^*\text{TiR} \) compounds is given in Scheme 1. With some extensions this mechanism is applicable for our lanthanide systems as well. It consists of a sequence of well-established elementary reactions such as acetylene insertion into M-C a-bonds and a-bond metathesis. The first step involves alkyne CH bond activation by the carbamates \( \text{Cp}^*\text{LnNH} = \text{SiMe}_2 \) and formation of acetylide, \( [\text{Cp}^*\text{LnNH} = \text{CR}] \), together with \( \text{CH}_3\text{SiMe}_2 \). Coordination and subsequent insertion of an alkyne into the Ln-C a-bond affords a substituted alkyl lanthanide. This undergoes another a-bond metathesis with an internal alkyne or alkyne-alkyne interaction. Higher oligomers, i.e. trimers and traces of tetramers, are formed as well when smaller alkynes such as propyne or n-pentyne are applied. For instance, propyne is oligomerized by 3 to a sole dimer (74%), two trimers (19% and 6%), and a tetramer (15%). However, the regioselectivity is retained and the dimer as well as the major trimer was identified as head-to-tail oligomers (NMR analysis, eq 7).

\[ \text{HC} = \text{CMe(xs)} \xrightarrow{2,3} \]

\[ \text{HC} = \text{CMe(xs)} \xrightarrow{2,3} \]

(10) Although it is clear that this trimer is a substituted allene, it proved not possible to distinguish by NMR spectroscopy whether 18 or one of its isomers is formed.
Alkyne Oligomerization by Lanthanide Carbyls

The extent of oligomerization, i.e. the dimer:higher oligomer ratio in the coupling of alkyl-substituted terminal alkynes by 1–3, is determined by the differences in activation energy ($\Delta AG^*$) for CH bond activation and insertion in step 4 (Scheme I, see also eq 10).

$\text{Cp}^*\text{LnR} + \text{HC}===\text{CR} \rightarrow \text{Cp}^*\text{Ln}\text{C}=$ [eq 10]

$\text{Cp}^*\text{Ln}R + \text{HC}===\text{CR} \rightarrow \text{Cp}^*\text{Ln}\text{C}=$ \[\text{C(R)R'}\text{ insertion (10)}\]

It appears that the value of $\Delta AG^*$ depends on steric factors such as the size of the metal and the bulk of the alkyne alkyl substituent. For a relatively small metal, such as yttrium, exclusively dimers are formed. This indicates that the metal activation energy for $\sigma$-bond metathesis in step 4 is much lower than that for insertion. Significant amounts of trimers were formed in the reactions of the much larger lanthanum and cerium. Hence, the difference in activation energy between CH bond activation and insertion is much smaller for lanthanum and cerium than for yttrium. Detailed kinetic and mechanistic studies will be required to solve the question whether for these large metals the energy for CH bond activation has increased or that of insertion has decreased. For the time being, we assume that the latter is the case because insertion reactions are generally more sensitive to steric effects than CH bond activations.

The oligomerization of alkyl-substituted alkynes by 1–3 leads to the exclusive formation of head-to-tail dimers. Hence, in the insertion step, the alkyne substituent is always pointing away from the $\text{Cp}^*$ rings. It is likely that this situation is energetically favored because it minimizes steric repulsions between the $\text{Cp}^*$ methyl groups and the alkyne substituent R. Thus, it is tempting to suggest that the regioselectivity of the reactions is sterically controlled. However, it is not possible to explain the stereochemical outcome of the reactions of 1–3 with phenylacetylene and (trimethylsilyl)acetylene with steric arguments only. In both cases significant amounts of head-to-head dimers are formed as well and this suggests that the product distributions for these large metals are not only sterically controlled but that electronic factors are also important. The mechanisms operating for trimer formation in the reactions of the lanthanum and cerium carbyls with (trimethylsilyl)acetylene and phenylacetylene, especially those resulting in the formation of allenes, are not understood yet. Several pathways are conceivable: subsequent reactions of free enynes with the active compounds $\text{Cp}^*\text{Ln}[\text{C}=$ [eq 10] such as 1,4-additions or insertion of a second molecule of phenylacetylene into the Ln–C bond of the alkenyl species followed by skeletal rearrangements. Trimer 17 contains two intact triple bonds and is likely formed by a consecutive reaction of an enyne, i.e. insertion of the enyne double bond into the lanthanide–acetylide bond followed by another $\sigma$-bond metathesis with phenylacetylene (Scheme II).

