Catalytic Oligomerization of Terminal Alkynes by Lanthanide Carbyls \((\eta^5-C_5\text{Me}_5)2\text{LnCH(SiMe}_3\text{)}2\) (Ln = Y, La, Ce)

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Vinylvinylidene ligand and one of the dppe phenyl rings. Vinylvinylidene, rather than allenylidene, products when for dehydration of hydroxyvinylidene intermediates to give aromatic stacking between the phenyl substituent on the vinylvinylidene ligand and one of the dppe phenyl rings.

Conclusions. These results clearly indicate a preference for dehydration of hydroxyvinylidene intermediates to give vinylvinylidene, rather than allenylidene, products when protons are available on the δ-carbon atom in the [Ru-(PMe3)2(Cp)]+ system. This supports the intermediacy of a vinylvinylidene complex, presumably [Ru(C==CH(Me)==CH2)(PPh3)2(Cp)]+, in the formation of dimer 7. Evidently, similar dimerization of 1 and 2 is prevented by the ring strain and the bridgehead double bonds, which would be present in similar dimers. Likewise, dimerization of 3 is prevented by the four additional methyl substituents, which interfere sterically and preclude the proton transfers from δ-carbons that accompany C—C bond making during the formation of 7. Deprotonations of the cationic vinylvinylidene complexes straightforwardly lead to enynyls. Cycloaddition of enynyl 4 with CS2 takes place in a [2 + 2] rather than a [4 + 2] fashion.

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Supplementary Material Available: Listings of positional and thermal parameters, bond distances, torsion angles, and least-squares planes (4 pages); a table of experimental and calculated structure factors for the structure of 1 (22 pages). Ordering information is available on any current masthead page.

Catalytic Oligomerization of Terminal Alkynes by Lanthanide Carbyls (η⁵-C₅Me₅)₂LnCH(SiMe₃)₂ (Ln = Y, La, Ce)

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Received November 1, 1990

Lanthanide and group 3 carbyls Cp*₅LnCH(SiMe₃)₂ (1, Ln = Y; 2, Ln = La; 3, Ln = Ce) are active catalyst precursors for the oligomerization of terminal alkynes H==CR (R = alkyl, aryl, SiMe₃). The regioselectivity and the extent of oligomerization depend strongly on the lanthanide applied as well as on the alkyne substituent R. For yttrium, alkyl-substituted alkynes are dimerized selectively to 2,4-disubstituted 1-buten-3-ynes whereas mixtures of two enyne isomers, i.e. 2,4-disubstituted 1-buten-3-ynes and 1,4-disubstituted 1-buten-3-ynes, are found for phenylacetylene and (trimethylsilyl)acetylene. The reactions with lanthanum and cerium produce, besides dimers, higher oligomers (trimers, tetramers) of various sorts (allenes and diynes). NMR studies indicate that lanthanide acetylides [Cp*₅LnC==CR]₉, formed by σ-bond metathesis between the carbyl and the alkyne CH bond, are the active species in the catalytic cycle. Two oligomeric cerium acetylides [Cp*₅CeC==CR]₉ (7, R = t-Bu; 20, R = Me) have been synthesized on a preparative scale. Spectroscopic data for these compounds suggest a significant contribution of the 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,

[1] The following abbreviations are used in this article: Ln = lanthanide or group 3 element; Cp* = η⁵-pentamethylyclopentadienyl ring; Iw = linewidths of NMR resonances at half maximum.


nistic studies have not been reported yet and the factors that govern regio- and stereoselectivity are not fully understood.

Extensive research in our group on titanium(III) carbyls, Cp*TiR, and by Japanese colleagues on less well-defined systems, Cp*TiCl/RMgX have shown that these catalyze the dimerization of terminal alkynes. The reactions are remarkably selective and give exclusively linear defined systems, Cp*TiCl/RMgX have shown that these coupling reactions appear to be rather sensitive to the size of the alkyne substituent R, and bulky alkynes such as tert-butylacetylene could not be dimerized. Recently, it was demonstrated that group 3 alkyls Cp*ScR6 and Cp*YR7 also catalyze the head-to-tail dimerization of propyne to 2-methyl-1-penten-3-yne.

