$$\textit{mer-(dppe)(CO)}_3W=C=C \begin{array}{c} CO_2Me \\ \diagdown \\ C - CO_2Me \\ \| \\ C \\ \diagup \diagdown \\ H \quad Ph \end{array}$$

13

$$(CO)_5Cr=C=C \begin{array}{c} CO_2Me \\ \diagdown \\ C - H \\ \| \\ C \\ \diagup \diagdown \\ MeO_2C \quad H \end{array}$$

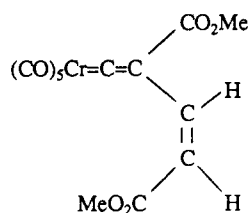**14**

ometry appears to minimize contacts between the [Re-(CO)$_2$(Cp)] groups at each end of the vinylvinylidene bridge. The reason for S-cis geometry in tungsten complex **13** is not obvious, but it may be a means of maximizing 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-(PMe$_3$)$_2$(Cp)]$^+$ system. This supports the intermediacy of a vinylvinylidene complex, presumably [Ru[C=CHC-(Me)=CH$_2$](PPh$_3$)$_2$(Cp)]$^+$, in the formation of dimer **7**.[3] 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 CS$_2$ takes place in a [2 + 2] rather than a [4 + 2] fashion.

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 (η^5-C$_5$Me$_5$)$_2$LnCH(SiMe$_3$)$_2$ (Ln = Y, La, Ce)

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Lanthanide and group 3 carbyls Cp*$_2$LnCH(SiMe$_3$)$_2$ (**1**, Ln = Y; **2**, Ln = La; **3**, Ln = Ce) are active catalyst precursors for the oligomerization of terminal alkynes HC≡CR (R = alkyl, aryl, SiMe$_3$). 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*$_2$LnC≡CR]$_n$, formed by σ-bond metathesis between the carbyls and the alkyne CH bond, are the active species in the catalytic cycle. Two oligomeric cerium acetylides [Cp*$_2$CeC≡CR]$_n$ (**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.[1,2] 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* = η^5-pentamethylcyclopentadienyl ring; lw = linewidths of NMR resonances at half maximum.

(2) (a) Keim, W.; Behr, A.; Röper, M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, p 371. (b) Winter, M. J. In *The Chemistry of the Metal–Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley and Sons: Chichester, U.K., 1985; Vol. 3, p 259. (c) Vollhardt, K. P. C. *Acc. Chem. Res.* 1977, *10*, 1.

Rh, Ru, Cu, or Cr, are known for the dimerization of terminal alkynes.[3] 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 alkyne CH bond activation, which produces the active metal acetylide, L$_n$MC≡CR. However, detailed mecha-

(3) (a) Yamazaki, H. *J. Chem. Soc., Chem. Commun.* 1976, 841. (b) Yoshikawa, S.; Kiji, J.; Furukawa, J. *Macromol. Chem.* 1977, *178*, 1077. (c) Ishikawa, M.; Ohskita, J.; Ito, Y.; Minato, A. *J. Organomet. Chem.* 1988, *346*, C58.
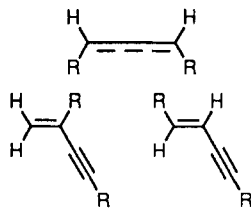
Figure 1. Different modes for 1-alkyne dimerization.

nistic 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(III) carbyls, Cp*$_2$TiR, and by Japanese colleagues[5] on less well-defined systems, Cp*$_2$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-buten-3-ynes. The 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*$_2$ScR[6] and Cp*$_2$YR[7] also catalyze the head-to-tail dimerization of propyne to 2-methyl-1-penten-3-yne.

With bent sandwich carbyls Cp*$_2$LnCH(SiMe$_3$)$_2$ of the early lanthanides lanthanum and cerium available,[8] 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,[9] 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*$_2$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 as the solvent and monitored with ^{1}H 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
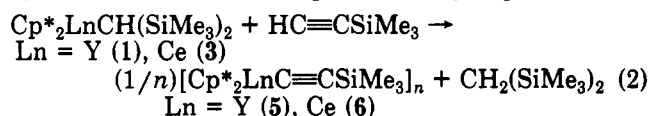
will be discussed in more detail further on.

