Organometallics **1993,** *12,* 2609–2617

Reversible Carbon–Carbon Bond Formation in Organolanthanide Systems. Preparation and Properties of Lanthanide Acetylides $[Cp^*_2LnC{\equiv}CR]_n$ and Their Rearrangement Products $[Cp^*_2Ln]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}RC_4R)$ (Ln = La, Ce, R = Alkyl)

H. J. Heeres,[†] J. Nijhoff, and J. H. Teuben*

Groningen Centre for Catalysis and Synthesis, Department of Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

R. D. Rogers

Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

Received December 30, 1992

The early lanthanide carbyls $Cp^*_2LnCH(SiMe_3)_2$[1] (**1**, Ln = Ce; **2**, Ln = La) react with terminal alkynes $HC{\equiv}CR$ (R = Me, *t*-Bu) to produce oligomeric acetylides $[Cp^*_2LnC{\equiv}CR]_n$ (**3**, Ln = Ce, R = Me; **4**, Ln = La, R = Me; **5**, Ln = Ce, R = *t*-Bu). The acetylides are not stable in solution and rearrange to give the carbon–carbon coupled products, $[Cp^*_2Ln]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}RC_4R)$ (**6**, Ln = Ce, R = Me; **7**, Ln = La, R = Me; **8**, Ln = Ce, R = *t*-Bu). The acetylide carbon–carbon coupling reaction is reversible in solution. Thermodynamic and kinetic parameters for this process were determined for the $[Cp^*_2LaC{\equiv}CMe]_n/[Cp^*_2La]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}MeC_4Me)$ couple: $\Delta G^\ominus = 4.5 \pm 0.4$ kJ/mol; $k_1 = 8.3(\pm0.4) \times 10^{-5}$ s^{-1}; $k_{-1} = 1.1(\pm0.7) \times 10^{-5}$ s^{-1}, and $\Delta G^\ddagger = 96.3(\pm0.1)$ kJ/mol (298 K). The molecular structures of **6** and **8** were determined by single-crystal X-ray diffraction and shown to consist of two Cp^*_2Ce units bridged by a conjugated RC_4R group. Cell data for **6**: monoclinic, $P2_1/n$, $a = 10.670(8)$ Å, $b = 25.081(9)$ Å, $c = 16.706(9)$ Å, $\beta = 102.41(7)°$, $D_{calcd}(Z = 4) = 1.37$ g·cm^{-3}. Least-squares refinement based on 4179 reflections converged to $R = 0.046$ and $R_w = 0.053$. Cell data for **8**: monoclinic, $P2_1/n$, $a = 11.376(6)$ Å, $b = 14.151(5)$ Å, $c = 15.541(4)$ Å, $\beta = 103.92(4)°$, $D_{calcd}(Z = 2) = 1.34$ g·cm^{-3}. Least-squares refinement based on 3502 reflections converged to $R = 0.031$ and $R_w = 0.040$. Protolysis of **6** and **7** with 2,6-di-*tert*-butyl-4-methylphenol affords (*E*)-2-hexen-4-yne, exclusively. Contrastingly, a mixture of enynes and butatrienes is formed upon protolysis of **8**. Both **5** and **8** catalyze the dimerization of *tert*-butylacetylene to 2,4-di-*tert*-butyl-1-buten-3-yne.

Introduction

Organometallics containing an acetylide moiety have played an important role in the development of organo-f-element chemistry.[2] Broadly applicable synthetic routes to this class of compounds have been developed, examples of which include salt metathesis between lanthanide halides and main group acetylides and σ-bond metathesis between lanthanide alkyls or hydrides and terminal alkynes (eq 1).

$$L_xLn\text{-}X + M{-}{\equiv}{-}R \longrightarrow {}^1\!/_n\,[L_xLn{-}{\equiv}{-}R]_n + MX \quad (1a)$$

$$L_xLn\text{-}R' + H{-}{\equiv}{-}R \longrightarrow {}^1\!/_n\,[L_xLn{-}{\equiv}{-}R]_n + R'H \quad (1b)$$