With bent sandwich carbyls Cp*LnCH(SiMe3)2 of the early lanthanides lanthanum and cerium available, 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, scandium, and yttrium, 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 produce trimers of various sorts as well. It was decided to carry out a detailed study aimed at scope, identification of various oligomers, and the identity of the catalytic species involved.

Results and Discussion

NMR Tube Experiments. The reactions of the yttrium and cerium carbyls, Cp*LnCH(SiMe3)2 (1, Ln = Y; 3, Ln = Ce) with an excess of alkynes HC=CR (R = Ph, SiMe3, t-Bu) were initially carried out in sealed NMR tubes with benzene-d6 as the solvent and monitored with 1H NMR spectroscopy. In all cases studied the excess alkyne was rapidly converted into a mixture of oligomers. In this section we will focus on the organolanthanides involved in the catalytic reaction; the alkyne oligomer distribution and identification of the individual oligomers will be discussed in more detail further on.

Addition of an excess of phenylacetylene to benzene-d6 solutions of 1 and 3 resulted in a quick catalytic reaction and after ca. 10 min, all alkyne was oligomerized. For yttrium, oligomerization was accompanied by the quantitative formation of [Cp*Y=C=CH2]n (4) and CH2(SiMe3)2 (eq 1).

$$\text{Cp*YCH(SiMe3)}_2 + \text{HC=CPh} \rightarrow \frac{1}{n}[\text{Cp*Y=C=CH2}]_n + \text{CH2(SiMe3)}_2 \quad (1)$$

The reaction of the cerium derivative with phenylacetylene produced a mixture of starting carbyl 3, small amounts of CH2(SiMe3)2, and several alkyne oligomers. However, in this case clear assignment of resonances arising from [Cp*CeC=CH2]n proved not possible.

Excess of (trimethylsilyl)acetylene was slowly converted (ca. 4 h) to a mixture of alkyne oligomers by solutions of 1 and 3. The acetylides [Cp*LnC≡CSiMe3]n (5, Ln = Y; 6, Ln = Ce) were formed quantitatively (eq 2).

$$\text{Cp*LnCH(SiMe3)}_2 + \text{HCC=CSIMe3} \rightarrow \text{Ln} = \text{Y} (1), \text{Ce} (3)$$

$$(1/n)[\text{Cp*LnC≡CSIMe3}]_n + \text{CH2(SiMe3)}_2 \quad (2)$$

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 alkyne oligomers present (vide infra).

Catalytic activity depends on the solvent applied. For instance, tert-butylacetylene was quickly oligomerized in benzene-d6 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 CH2(SiMe3)2. However, the reaction of 3 with tert-butylacetylene in a coordinating solvent such as THF-d8 only resulted in a stoichiometric reaction and the formation of Cp*CeC≡C-t-Bu•THF-d8 (8-9) together with CH2(SiMe3)2 (eq 3).

$$3 + \text{HCC=t-Bu} \rightarrow \text{Cp*CeC≡C-t-Bu•THF-d8} + \text{CH2(SiMe3)}_2 \quad (3)$$

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 alkyne oligomerization involved addition of a large excess of alkyne (>45 mmol of alkyne/mmole 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 alkyne oligomers were analyzed by GC, GC/MS, and NMR spectroscopy.

Alkyne HC≡CR (R = n-Pr, t-Bu, SiMe3, Ph) are oligomerized exclusively to dimers by solutions of Cp*YCH(SiMe3)2 (1). The regioselectivity of the reactions strongly depends on alkyne applied. Alkynes with alkyl substituents (n-Pr, t-Bu) are very selectively coupled to head-to-tail dimers, 2,4-disubstituted 1-butene-3-yne (eq 4, Table 1).

$$2\text{HC≡CR} \rightarrow \frac{1}{2}[\text{Cp*Y=C=C=CH2}]_2 + \text{CH2(SiMe3)}_2 \quad (4)$$
Table I. Product Distributions for the Oligomerization of Terminal Alkynes by Compounds Cp*2LnCH(SiMes)2 (Ln = Y, La, and Ce)

<table>
<thead>
<tr>
<th></th>
<th>dimers*</th>
<th>trimers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>Y</td>
<td>n-Pr</td>
<td>100</td>
</tr>
<tr>
<td>La</td>
<td>Me</td>
<td>78</td>
</tr>
<tr>
<td>Ce</td>
<td>Me</td>
<td>74</td>
</tr>
<tr>
<td>n-Pr</td>
<td>91</td>
<td>9</td>
</tr>
<tr>
<td>t-Bu</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Ph</td>
<td>89</td>
<td>11</td>
</tr>
</tbody>
</table>

* Type A, H,C=CRC=CR; type B, R(H)C=C(H)C=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,Cdisubstituted 1-buten-3-ynes (eq 5, Table I).