Addition of an excess of phenylacetylene to benzene-d_6 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*$_2$YC≡CPh]$_n$ (4) and CH$_2$(SiMe$_3$)$_2$ (eq 1).

$$Cp*_2YCH(SiMe_3)_2 + HC≡CPh →$$
$$\underset{1}{}$$
$$\underset{4}{(1/n)[Cp*_2YC≡CPh]_n + CH_2(SiMe_3)_2} \quad (1)$$
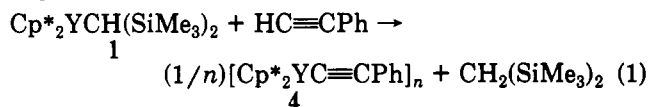
The reaction of the cerium derivative with phenylacetylene produced a mixture of starting carbyl 3, small amounts of CH$_2$(SiMe$_3$)$_2$, and several alkyne oligomers. However, in this case clear assignment of resonances arising from [Cp*$_2$CeC≡CPh]$_n$ proved not possible.

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*$_2$LnC≡CSiMe$_3$]$_n$ (5, Ln = Y; 6, Ln = Ce) were formed quantitatively (eq 2).

$$Cp*_2LnCH(SiMe_3)_2 + HC≡CSiMe_3 →$$
$$Ln = Y (1), Ce (3)$$
$$(1/n)[Cp*_2LnC≡CSiMe_3]_n + CH_2(SiMe_3)_2 \quad (2)$$
$$Ln = Y (5), Ce (6)$$

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-d_6 solutions of 3. Like the reaction with phenylacetylene, a mixture of the starting carbyl 3 and [Cp*$_2$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_8 only resulted in a stoichiometric reaction and the formation of Cp*$_2$CeC≡C-*t*-Bu·THF-d_8 (8-d_8) together with CH$_2$(SiMe$_3$)$_2$ (eq 3). Catalytic alkyne oligomerization

$$3 + HC≡C-t-Bu \xrightarrow{THF-d_8}$$
$$\underset{8-d_8}{Cp*_2CeC≡C-t-Bu·THF-d_8 + CH_2(SiMe_3)_2} \quad (3)$$
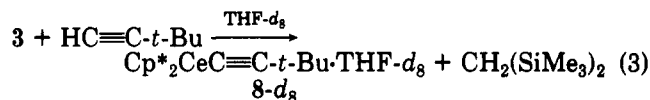
was not observed and even after several weeks at room temperature, the remainder of the *tert*-butylacetylene was unchanged.

Preparative Catalytic Oligomerization. The standard reaction procedure for preparative alkyne oligomerization involved addition of a large excess of alkyne (>45 mmol of alkyne/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 alkyne oligomers were analyzed with 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*$_2$YCH(SiMe$_3$)$_2$ (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-buten-3-ynes (eq 4, Table I).

$$2HC≡CR \xrightarrow{1} \quad (4)$$
$$R = alkyl$$
$$R = n\text{-Pr } (9), t\text{-Bu } (10)$$
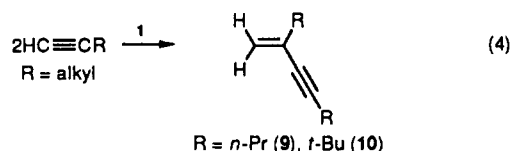
(4) ten Cate, L. C.; Agricola, F. T.; Heeres, H. J.; Jansen, H.; Luinstra, G. A.; Pattiasina, J. W.; de Boer, J. L.; Meetsma, A.; Teuben, J. H.; Spek, A. L. To be published.

(5) Akita, M.; Yasuda, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 480.

(6) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

(7) den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053.

(8) (a) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091. (b) Heeres, H. J.; Renkema, J.; Booij, M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1988**, *7*, 2495.