The molecular structures of several compounds have been determined by single-crystal X-ray diffraction, and most have been shown to be oligomeric with bridging acetylide ligands.[3] However, virtually nothing is known about the reactivity of well-defined organolanthanide acetylides, and especially their catalytic properties are largely unexplored. This is rather surprising because Shen and co-workers[4] have demonstrated that heterogeneous Ziegler systems based on lanthanides are excellent catalysts for the highly *cis*-stereospecific polymerization of alkynes such as acetylene and phenylacetylene. Studies on soluble lanthanide acetylides might give valuable information on the mechanism of these polymerizations.

We have recently reported[5] that solutions of the cerium carbyl $Cp^*_2CeCH(SiMe_3)_2$ (**1**) catalyze the head to tail oligomerization of alkyl-substituted terminal alkynes to 2,4-disubstituted enynes. Workup of the reaction mixture afforded red-brown crystals which were identified as the acetylides $[Cp^*_2CeC{\equiv}CR]_n$. The observed reduction of the $\nu(C{\equiv}C)$ to below 1600 cm^{-1} was assumed to be the result of bridging, side-on bonding of the acetylide ligands.

[†] Present address: Koninklijke/Shell-Laboratorium Amsterdam, Shell Research BV, Postbus 3003, 1003 AA Amsterdam, The Netherlands.

(1) The following abbreviations are used in this paper: Ln = lanthanide or group 3 element; Cp* = η^5-C_5Me_5 ligand; HOAr = 2,6-di-*tert*-butyl-4-methylphenol; OAr = 2,6-di-*tert*-butyl-4-methylphenoxide; lw = line width of the NMR resonances at half-maximum.

(2) (a) Atwood, J. L.; Hains, C. F.; Tutsui, M.; Gebala, A. E. *J. Chem. Soc., Chem. Commun.* **1973,** 452. (b) Tutsui, M.; Ely, N. *J. Am. Chem. Soc.* **1974,** *96,* 4042. (c) Evans, W. J.; Wayda, A. L. *J. Organomet. Chem.* **1980,** *202,* C6. (d) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 21. (e) Nast, R. *Coord. Chem. Rev.* **1982,** *47,* 90. (f) Den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987,** *6,* 2053.

(3) (a) Atwood, J. L.; Hunter, W. E.; Wayda, J. L.; Evans, W. J. *Inorg. Chem.* **1981,** *20,* 4115. (b) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1983,** *2,* 709. (c) Evans, W. J.; Drummond, D. K.; Hanusa, T. P.; Olofson, J. M. *J. Organomet. Chem.* **1989,** *376,* 311. (d) Shen, Q.; Zheng, D.; Lin, L.; Lin, Y. *J. Organomet. Chem.* **1990,** *391,* 307.

(4) Shen, Z. *Inorg. Chim. Acta* **1987,** *140,* 7.

(5) Heeres, H. J.; Teuben, J. H. *Organometallics* **1991,** *10,* 1980.

0276-7333/93/2312-2609$04.00/0 © 1993 American Chemical Society

Table I. ^{1}H- and ^{13}C-NMR Spectroscopic Data for 4–7

$[Cp^*_2LaC{\equiv}CMe]_n$ (**4**)	2.19	s, 30H, Cp*	toluene-d_8, −10 °C
	1.45	s, 3H, Me	
	156.2	s, *C*≡CMe	
	120.9	s, Cp*	
	117.0	s, C≡*C*Me	
	12.8	q, $^1J_{CH}$ = 126 Hz, Cp*	
	7.2	q, $^1J_{CH}$ = 131 Hz, C≡C*Me*	
$[Cp^*_2CeC{\equiv}C\text{-}t\text{-}Bu]_n$ (**5**)	6.24	s, 30H, lw = 33 Hz, Cp*	toluene-d_8, −20 °C
	−14.4	s, 9H, lw = 260 Hz, *t*-Bu	
$[Cp^*_2Ce]_2(C_4Me_2)$ (**6**)	2.78	s, 30H, lw = 12 Hz, Cp*	benzene-d_6, 21 °C
	−13.3	s, 3H, lw = 35 Hz, Me	
$[Cp^*_2La]_2(C_4Me_2)$ (**7**)	2.38	s, 6H, Me	benzene-d_6, 21 °C
	2.06	s, 30H, Cp*	
	208.6	s, Me*C*=C=	
	153.9	s, MeC=*C*=	
	119.2	s, Cp*	
	16.1	q, $^1J_{CH}$ = 127 Hz, *Me*C=C=	
	11.2	q, $^1J_{CH}$ = 124 Hz, Cp*	