The lanthanum- and cerium-catalyzed couplings of terminal alkynes are generally less selective than for yttrium, and in addition to dimers, higher oligomers are formed as well. Both lanthanum and cerium behave essentially identical, and distinct differences in selectivity and activity are not observed. The extent of oligomerization as well as the regioselectivity appears to depend strongly on the alkyne substituent R (Table I), and there are remarkable differences between alkyl-substituted alkynes on one side and (trimethylsilyl)acetylene and phenylacetylene on the other.

In the case of alkyl-substituted alkynes, the size of the alkyne substituent R determines the dimer-higher oligomer ratio. Alkynes with bulky groups such as tert-butylacetylene are very selectively coupled to 2,4-disubstituted 1-buten-3-ynes (eq 6).

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 (1%). 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).

```
HC=CMex(s) + 2.3  H/CMe + + H/CMe + + H/CMe + +  
```

![Diagram](image_url)

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-ynes (13), and two trimers (eq 8, Table I).

```
HC=CPh(xs) + 2.3  H/CPh + + H/CPh + + +  
```

![Diagram](image_url)

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-ynes (13), and two trimers (eq 8, Table I). One of the trimers contains two intact triple bonds (NMR analysis) and was identified as 1,3,6-triphenyl-1,5-hexadiyne (17). The second trimer contains an allenic fragment (NMR analysis) and is likely a substituted allene such as 18.

Reaction of 2 and 3 with (trimethylsilyl)acetylene produced a mixture with four major products: head-to-tail dimer 12, head-to-head dimer 14, and two trimers (eq 9). The major trimer was identified as a substituted allene such as 19A or 19B. Unfortunately, the other trimer could not be identified.

```
HC=CMe3(xs) + 2.3  H/CMe + + H/CMe + + +  
```

![Diagram](image_url)

**Proposed Catalytic Cycle.** A plausible reaction pathway for the dimerization of terminal alkynes by Cp*2ScR and Cp*2TiR compounds is given in Scheme I. 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 carbyls Cp*2LnCH(SiMes)2 and formation of acetylide, [Cp*2LnC==CR]2, together with CH2(SiMes)2. Coordination and subsequent insertion of an alkyne into the Ln-C a-bond affords a substituted alkenyl lanthanide. This undergoes another a-bond metathesis with an integer.

---

(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.

coming alkyne, thus regenerating the active acetylide and producing free enynes.

The first step in the mechanism, i.e. \( \sigma \)-bond metathesis between a \( \text{Ln}-\text{C} \) \( \sigma \)-bond and an alkyne \( \text{CH} \) bond, appears to be a general reaction for lanthanide and group 3 carbyls.\(^{12} \) Marks and co-workers\(^{12} \) determined bond enthalpies for a series of \( \text{Cp}^*\text{SmR} \) compounds \( (\text{R} = \text{CH(SiMe}_3)_2, \text{C}_2\text{H}_5, \text{C}_2\text{CPh}, \text{and H}) \) and analyzed the thermodynamics of samarium-centered reactions. They calculated the \( \text{CH} \) bond metathesis reaction of \( \text{Cp}^*\text{SmCH(SiMe}_3)_2 \) with phenylacetylene to be rather exothermic \( (\Delta H_{\text{prod}} = -76 \text{ kJ/mol}) \); although the reaction is entropically unfavorable since four particles form three \( (-\Delta S = +20 \text{ to } +40 \text{ kJ/mol at room temperature}) \). It is reasonable to assume that the thermodynamics for cerium are essentially that of samarium.