**Preparation, Characterization, and Catalytic Behavior of Cerium Acetylides.** NMR studies clearly expressed that the acetylides $\text{[Cp}^*\text{LnC}=$ [eq 10] play a crucial role in the oligomerization reaction (vide supra). Therefore, a number of cerium acetylides have been prepared to find out whether these are indeed the active species in the catalytic cycle. Furthermore, we thought it interesting to study structure and bonding of the alkynyl unit in these

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(14) Evans, W. J. Polyhedron 1987, 6, 803.


novel early lanthanide acetylenides in more detail.

The cerium acetylenides, \([\text{Cp}^*\text{CeC}==\text{CR}]_n\) \((R = \text{Me, t-Bu); 20, R = \text{Me}}\), were prepared by addition of an excess of alkyn to benzene (7) or pentane solutions (20) of \(\text{Cp}^*\text{CeCH(SiMe}_3\text{)}_2\) and isolated as red-brown crystals. Elemental analyses and \(^1\text{H} NMR\) data (Table II) are consistent with the formulas given.

Both compounds are poorly soluble in aliphatic and aromatic hydrocarbon solvents, a strong indication that 7 and 20 are oligomeric. Related compounds, i.e. \([\text{Cp}^*\text{ErC}==\text{C-t-Bu}]_2\)24 and \([\text{Cp}^*\text{H}_2\text{Me})_2\text{SmC}==\text{C-t-Bu}]_2\)12b have been shown by X-ray diffraction to be dimeric with asymmetrical alkynyl bridges (Figure 2, structure A). IR spectra for these and other lanthanide acetylenides show characteristic \(\nu(C==C)\) absorptions between 2090 and 2020 cm\(^{-1}\).2,4 However 7 and 20 have no IR bands in this specific area. Instead, absorptions are present at 1550 (m) cm\(^{-1}\) for 7 and at 1600 (m) cm\(^{-1}\) for 20 and this indicates a significant reduction of the C=CC bond order in these acetylenides. In analogy with \([\text{L}^2\text{MC}==\text{CR}]_n\) compounds (L = cyclopentadienyl type ligand; M = Ti and Zr),18 we assume that 7 and 20 possess bridging alkynyl ligands with a significant contribution of the alkyn \(\pi\)-system in the bonding with the metal (Figure 2, structure B). However, the evidence obtained does not allow a detailed description and X-ray structure determinations will have to give the definite answer. Regrettably, suitable single crystals for

Table II. \(^1\text{H} NMR Data for Compounds \([\text{Cp}^*\text{CeC}==\text{CR}]_n\) \((R = \text{Me, t-Bu); and } \text{Cp}^*\text{CeC}==\text{C-t-Bu})_n\text{THF}^a\)

<table>
<thead>
<tr>
<th>compd</th>
<th>(\delta)</th>
<th>(J^a)</th>
<th>(\nu^a)</th>
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<tr>
<td>([\text{Cp}^*\text{CeC}==\text{C-t-Bu}]_n) (7)</td>
<td>4.65</td>
<td>30</td>
<td>25</td>
<td>Cp*</td>
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<tr>
<td>([\text{Cp}^*\text{CeC}==\text{C-t-Bu})_n\text{THF} (8)</td>
<td>3.97</td>
<td>30</td>
<td>13</td>
<td>Cp*</td>
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<tr>
<td>([\text{Cp}^*\text{CeC}==\text{CMe}]_n) (20)</td>
<td>2.78</td>
<td>30</td>
<td>12</td>
<td>Cp*</td>
</tr>
</tbody>
</table>

*a Benzene-d\(_6\), 21 °C; all resonances are singlets. *Integrated intensities of the resonances. *Line widths of the resonances at half-maximum (Hz).