(9) Ionic radii (6-coordinate compounds): La^{3+}, 1.03 Å; Ce^{3+}, 1.01 Å, Y^{3+}, 0.90 Å; Sc^{3+}, 0.75 Å; Ti^{3+}, 0.67 Å. See: Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

Table I. Product Distributions for the Oligomerization of Terminal Alkynes by Compounds Cp*₂LnCH(SiMe₃)₂ (Ln = Y, La, and Ce)

| M | R | dimers[a] | | trimers |
		A	B	
Y	n-Pr	100		
	t-Bu	100		
	SiMe₃	20	80	
	Ph	89	11	
La	Me[b]	78		17 4
	n-Pr	91		9
	t-Bu	100		
	SiMe₃	4	45	47 4
	Ph		86	13 1
Ce	Me[b]	74		19 6
	n-Pr	96		4
	i-Pr	99		1
	i-Bu	97		3
	t-Bu	100		
	SiMe₃	7	61	27 5
	Ph		82	16 2

[a] Type A, $H_2C=CRC\equiv CR$; type B, $R(H)C=C(H)C\equiv CR$.
[b] Traces of tetramers (ca. 1%) present as well.

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).

R = Ph (11), SiMe₃ (12)

$$\tag{5}$$

R = Ph (13), SiMe₃ (14)
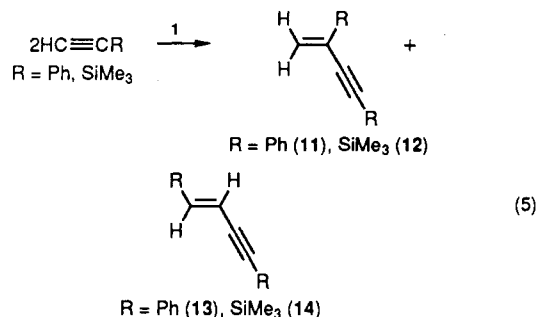
The lanthanum- and cerium-catalyzed couplings of terminal alkynes are generally less selective than for yttrium, and in addition to dimers, higher oligomers are formed as well. Both lanthanum and cerium behave essentially identical, and distinct differences in selectivity and activity are not observed. 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).


$$\tag{6}$$

10
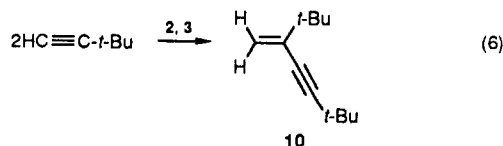
Higher oligomers, i.e. trimers and traces of tetramers, are formed as well when smaller alkynes such as propyne or n-pentyne are applied. For instance, propyne is oligomerized by **3** to a sole dimer (74%), two trimers (19% and 6%), and a tetramer (1%). However, the regioselectivity is retained and the dimer as well as the major trimer

was identified as head-to-tail oligomers (NMR analysis, eq 7).


$$\tag{7}$$

15   16
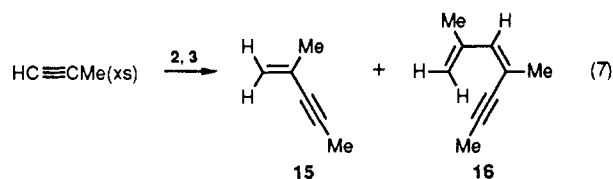
The lanthanum- and cerium-catalyzed oligomerizations of phenylacetylene and (trimethylsilyl)acetylene give, in addition to dimers, significant amounts of trimers as well. NMR spectroscopy shows that these are not simply head-to-tail or head-to-head trimers. Phenylacetylene is oligomerized to a mixture of a single dimer, 1,4-diphenyl-1-buten-3-yne (**13**), and two trimers (eq 8, Table

$$\tag{8}$$

17
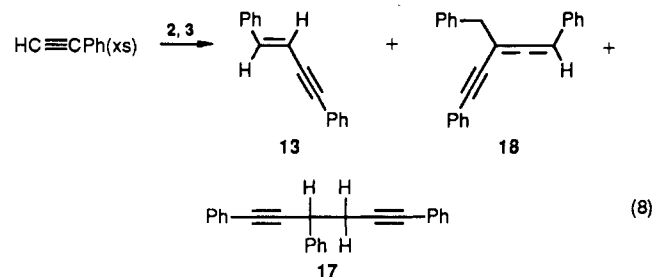
I). One of the trimers contains two intact triple bonds (NMR analysis) and was identified as 1,3,6-triphenyl-1,5-hexadiyne (**17**). The second trimer contains an allenic fragment (NMR analysis) and is likely a substituted allene such as **18**.[10]

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.