A number of cerium acetylides, \( [\text{Cp}^*\ce{CeC=CR}]_n \) \( (\text{R} = \text{Me}, \text{t-Bu}) \), have been made on a preparative scale. Spectroscopic data as well as their low solubility in hydrocarbon solvents favor an oligomeric structure (vide infra). However, oligomeric organometallics with bridging ligands are generally less reactive than the corresponding, coordinatively unsaturated monomeric species.\(^{14} \) Hence, it is reasonable to assume that the active species in the catalytic cycle are monomeric acetylides with terminal alkynyl ligands which have enough space available for alkyne coordination, a prerequisite for catalytic activity.

The acetylides are the sole organolanthanides that could be detected in the course of the catalytic reactions (NMR analysis). This argues that alkyne insertion into the \( \text{Ln}-\text{acetylide} \) bond is the rate-determining step in the catalytic cycle. In some cases acetylide formation is not quantitative and mixtures of the acetylide and the starting carbyl are formed. This indicates that the rate of \( \sigma \)-bond metathesis between the carbyls and the alkyne \( \text{CH} \) bond (step 1) is slower than \( \sigma \)-bond metathesis with the metal–alkynyl bond in the catalytic cycle (step 4). It is likely that these differences in the rate of \( \sigma \)-bond metathesis are related to the size of the alkynyl substituent; i.e. the reactivity of a bulky \( \text{CH(SiMe}_3)_2 \) group is much lower than that of a less hindered alkynyl group.

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 \( (\Delta AG^\ddagger) \) for \( \text{CH bond activation and insertion in step} 4 \) (Scheme I, see also eq 10).

\[
\begin{align*}
\text{Cp}^*\text{LnR} + \text{HC}=\text{CR} & \rightarrow \text{Cp}^*\text{Ln} \text{CH=CR} \\
\text{Cp}^*\text{Ln} \text{CH=CR} + \text{RH} & \rightarrow \text{Cp}^*\text{Ln} \text{CHCH}_2 \text{CR} \quad (\text{insertion} 10)
\end{align*}
\]

It appears that the value of \( \Delta AG^\ddagger \) 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,\(^{8} \) exclusively dimers are formed. This indicates that for this metal the 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 \( \text{CH} \) 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 \( \text{CH} \) 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 \( \text{CH} \) bond activations.\(^{15} \)

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 \( \text{R} \) is always pointing away from the \( \text{Cp}^* \) rings. It is likely that this situation is energetically favored because it minimizes sterical repulsions between the \( \text{Cp}^* \) methyl groups and the alkyne substituent \( \text{R} \). 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 \( \text{Cp}^*\text{LnC=CR} \), such as 1,4-additions\(^{16} \) or insertion of a second molecule of phenylacetylene into the \( \text{Ln}-\text{C} \) 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 \( [\text{Cp}^*\text{LnC}=\text{CR}] \), 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
and X-ray structure determinations will have to give the evidence obtained does not allow a detailed description. We assume that a definite answer. Regretfully, suitable single crystals for bonding with the metal (Figure 2).

**Table II.** $^1$H NMR Data for Compounds $[\text{Cp}^*\text{C}=\text{CR}]_x$ (R = Me, t-Bu) and $[\text{Cp}^*\text{C}=\text{C}-\text{t-Bu}^{3}\text{THF}]^a$