Conclusion Remarks

Lanthanide carbyls, \([\text{Cp}^*\text{LnCH(SiMe}_3\text{)}_2\) \((\text{Ln} = \text{Y, La, Ce})\), are very active catalysts for the oligomerization of terminal alkynes by a mechanism that consists of several insertions and \(\sigma\)-bond metatheses. However, the coupling reactions are less selective than for extensively studied \(\text{Cp}^*\text{Ti}^{III}\) systems and, in addition to a lowering of regioselectivity, higher alkyn oligomers are formed as well. Remarkable differences in regioselectivity were observed between alkyl-substituted alkynes on one side and (tris-methylsilyl)acetylene and phenylacetylene on the other. This indicates not only that the stereochemical outcome of alkyn insertion is sterically controlled but that electronic effects are important as well.

A delicate balance between alkyn CH bond formation and alkyn insertion determines the dim:higher oligomer ratio. In contrast to yttrium, significant amounts of higher oligomers are found for the lanthanum- and cerium-cata-

both 7 and 20 could not be obtained so far.

That the lanthanide-acetylides are indeed the active species in the catalytic cycle is supported by the following experiment. As in the case of \(\text{Cp}^*\text{CeCH(SiMe}_3\text{)}_2\) an excess of tert-butylacetylene is dimerized by benzene-d\(_6\) suspensions of 7 to 2,4-di-tert-butyl-1-butene-3-ynyl exclusively. Complete conversion was observed within 10 min at room temperature, which is comparable to the activity found for \(\text{Cp}^*\text{CeCH(SiMe}_3\text{)}_2\).

Catalytic activity was shown to depend on the solvent used, and for instance, neither dimerization nor oligomerization was observed when the reactions were carried out in THF. This led to the conclusion that THF blocks the free coordination sites at the metal which are necessary for coordination of an alkyn, a prerequisite for catalytic activity. Indeed, \(\text{Cp}^*\text{CeCH(SiMe}_3\text{)}_2\) reacts with tert-butylacetylene in THF to yield the THF adduct of 7, \(\text{Cp}^*\text{CeC}==\text{C-t-Bu})_n\text{THF} (8)\). \(^1\text{H} NMR\) spectra of 8 are consistent with the proposed stoichiometry and show a singlet for the \(\text{Cp}^*\) and t-Bu groups together with two broad, high-field shifted resonances for the \(\alpha\)- and \(\beta\)-THF hydrogens (Table II). IR spectra display a clear \(\nu(C==C)\) absorption at 2060 cm\(^{-1}\). This value is in the range (2080–2060 cm\(^{-1}\)) for a number of \(\text{Cp}^*\text{LnCH(SiMe}_3\text{)}_2\) compounds (Ln = Y and Sm19). Typical absorptions of THF coordinated to a Ln\(^{III}\) center are present at 1020 and 865 cm\(^{-1}\).20

Conclusion Remarks

Lanthanide carbyls, \(\text{Cp}^*\text{LnCH(SiMe}_3\text{)}_2\) \((\text{Ln} = \text{Y, La, Ce})\), are very active catalysts for the oligomerization of terminal alkynes by a mechanism that consists of several insertions and \(\sigma\)-bond metatheses. However, the coupling reactions are less selective than for extensively studied \(\text{Cp}^*\text{Ti}^{III}\) systems and, in addition to a lowering of regioselectivity, higher alkyn oligomers are formed as well. Remarkable differences in regioselectivity were observed between alkyl-substituted alkynes on one side and (tris-methylsilyl)acetylene and phenylacetylene on the other. This indicates not only that the stereochemical outcome of alkyn insertion is sterically controlled but that electronic effects are important as well.