$$\tag{9}$$

19A   19B
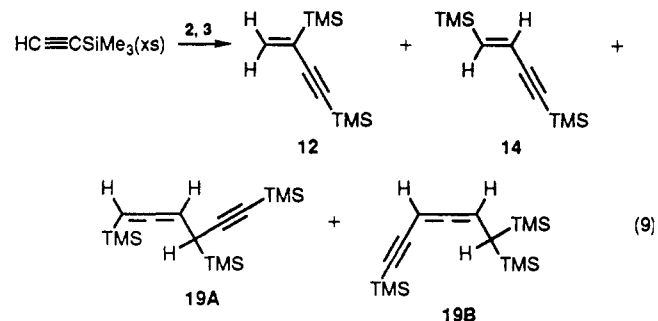
Proposed Catalytic Cycle. A plausible reaction pathway for the dimerization of terminal alkynes by Cp*₂ScR and Cp*₂TiR compounds is given in Scheme I.[4,5,7,11] With some extensions this mechanism is applicable for our lanthanide systems as well. It consists of a sequence of well-established elementary reactions such as acetylene insertion into M–C σ-bonds and σ-bond metathesis. The first step involves alkyne CH bond activation by the carbyls Cp*₂LnCH(SiMe₃)₂ and formation of acetylides, [Cp*₂LnC≡CR]ₙ, together with CH₂(SiMe₃)₂. Coordination and subsequent insertion of an alkyne into the Ln–C σ-bond affords a substituted alkenyl lanthanide. This undergoes another σ-bond metathesis with an in-

(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.

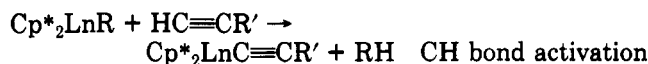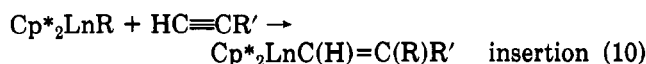(11) Christ, C. S.; Eyler, R. R.; Richardson, D. E. *J. Am. Chem. Soc.* 1990, *112*, 596.

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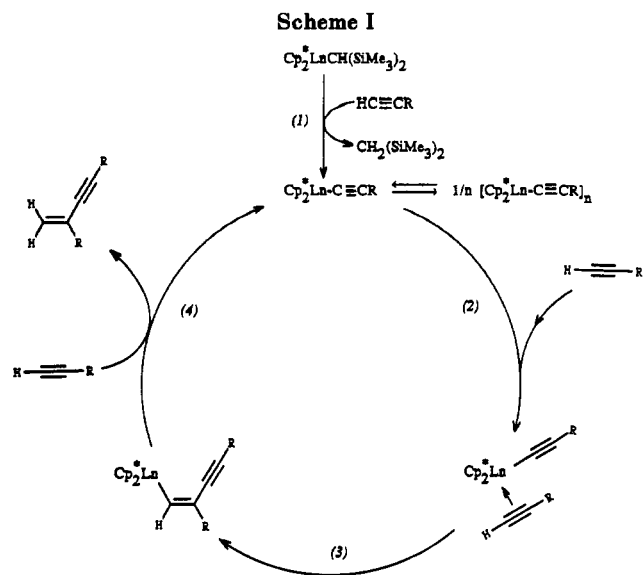
coming alkyne, thus regenerating the active acetylide and producing free enynes.

The first step in the mechanism, i.e. σ-bond metathesis between a Ln–C σ-bond and an alkyne CH bond, appears to be a general reaction for lanthanide and group 3 carbyls.[7,12] Marks and co-workers[13] determined bond enthalpies for a series of Cp*$_2$SmR compounds (R = CH(SiMe$_3$)$_2$, η^3-C$_3$H$_5$, C≡CPh, and H) and analyzed the thermodynamics of samarium-centered reactions. They calculated the CH bond metathesis reaction of Cp*$_2$SmCH(SiMe$_3$)$_2$ with phenylacetylene to be rather exothermic (ΔH_{calcd} = −76 kJ/mol); although the reaction is entropically unfavorable since four particles form three ($-T\Delta S$ = +20 to +40 kJ/2 mol of Sm at room temperature). It is reasonable to assume that the thermodynamics for cerium are essentially that of samarium.