<table>
<thead>
<tr>
<th>compd</th>
<th>$\delta$</th>
<th>$^3J$</th>
<th>$\delta^1$</th>
<th>assgmt</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Cp}^*\text{C}=\text{C}-\text{t-Bu}]_x$ (7)</td>
<td>4.65</td>
<td>30</td>
<td>25</td>
<td>$\text{Cp}$*</td>
</tr>
<tr>
<td>$[\text{Cp}^*\text{C}=\text{C}-\text{t-Bu}]_x$ (7)</td>
<td>-5.0</td>
<td>9</td>
<td>10</td>
<td>$t$-Bu</td>
</tr>
<tr>
<td>$[\text{Cp}^*\text{C}=\text{C}-\text{t-Bu}]_x$ (7)</td>
<td>3.97</td>
<td>30</td>
<td>13</td>
<td>$\text{Cp}$*</td>
</tr>
<tr>
<td>$[\text{Cp}^*\text{C}=\text{C}-\text{t-Bu}]_x$ (7)</td>
<td>-1.98</td>
<td>9</td>
<td>4</td>
<td>$t$-Bu</td>
</tr>
<tr>
<td>$[\text{Cp}^*\text{C}=\text{C}-\text{t-Bu}]_x$ (7)</td>
<td>-7.49</td>
<td>4</td>
<td>80</td>
<td>$\beta$-THF</td>
</tr>
<tr>
<td>$[\text{Cp}^*\text{C}=\text{C}-\text{t-Bu}]_x$ (7)</td>
<td>-22.0</td>
<td>4</td>
<td>180</td>
<td>$\alpha$-THF</td>
</tr>
<tr>
<td>$[\text{Cp}^*\text{C}=\text{C}-\text{t-Bu}]_x$ (7)</td>
<td>2.78</td>
<td>30</td>
<td>12</td>
<td>$\text{Cp}$*</td>
</tr>
<tr>
<td>$[\text{Cp}^*\text{C}=\text{C}-\text{t-Bu}]_x$ (7)</td>
<td>-13.3</td>
<td>3</td>
<td>35</td>
<td>Me</td>
</tr>
</tbody>
</table>

*a* Benzene-$d_6$, 21 °C; all resonances are singlets. b Integrated intensities of the resonances. c Line widths of the resonances at half-maximum (Hz).

novel early lanthanide acetylides in more detail.

The cerium acetylides, $[\text{Cp}^*\text{C}=\text{CeC}=\text{CR}]_x$ (R = Me, pentane solutions (20) of $[\text{Cp}^*\text{C}=\text{CeCH(SiMe}_3)_2]$ and isolated as red-brown crystals. Elemental analyses and $^1$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. $[\text{Cp}_2\text{Er}=\text{C}-\text{t-Bu}]_2$ and $[\text{Cp}_2\text{Me}_2\text{Sm}=\text{C}-\text{t-Bu}]_2$ 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 acetylides show characteristic $\nu(\text{C}=$) absorptions between 2090 and 2020 cm$^{-1}$. 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=C bond order in these acetylides. In analogy with $[\text{L}_3\text{MC}=\text{CR}]_x$, compounds (L = cyclopentadienyl type ligand; M = Ti and Zr), we assume that 7 and 20 possess bridging alkynyl ligands with a significant contribution of the alkynyl $\pi$-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. Regretably, suitable single crystals for 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 $[\text{Cp}^*\text{C}=\text{CeCH(SiMe}_3)_2]$ an excess of tert-butylacetylene is dimerized by benzene-$d_6$ suspensions of 7 to 2,4-di-tert-butyl-1-buten-3-yne exclusively. Complete conversion was observed within 10 min at room temperature, which is comparable to the activity found for $[\text{Cp}^*\text{C}=\text{CeCH(SiMe}_3)_2]$.

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 alkynyl, a prerequisite for catalytic activity. Indeed, $[\text{Cp}^*\text{C}=\text{CeCH(SiMe}_3)_2]$ reacts with tert-butylacetylene in THF to yield the THF adduct of 7, $[\text{Cp}^*\text{C}=\text{CeCH(SiMe}_3)_2\text{THF}]$. $^1$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 $\nu(\text{C}=$) absorption at 2060 cm$^{-1}$. This value is in the range (2080–2060 cm$^{-1}$) for a number of $[\text{Cp}^*\text{Ln}=\text{CR}-\text{THF}](\text{Ln} = \text{Y}^3$ and Sm$^{3+}$). Typical absorptions of THF coordinated to a Ln$^{3+}$ center are present at 1020 and 865 cm$^{-1}$.

Concluding Remarks

Lanthanide carbyls, $[\text{Cp}^*\text{Ln}=\text{CH(SiMe}_3)_2](\text{Ln} = \text{Y}, \text{La}, \text{and Ce})$, 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 $\text{Cp}_2\text{Ti}^{	ext{III}}$ systems and, in addition to a lowering of regioselectivity, higher alkynyl oligomers are formed as well. Remarkable differences in regioselectivity were observed between alkyl-substituted alkynes on one side and (tri-methylsilyl)acetylene and phenylacetylene on the other. This indicates not only that the steric demand of the alkynyl insertion is sterically controlled but that electronic effects are important as well.