A delicate balance between alkyn CH bond formation and alkyn insertion determines the dim:higher oligomer ratio. In contrast to yttrium, significant amounts of higher oligomers are found for the lanthanum- and cerium-catalyzed reactions. Thus, the difference in activation energy
between alkyne CH bond activation and alkyne insertion for large lanthanides is much smaller than that for the coordinatively more saturated group 3 elements.

Experimental Section

General Considerations. All compounds are extremely airsensitive, and manipulations were carried out by using Schlenk, vacuum line, or glovebox techniques under nitrogen or argon. Benzene, toluene, Et2O, THF, pentane, and hexane were distilled from Na/K alloy under nitrogen. NMR solvents (benzene-d6, toluene-d8, THF-d8, cyclohexane-d10) were distilled from Na or K2CO3. 1-Butyne, 3,3-dimethyl-1-butyne, 3-methyl-1-butyne, 4-methyl-1-pentyne, (trimethylsilyl)acetylene, and phenylacetylene were distilled under vacuum and stored on molecular sieves (4 Å) under nitrogen. Propyne (Matheson, C.P.) was used as purchased.

IR spectra were recorded on a Pye-Unicam SP3-300 or a Mattson-4020 Galaxy FT-IR spectrophotometer using Nujol mulls between KBr disks. NMR spectra were recorded on Nicolet NT-200, Brucker WH-90, and Varian VXR-300 spectrometers. Chemical shifts are reported as parts per million relative to TMS (δ 6 0.00 ppm). 13C NMR chemical shifts are referenced to an NMR tube charged with 19.7 mg (0.04 mmol) of 1 in HP 8980-A instrument equipped with a HP 3390 integrator using a Forapack Q or an OV-101 capillary column. The GC response factors of the NMR tubes were determined by GC integrated detection, were assumed to be linearly related to their carbon number. GC/MS analyses were carried out on a Finnigan 3300 or a Ribermag R 10-10 C instrument operating at 70 eV using a CP Sil 5 column. Elemental analyses were performed at the Microanalytical Department of this institute. All found percentages are the average of at least two independent determinations.

**NMR Tube Reaction of Cp*YCH(SiMe3)2 (1) with Excess HC≡CSiMe3**

To an NMR tube charged with 19.7 mg (0.04 mmol) of 1 in benzene-d6 (3.0 mL) was added HC≡CSiMe3. The quantitative conversion of 1 to [Cp*YCH(SiMe3)] (δ (Cp*) = 1.97 ppm) and Cp*SiMe3. All HC≡CSiMe3 was dimerized to a mixture of 11.00 (90%) and 13.00 (10%).

**NMR Tube Reaction of Cp*YCH(SiMe3)2 (1) with Excess (Trimethylsilyl)acetylene**

A 100-μL (0.71 mmol) aliquot of HC≡CSiMe3 was added to an NMR tube charged with 19.4 mg (0.04 mmol) of 1 in ca. 0.4 mL of benzene-d6. After 20 min, characteristic resonances of CH2SiMe3 were present. The reaction mixture was then analyzed by GC, GC/MS, and NMR spectroscopy. Product distributions are given in Table I.

The oligomerization of propyne with the lanthanum derivative was performed analogously with 101 mg (0.18 mmol) of Cp*LaCH(SiMe3)2 in toluene (15 mL) was exposed to 170 mmol of propyne at room temperature. Upon addition of the solution instantaneously changed from red to purple and the solvent started to reflux. After ca. 1 min, the solution turned green. The propyne uptake slowly decreased in time. After 3 h, the reaction was quenched by air exposure and the crude reaction mixture was analyzed by GC (Table I) and GC/MS. The total propyne uptake varied between 25 and 50 mmol. The oligomerization of propyne with the lanthanum derivative was performed analogously with 101 mg (0.18 mmol) of Cp*LaCH(SiMe3)2 in toluene (15 mL). The total uptake of propyne varied between 34 and 56 mmol. The product distribution of the oligomers is given in Table I.