Recently, we succeeded in the preparation of single crystals of $[Cp^*_2CeC{\equiv}CR]_n$ for R = Me (**6**) and *t*-Bu (**8**). X-ray diffraction studies revealed that our earlier assumption with respect to the molecular structures of **6** and **8** is incorrect and that the acetylide ligands in both compounds are coupled to form bridging RC_4R moieties. This contribution describes the molecular structure of **6** and **8** and provides evidence that acetylide carbon–carbon coupling in these early lanthanide systems proceeds *via* initial acetylide formation and, more surprisingly, that acetylide coupling is reversible at ambient temperatures. Furthermore, the implication of this rearrangement on the catalytic performance of the acetylides will be discussed.

Results and Discussion

Synthesis and Characterization of Lanthanide Acetylides. Treatment of pentane solutions of $Cp^*_2CeCH(SiMe_3)_2$ (**1**) or $Cp^*_2LaCH(SiMe_3)_2$ (**2**) with an excess of propyne and/or *tert*-butylacetylene resulted in the formation of acetylides $[Cp^*_2LnC{\equiv}CR]_n$ (**3**, Ln = Ce, R = Me; **4**, Ln = La, R = Me; **5**, Ln = Ce, R = *t*-Bu) (eq 2).

$$Cp^*_2LnCH(SiMe_3)_2 + H{-}{\equiv}{-}R \longrightarrow {}^1/_n\,[Cp^*_2Ln{-}{\equiv}{-}R]_n + CH_2(SiMe_3)_2 \qquad (2)$$

1, Ln = Ce
2, Ln = La

3, Ln = Ce, R = Me
4, Ln = La, R = Me
5, Ln = Ce, R = ^{t}Bu

The compounds were isolated as purple (**3** and **5**) or white (**4**) thermolabile powders in good yields (68–91%). IR spectra display a characteristic C≡C triple bond stretching vibration at 2035 cm^{-1} (**3** and **4**) and at 2005 cm^{-1} (**5**), which is significantly lower than for free propyne (2140 cm^{-1}).[6] Similar reduction of the C≡C stretching vibration was observed for related lanthanide acetylides.[2,3]

^{1}H- and ^{13}C-NMR spectroscopic data for **4** and **5** are given in Table I and are in agreement with the proposed stoichiometry. As expected for a paramagnetic cerium(III) organometallic,[7] the resonances for **5** are isotropically shifted and present at δ 6.24 (lw = 33 Hz, Cp*) and −14.4 (lw = 260 Hz, *t*-Bu). ^{1}H-NMR spectra for the methylacetylide **3** could not be obtained due to the poor thermal stability of this compound.

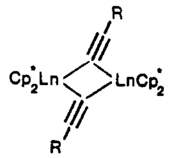
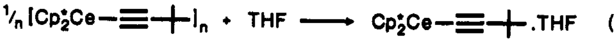


Figure 1. Acetylide bonding in organolanthanide compounds.

In analogy with structurally characterized lanthanide acetylides like $[Cp_2ErC{\equiv}C\text{-}t\text{-}Bu]_2$,[3a] $[(C_5H_4Me)_2SmC{\equiv}C\text{-}t\text{-}Bu]_2$,[3b] and $[(C_5H_4\text{-}t\text{-}Bu)_2SmC{\equiv}CPh]_2$,[3d] it is reasonable to assume that **3**, **4**, and **5** are dimers with asymmetrically bridging, σ-bonded acetylide ligands (Figure 1).[8] However, the exact degree of association is as yet unknown. Determination of the nuclearity by solution molecular weight determinatons were unsuccessful due to the limited solubility and thermal instability (*vide infra*) of the acetylides studied.