A delicate balance between alkynyl CH bond formation and alkynyl insertion determines the dimer: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 air-sensitive, and manipulations were carried out by using Schlenk, vacuum line, or glovebox techniques under nitrogen or argon. Solvents were distilled from Na or vacuum-transferred and stored on molecular sieves (4 Å). Sensitive reactions were carried out by using Schlenk, glovebox techniques under nitrogen or argon, or TMS (δ 0.00 ppm). 13C NMR chemical shifts are referenced to TMS (δ 0.00 ppm) and protons are referenced to residual protons in each NMR solvent (benzene-d6, δ 7.16; chloroform-d, δ 7.22; THF-d8, δ 3.36 ppm) or TMS (δ 0.00 ppm). 1H NMR chemical shifts are referenced to carbon resonances of the solvent (benzene-d6, δ 128.96; toluene-d8, δ 7.02; chloroform-d, δ 7.22; cyclohexane-d10, δ 1.36 ppm) or TMS (δ 0.00 ppm). NMR spectroscopy was performed using a HP 5890-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 solvents were determined by GC analysis using a column of 10% Apiezon L. GC-MS data are reported as ion abundances corrected for isotopic distribution. NMR data are given in Table I.

**Tube Reaction of Cp*CeC=C(SiMe3)2 (3) with Excess tert-Butylacetylene.** A 250-μL (1.97 mmol) aliquot of tert-butylacetylene was added to an NMR tube charged with 43 mg (0.09 mmol) of 3 in benzene-d6. Upon addition the solution turned purple and the solvent started to reflux. An NMR spectrum after 10 min indicated the presence of unreacted 3, CH2(SiMe3)2, the quantitative conversion of tert-butylacetylene to 2,4-di-tert-butyl-1-butene-3-yne (10%), and characteristic resonances of [Cp*CeC=C-t-Bu]2 (7).

**Tube Reaction of Cp*CeC=C(SiMe3)2 (3) with Excess tert-Butylacetylene in THF-d8.** A 50-μL (0.41 mmol) aliquot of tert-butylacetylene was added to an NMR tube containing 30.0 mg (0.05 mmol) of 3 in THF-d8 (0.5 mL). NMR spectroscopy indicated the qualitative formation of Cp*CeC=C-t-Bu[THF]2 (8-d3) and CH2(SiMe3)2. Excess tert-butylacetylene was invisible present, and resonances of the dimer 2,4-di-tert-butyl-1-butene-3-yne (10%) were not observed.

**Catalytic Oligomerization of HC=CR (R = n-Pr, t-Pr, t-Bu, i-Bu, t-Bu, Ph, SiMe3) by Cp*CeCH(SiMe3)2 (3).** Alkyne (45–90 mmol) were added to hexane solutions (7–14 mL) of Cp*CeCH(SiMe3)2 (0.06–0.14 mmol; catalyst/substrate ratios ranging from 1:45:1 to 1:190). Upon addition the color of the solutions instantaneously changed from red to purple and then within 1 min to green. The reactions were exothermic, and in several cases the solvent started to reflux. After stirring for 2.5 h at room temperature, the reactions were quenched by exposing the reaction mixtures to air and the composition was determined by GC. The reaction mixtures were taken up into CH2Cl2 and passed over a column of silica to remove inorganic residues. 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.

**Catalytic Oligomerization of Alkynes HC=CR (R = n-Pr, t-Bu, SiMe3, Ph) by Cp*LnCH(SiMe3)2 (1, Ln = Y; 2, Ln = La).** The reactions were carried out by a procedure similar to the one given for the reactions with Cp*CeCH(SiMe3)2. However, the composition of the reaction mixture was determined by GC and GC/MS only and the oligomers were not separated from the catalyst residues. Catalyst concentrations between 8 × 10−4 and 1 × 10−2 mol/L were applied, catalysis was determined by GC (Table I), and GC/MS. The total propyne uptake varied between 80 and 50 mol.

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 the color 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 36 and 50 mol.