A number of cerium acetylides, [Cp*$_2$CeC≡CR]$_n$ (R = Me, 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 Ln–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 σ-bond metathesis between the carbyls and the alkyne CH bond (step 1) is slower than σ-bond metathesis with the metal–alkenyl bond in the catalytic cycle (step 4). It is likely that these differences in the rate of σ-bond metathesis are related to the size of the alkyl substituent; i.e. the reactivity of a bulky CH(SiMe$_3$)$_2$ group is much lower than that of a less hindered alkenyl 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 ($\Delta\Delta G^{\ast}$) for CH bond activation and insertion in step 4 (Scheme I, see also eq 10).

$$Cp^*{}_2LnR + HC≡CR' \rightarrow$$
$$Cp^*{}_2LnC(H)=C(R)R' \quad \text{insertion (10)}$$

$$Cp^*{}_2LnR + HC≡CR' \rightarrow$$
$$Cp^*{}_2LnC≡CR' + RH \quad \text{CH bond activation}$$

It appears that the value of $\Delta\Delta G^{\ast}$ 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,[9] exclusively dimers are formed. This indicates that for this metal the activation energy for σ-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.[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 R is always pointing away from the Cp* rings. It is likely that this situation is energetically favored because it minimizes steric repulsions between the 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 Cp*$_2$LnC≡CR, such as 1,4-additions[16] 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 σ-bond metathesis with phenylacetylene (Scheme II).

Preparation, Characterization, and Catalytic Behavior of Cerium Acetylides. NMR studies clearly expressed that the acetylides [Cp*$_2$LnC≡CR]$_n$ 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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(13) Nolan, S. P.; Stein, D.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7844.

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

(15) Burger, B. J.; Thompson, M. E.; Cotton, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566.
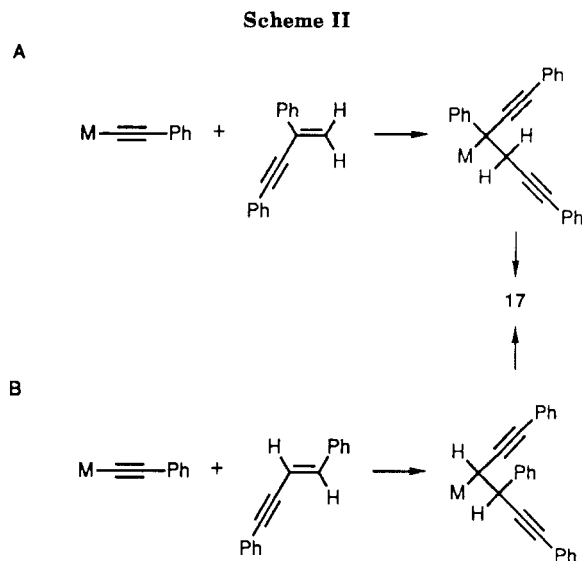
(16) Kusumoto, T.; Hiyama, T. *Chem. Lett.* **1985**, 1405.

Scheme II

A

B

Table II. ¹H NMR Data for Compounds [Cp*₂CeC≡CR]ₙ (R = Me, *t*-Bu) and Cp*₂CeC≡C-*t*-Bu•THF[a]

compd	δ	I[b]	lw[c]	assgnt
[Cp*₂CeC≡C-*t*-Bu]ₙ (7)	4.65	30	25	Cp*
	-5.0	9	10	*t*-Bu
Cp*₂CeC≡C-*t*-BuCTHF (8)	3.97	30	13	Cp*
	-1.98	9	4	*t*-Bu
	-7.49	4	80	β-THF
	-22.0	4	180	α-THF
[Cp*₂CeC≡CMe]ₙ (20)	2.78	30	12	Cp*
	-13.3	3	35	Me