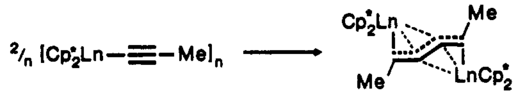
The oligomeric structure of the acetylides may be broken up by the action of a Lewis base. Addition of THF to solutions of **5** affords a monomeric adduct, $Cp^*_2CeC{\equiv}C\text{-}t\text{-}Bu{\cdot}THF$ (**9**, eq 3), a known compound which was prepared by treatment of $Cp^*_2CeCH(SiMe_3)_2$ with *tert*-butylacetylene in the presence of THF.[5]



(3)

5 9

Thermolysis and the Formation of Compounds $[Cp^*_2Ln]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}RC_4R)$ (6, Ln = Ce, R = Me; 7, Ln = La, R = Me; 8, Ln = Ce, R = *t*-Bu). The methylacetylides **3** and **4** are unstable in hydrocarbon solution and transform within 1 day at room temperature. Workup afforded brown-red and red crystals, respectively, identified as $[Cp^*_2Ln]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}MeC_4Me)$ (**6**, Ln = Ce; **7**, Ln = La, eq 4), formed by coupling of the α-carbon atoms of the acetylide ligands.



(4)

3, Ln = Ce
4, Ln = La

6, Ln = Ce
7, Ln = La

NMR tube reactions for **4** indicate that thermolysis is a very clean process with **7** being the sole organolanthanide formed. The half-life for the coupling reaction for **4** was determined (NMR spectroscopy) to be 3.2 h at room temperature. A more elaborate discussion on the kinetics of the carbon–carbon coupling reaction will be given further on.

IR spectra for **6** and **7** are essentially superimposable and suggest a close relationship in molecular structures. Bands of medium intensity are present at 1600 (**6**) and

---

[6] Duncan, J. L.; McKean, D. C.; Nivellini, G. D. *J. Mol. Structure* **1976**, *32*, 255.

[7] (a) Fischer, R. D. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragala, I. L., Eds.; D. Riedel: Dordrecht, 1985; p 277. (b) Evans, W. J.; Hozbor, M. A. *J. Organomet. Chem.* **1987**, *326*, 299.

[8] One of the reviewers informed us that they had recently solved the crystal structure of $[Cp^*_2SmC{\equiv}C\text{-}t\text{-}Bu]_n$ (unpublished results). This acetylide crystallizes as a loosely joined dimer with terminal acetylide ligands and bridging Cp* ligands. Although La and Ce are larger than Sm and steric crowding of the four Cp* ligands would be less for the former elements, acetylides 3–5 might have related molecular structures.

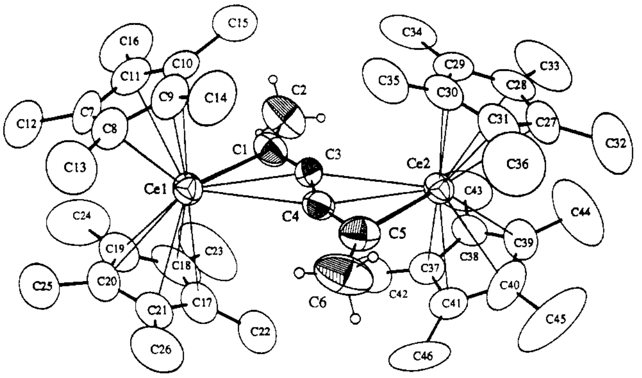
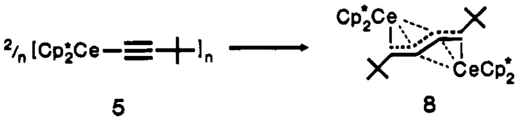


Figure 2. Molecular structure and atom labeling scheme for 6.