**Preparation of [Cp*CeC=C-t-Bu]2 (7), tert-Butylacetylene (2.0 mL, 16 mmol) was added to a stirred solution of 574 mg (1.00 mmol) of Cp*CeC=C(SiMe3)2 in 20 mL of benzene-d6. Upon addition the solution instantaneously turned purple. After stirring for 40 h at room temperature, a red-brown suspension had formed. Benzoic (20 mL) was added, and the suspension was heated until all solid had dissolved. Cooling to room temperature gave 115 mg (0.23 mmol, 23%) of 7 as deep red crystals. IR (cm−1): 2720 (w), 1550 (s), 1380 (m), 1360 (w), 1285 (w), 1200 (w), 1100 (m), 800 (m), 730 (s), 690 (w), 542 (m). Elemental analyses were given in Table II. Anal. Caled for C39H33Ce: C, 63.51; H, 8.00. Found: C, 63.47; H, 7.98. The compound is insufficiently soluble for recrystallization in benzene.

**Preparation of [Cp*Ce=C═CMe]2 (20), Excess propyne (228 mg, 1.26 mmol) of Cp*CeCH(SiMe3)2 in pentane (40 mL). Upon addition the solution instantaneously changed from red to purple and a pink-purple solid deposited. After ca. 15 min, the propyne atmosphere was..."
replace boron center can be systematically varied by appropriate derivative chemistry is known whereby the properties of the bond extensively. 2-11 However, until recently there was Part of this success is due to the fact that a versatile de-
systems that have been studied, the complex M-B inter-
fragments as borane substituents on reactivity and prop-


Catalytic Dimerization of tert-Butylacetylene by [Cp*2Ce=CH-t-Bu] (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-yn-ye (10).

Preparation of Cp*2Ce=C(=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*2CeCH(SiMe3)2 in pentane/THF (11 mL, 10%). 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), 1760 (m), 1245 (s), 1200 (w), 1020 (m), 865 (m), 715 (m), 480 (m). NMR data are given in Table II. Anal. Calcd for Cp*2CeO: C, 63.91; H, 8.40; Ce, 24.85. Found: C, 63.97; H, 8.48; Ce, 24.78.

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


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The preparation and characterization of the compounds [HFe4(CO)12C]BXY (X = Y = H, Cl, Br; X = H, Y = Cl, Br, OH) are described. Geometric, spectroscopic, and Fenske–Hall quantum-chemical parameters demonstrate that these compounds are usefully described as tricoordinate boron compounds parametrized with a carbido cluster. The carbido cluster [HFe4(CO)12C], as a substituent, is shown to be both a sterically demanding ligand and a strong π donor to the boron center. The anticipated differences in the reactivity of these compounds with AlX3, NEt3, H2O, and THF as X and Y are varied reflect the unusual properties of this compound type. Single-crystal X-ray diffraction studies of [HFe4(CO)12C]BH (X = Cl, Br) are reported. In both cases crystals form in the monoclinic system of space group P21/m with the following unit cell parameters: X = _Cl, a = 8.081 (2) Å, b = 15.730 (3) Å, c = 8.936 (2) Å, β = 113.41 (2)°, V = 1042.3 (4) Å3, Z = 2; X = Br, a = 8.276 (6) Å, b = 15.749 (11) Å, c = 8.993 (6) Å, β = 114.36 (6)°, V = 1067.7 (1.5) Å3, Z = 2. The solution for X = Cl was by direct methods (R(F) = 3.27%, R(wf) = 3.55 for 1656 independent reflections (F > 2σ(F)), whereas for X = Br it was by isomorphous analogy to the solution for X = Cl (R(F) = 3.97%, R(wf) = 4.11% for 1859 independent reflections (F > 2σ(F))).

The usefulness of boranes as reagents is well-known.1 Part of this success is due to the fact that a versatile derivative chemistry is known whereby the properties of the boron center can be systematically varied by appropriate sterically and electronic factors associated with the substituents at the boron center. The effect of transition-metal fragments as borane substituents on reactivity and properties is less well understood. On the other hand, in those systems that have been studied, the complex M–B interactions are known to change the reactivity of the B–H bond extensively.2–11 However, until recently there was no report of a boron hydride substituted with a mononuclear transition-metal fragment, e.g. LMBH2. An example from our own laboratories is (CO)2CoBH2TF2,12 and the closely related complex (CO)2[η5-dppm]Co(μ-dppm)BH2 has now been isolated and crystallographically charac-