[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, [Cp*₂CeC≡CR]ₙ (7, R = *t*-Bu; 20, R = Me), were prepared by addition of an excess of alkyne to benzene (7) or pentane solutions (20) of Cp*₂CeCH(SiMe₃)₂ and isolated as red-brown crystals. Elemental analyses and ¹H 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. [Cp₂ErC≡C-*t*-Bu]₂[12a] and [(C₅H₄Me)₂SmC≡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 acetylides show characteristic ν(C≡C) absorptions between 2090 and 2020 cm⁻¹.[7,17] 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 [L₂MC≡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 alkyne π-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
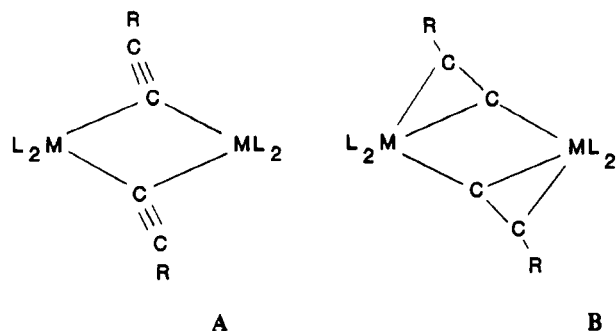

Figure 2. Two of the possible bonding modes for bridging alkynyl ligands.

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 Cp*₂CeCH(SiMe₃)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 Cp*₂CeCH(SiMe₃)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 alkyne, a prerequisite for catalytic activity. Indeed, Cp*₂CeCH(SiMe₃)₂ reacts with *tert*-butylacetylene in THF to yield the THF adduct of 7, Cp*₂CeC≡C-*t*-Bu·THF (8). ¹H NMR spectra of 8 are consistent with the proposed stoichiometry and show a singlet for the Cp* and *t*-Bu groups together with two broad, high-field shifted resonances for the α- and β-THF hydrogens (Table II). IR spectra display a clear ν(C≡C) absorption at 2060 cm⁻¹. This value is in the range (2080–2060 cm⁻¹) for a number of Cp*₂LnC≡CR·L compounds (Ln = Y⁷ and Sm¹⁹). Typical absorptions of THF coordinated to a Ln³⁺ center are present at 1020 and 865 cm⁻¹.²⁰

Concluding Remarks

Lanthanide carbyls, Cp*₂LnCH(SiMe₃)₂ (Ln = Y, La, and Ce), are very active catalysts for the oligomerization of terminal alkynes by a mechanism that consists of several insertions and σ-bond metatheses. However, the coupling reactions are less selective than for extensively studied Cp*₂Ti^III systems and, in addition to a lowering of regioselectivity, higher alkyne oligomers are formed as well. Remarkable differences in regioselectivity were observed between alkyl-substituted alkynes on one side and (trimethylsilyl)acetylene and phenylacetylene on the other. This indicates not only that the stereochemical outcome of alkyne insertion is sterically controlled but that electronic effects are important as well.

A delicate balance between alkyne CH bond formation and alkyne 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

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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. Benzene, toluene, Et_2O, THF, pentane, and hexane were distilled from Na/K alloy under nitrogen. NMR solvents (benzene-d_6, toluene-d_8, THF-d_8, cyclohexane-d_{12}) were distilled from Na or Na/K alloy. Carbyls $Cp*_2LnCH(SiMe_3)_2$ (Ln = Y,[21] La,[8] and Ce[8]) were prepared according to published procedures. 1-Pentyne, 3,3-dimethyl-1-butyne, 3-methyl-1-butyne, 4-methyl-1-pentyne, (trimethylsilyl)acetylene, and phenylacetylene were distilled or vacuum-transferred 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 in parts per million relative to TMS (δ = 0.00 ppm). Proton spectra are referenced to residual protons in deuterated solvents (benzene-d_6, δ 7.15; THF-d_8, δ 1.72; toluene-d_8, δ 7.02; chloroform-d_1, δ 7.22; cyclohexane-d_{12}, δ 1.36 ppm) or TMS (δ 0.00 ppm). ^{13}C NMR chemical shifts are referenced to carbon resonances of the solvent (benzene-d_6, δ 127.96; toluene-d_8, δ 20.4; chloroform-d_1, δ 77.0; THF-d_8, δ 25.5; cyclohexane-d_{12}, δ 26.6 ppm). Gas chromatography was performed with a HP 5890-A instrument equipped with a HP 3390 integrator using a Porapack Q or an OV-101 capillary column. The GC response factors of the oligomers, using flame ionization 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 $Cp*_2YCH(SiMe_3)_2$ (1) with Excess HC≡CPh. A 100-μL (0.92 mmol) aliquot of HC≡CPh was added to an NMR tube charged with 19.7 mg (0.04 mmol) of 1 in benzene-d_6 (0.3 mL). Upon addition the solution turned yellow and the solvent started to refluux gently. NMR showed the quantitative conversion of 1 to $[Cp*_2YC≡CPh]_n$ ($\delta(Cp*)$ = 1.97 ppm) and $CH_2(SiMe_3)_2$. All HC≡CPh was dimerized to a mixture of 11 (90%) and 13 (10%).