**Preparation of [Cp*CeC≡CH(SiMe3)2] (7). tert-Butylacetylene**

To an NMR tube charged with 15 mg (0.23 mmol) of 7 as deep red crystals. IR (cm−1): 2720 (w), 1550 (m), 1380 (m), 1390 (w), 1335 (w), 1280 (w), 1290 (w), 1010 (m), 980 (m), 730 (m), 540 (m), 420 (m). The compound was obtained in 72% yield. Anal. Caled. For C23H26Ce: C, 63.51; H, 8.00. Found: C, 63.47; H, 7.98. The compound is insufficiently soluble for cryoscopic analysis.

**NMR Tube Reaction of Cp*LaCH(SiMe3)2 (3) with Excess Propyne**

Propyne (1.06 mmol) was condensed into an NMR tube charged with 36 mg (0.66 mmol) of 3 in benzene-d6 (0.4 mL). Upon addition the solution turned purple and subsequently green. NMR spectroscopy indicated the quantitative formation of CH2SiMe3. After 3 h, the solution was orange and a compound was observable in the NMR tube.

13C NMR chemical shifts are referenced to TMS (δ 6 0.00 ppm). 13C NMR chemical shifts are referenced to carbon resonances of the solvent (benzene-d6, δ 7.02; chloroform-d6, δ 7.22; cyclohexane-d10, δ 1.36 ppm) or TMS (δ 6 0.00 ppm). The solvent was then removed by rotary evaporation and the oligomers were analyzed by GC, GC/MS, and NMR spectroscopy. Product distributions are given in Table I.
replaced by nitrogen, the solvent was filtered off, and the pink residue was washed with pentane (2 × 5 mL). The solid was dried in vacuo, during which the color slowly changed from pink to red-brown, dissolved in toluene (20 mL), and subsequently cooled to −80 °C. Workup gave 100 mg (0.22 mmol, 18%) of 20 as red-brown crystals. IR (cm⁻¹): 2710 (w), 2120 (w), 1600 (m), 1030 (m), 940 (m), 800 (m), 730 (w), 450 (m). NMR data are given in Table II. Anal. Calcd for C₂H₂Ce: C, 63.44; H, 7.40; Ce, 31.16. Found: C, 61.69; H, 7.34; Ce, 31.25.

Catalytic Dimerization of tert-Butylacetylene by [Cp*₂CeC≡C-t-Bu]₂ (7). A 50-mL (0.4 mmol) aliquot of tert-butylacetylene was added to an NMR tube containing a suspension of 10.0 mg (0.02 mmol) of 7 in benzene-d₆ (0.5 mL). Upon addition the solution turned purple and subsequently red-brown. NMR analysis showed that all tert-butylacetylene had selectively been dimerized to 2,4-di-tert-butyl-1-buten-3-yne.

Preparation of Cp*₅CeC≡C-t-Bu·THF (8). tert-Butylacetylene (0.1 mL, 0.8 mmol) was added to a stirred solution of 205 mg (0.38 mmol) of Cp*₅CeCH(SiMe₃)₂ in pentane/THF (11 mL, 1:1). Upon addition the color of the solution changed from red to orange. The solution was evaporated to dryness to remove THF, and the residue was redissolved in pentane (10 mL). Concentration and cooling to −80 °C gave 88 mg (0.16 mmol, 44%) of 8 as orange-red crystals. IR (cm⁻¹): 2725 (w), 2140 (w), 2060 (m), 1360 (m), 1245 (s), 1200 (w), 1020 (s), 865 (m), 715 (m), 480 (m). NMR data are given in Table II. Anal. Calcd for C₆H₄CeO: C, 63.91; H, 8.40; Ce, 24.85. Found: C, 63.97; H, 8.47; Ce, 27.46.

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Supplementary Material Available: A text section containing the spectroscopic characterization of the alkynyl oligomers 9–19 (4 pages). Ordering information is given on any current masthead page.