NMR Tube Reaction of $Cp*_2YCH(SiMe_3)_2$ (1) with Excess (Trimethylsilyl)acetylene. A 100-μL (0.71 mmol) aliquot of HC≡CSiMe$_3$ was added to an NMR tube charged with 19.4 mg (0.04 mmol) of 1 in ca 0.4 mL of benzene-d_6. After ca. 20 min, characteristic resonances of $CH_2(SiMe_3)_2$, $[Cp*_2YC≡CSiMe_3]_n$ (5) ($\delta(Cp*)$ = 1.94 ppm), unreacted HC≡CSiMe$_3$, and dimers 12 and 14 were present. After ca. 4 h, all HC≡CSiMe$_3$ was converted into 12 (30%) and 14 (70%).

NMR Tube Reaction of $Cp*_2CeCH(SiMe_3)_2$ (3) with Excess (Trimethylsilyl)acetylene. A 200-μL (1.42 mmol) aliquot of (trimethylsilyl)acetylene was added to an NMR tube containing 11.3 mg (0.02 mmol) of 3 in benzene-d_6 (0.3 mL). After 2 h, characteristic resonances of 3 had disappeared and a novel organocerium compound was formed, which was tentatively identified as $[Cp*_2CeC≡CSiMe_3]_n$ (resonances at δ 5.0 ppm (s, 30 H) and -2.8 ppm (s, 9 H)). After 4 h, the excess (trimethylsilyl)-acetylene was oligomerized to a mixture of dimers and trimers. At this stage of the reactions at least two organocerium compounds were present in the reaction mixture (NMR analysis).

NMR Tube Reaction of $Cp*_2CeCH(SiMe_3)_2$ (3) with Excess Propyne. Propyne (1.06 mmol) was condensed into an NMR tube charged with 36 mg (0.06 mmol) of 3 in benzene-d_6 (0.4 mL). Upon addition the solution turned purple and subsequently green. NMR spectroscopy indicated the quantitative formation of $CH_2(SiMe_3)_2$, at least six broad resonances arising from organocerium compounds, and the presence of 2,4-dimethyl-1-buten-3-yne (15, 75%)

and (Z)-2,4-dimethyl-1,3-heptadien-5-yne (16, 25%).

NMR Tube Reaction of $Cp*_2CeCH(SiMe_3)_2$ (3) with Excess *tert*-Butylacetylene. A 230-μL (1.87 mmol) aliquot of *tert*-butylacetylene was added to an NMR tube charged with 43 mg (0.09 mmol) of 3 in benzene-d_6. Upon addition the color of the solution turned purple and the solvent started to reflux. An NMR spectrum after 10 min indicated the presence of unreacted 3, $CH_2(SiMe_3)_2$, the quantitative conversion of *tert*-butylacetylene to 2,4-di-*tert*-butyl-1-buten-3-yne (10), and characteristic resonances of $[Cp*_2CeC≡C-t-Bu]_n$ (7).

NMR Tube Reaction of $Cp*_2CeCH(SiMe_3)_2$ (3) with Excess *tert*-Butylacetylene in THF-d_8. 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-d_8 (0.5 mL). NMR spectroscopy indicated the quantitative formation of $Cp*_2CeC≡C-t-Bu·THF-d_8$ (8-d_8) and $CH_2(SiMe_3)_2$. Excess *tert*-butylacetylene was invariable present, and resonances of the dimer 2,4-di-*tert*-butyl-1-buten-3-yne (10) were not observed.

Catalytic Oligomerization of HC≡CR (R = *n*-Pr, *i*-Pr, *i*-Bu, *t*-Bu, Ph, SiMe$_3$) by $Cp*_2CeCH(SiMe_3)_2$ (3). Alkynes (45–90 mmol) were added to hexane solutions (7–14 mL) of $Cp*_2CeCH(SiMe_3)_2$ (0.06–0.14 mmol; catalyst:substrate ratios ranging from 1:45 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 CH_2Cl_2 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, SiMe$_3$, Ph) by $Cp*_2LnCH(SiMe_3)_2$ (1, Ln = Y; 2, Ln = La). The reactions were carried out by following a procedure similar to the one given for the reactions with $Cp*_2CeCH(SiMe_3)_2$. 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^{-3} and 1 × 10^{-2} mol/L were applied, catalyst:substrate ratios varied between 1:130 and 1:230. The product distributions are given in Table I.

Catalytic Oligomerization of Propyne by $Cp*_2LnCH(SiMe_3)_2$ (2, Ln = La; 3, Ln = Ce). A solution of 86 mg (0.15 mmol) of 3 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 mmol.

The oligomerization of propyne with the lanthanum derivative was performed analogously with 101 mg (0.18 mmol) of $Cp*_2LaCH(SiMe_3)_2$ 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 $[Cp*_2CeC≡C-t-Bu]_n$ (7). *tert*-Butylacetylene (2.0 mL, 16 mmol) was added to a stirred solution of 574 mg (1.00 mmol) of $Cp*_2CeCH(SiMe_3)_2$ in benzene (20 mL). Upon addition the solution instantaneously turned purple. After stirring for 40 h at room temperature, a red-brown suspension had been formed. Benzene (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 (m), 1380 (m), 1360 (w), 1335 (w), 1260 (w), 1200 (w), 1020 (m), 880 (m), 730 (m), 560 (m), 420 (m). NMR data are given in Table II. Anal. Calcd for $C_{26}H_{39}Ce$: C, 63.51; H, 8.00. Found: C, 63.47; H, 7.98. The compound is insufficiently soluble for cryoscopy in benzene.

Preparation of $[Cp*_2CeC≡CMe]_n$ (20). Excess propyne was allowed to react with 718 mg (1.26 mmol) of $Cp*_2CeCH(SiMe_3)_2$ in pentane (40 mL). Upon addition the color of the solution instantaneously changed from red to purple and a pink-purple solid deposited. After ca. 15 min, the propyne atmosphere was

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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 (w), 730 (w), 450 (m). NMR data are given in Table II. Anal. Calcd for $C_{23}H_{33}Ce$: C, 61.44; H, 7.40; Ce, 31.16. Found: C, 61.59; H, 7.34; Ce, 31.25.

Catalytic Dimerization of tert-Butylacetylene by [Cp*₂CeC≡C-t-Bu]ₙ (7). A 50-μL (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-d_6 (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 (10).

Preparation of Cp*₂CeC≡C-t-Bu·THF (8). tert-Butylacetylene (0.1 mL, 0.8 mmol) was added to a stirred solution of

205 mg (0.36 mmol) of Cp*₂CeCH(SiMe₃)₂ in pentane/THF (11 mL, 10:1). 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 $C_{30}H_{47}CeO$: C, 63.91; H, 8.40; Ce, 24.85. Found: C, 63.97; H, 8.47; Ce, 24.76.

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

A Carbido Cluster as a Bulky π Donor Ligand. Preparation and Characterization of [HFe₄(CO)₁₂C]BXY (X = Y = H, Cl, Br; X = H, Y = Cl, Br, OH)

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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 substituted 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 unanticipated 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]BHX (X = Cl, Br) are reported. In both cases crystals form in the monoclinic system of space group $P2_1/m$ 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 ($F_o > 5\sigma F_o$)), whereas for X = Br it was by isomorphous analogy to the solution for X = Cl ($R(F)$ = 3.97%, $R(wF)$ = 4.11% for 1889 independent reflections ($F_o > 5\sigma F_o$)).

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 steric 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. L_xMBH_2. An example from our own laboratories is (CO)₄CoBH₂·THF,[12] and the closely related complex (CO)₂(η¹-dppm)Co(μ-dppm)BH₂ has now been isolated and crystallographically charac-

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