1605 (7) cm^{-1} which implies that the carbon–carbon triple bond order is significantly reduced. The molecular structure of the cerium derivative 6 was determined by an X-ray diffraction study (Figure 2) and reveals a MeC_4Me unit bonded as a dimetalated butatriene with additional interactions with the cerium atoms (*vide infra*).

The characterization of 6 and 7 in solution was carried out by NMR spectroscopy. Especially informative are the ^{13}C-NMR chemical shifts for the C_4 moiety in diamagnetic 7 (Table I). In the ^{13}C-NMR spectrum, the terminal carbon resonance is present at δ 208.6 ppm, which is significantly downfield shifted compared to 1,4-di-*tert*-butylbutatriene (δ 118.2 ppm).[9] A similar downfield shift was reported for dilithiated 1,4-di-*tert*-butylbutatriene (δ 197.0 ppm).[9] The effect of metalation is less pronounced for the internal carbon atoms, and the chemical shift for 7 (δ 153.9 ppm) differs only slightly from that of 1,4-di-*tert*-butylbutatriene (δ 160.6 ppm).[9] The cerium *tert*-butylacetylide 5 is, like 6 and 8, not stable in solution and rearranges to the coupled product $[Cp^*_2Ce]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_4(t\text{-}Bu)_2)$ (8, eq 5).[10] The rate of coupling is much slower than for the methyl derivatives 3 and 4, and the half-life is on the order of days instead of hours.



5 8 (5)

An IR spectrum of 8 shows a clear band at 1560 cm^{-1}, which is somewhat lower than for the methyl analogs 6 and 7 but a strong indication for a close resemblance in molecular structures. This was confirmed by an X-ray diffraction study (Figure 3).

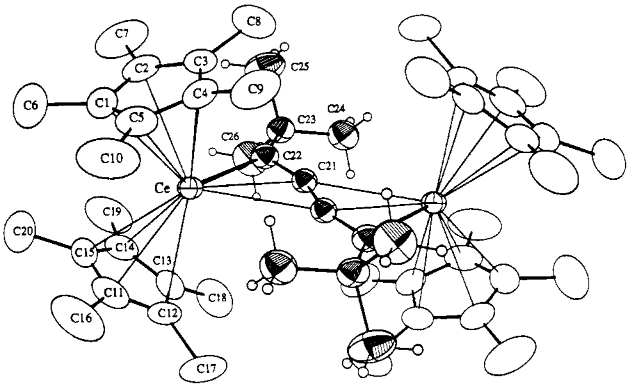


Figure 3. Molecular structure and atom labeling scheme for 8.

While this investigation was in progress, Evans and coworkers[11] reported that treatment of $[Cp^*_2SmH]_2$ or $Cp^*_2SmCH(SiMe_3)_2$ with phenylacetylene afforded a related carbon–carbon coupled product, $[Cp^*_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}PhC_4Ph)$. However, in contrast to cerium, the intermediate acetylide $[Cp^*_2SmC{\equiv}CPh]_n$ was neither isolated nor observed spectroscopically.[12] These differences in stability between cerium and samarium acetylides might be related to the differences in ionic radii between trivalent cerium (1.143 Å)[13] and trivalent samarium (1.079 Å).[13] For the latter, bridging acetylides might be strongly destabilized as a result of severe steric repulsion between the cyclopentadienyl rings and acetylide substituents. However, different acetylide substituents were applied (*tert*-butyl/methyl for cerium versus phenyl for samarium), and thus electronic effects cannot be excluded *a priori*.

Acetylide carbon–carbon coupling has not been observed for lanthanide acetylides with sterically less demanding cyclopentadienyl groups such as the unsubstituted or monoalkyl-substituted cyclopentadienyl ligands.[3] These acetylides are thermally stable and can be isolated and manipulated at ambient temperatures, suggesting that the steric crowding around the metal center plays an important role in the stability of lanthanide acetylides. Evans' and our results suggest that acetylide coupling is a general reaction pathway for organolanthanide acetylides supported by two pentamethylcyclopentadienyl ligands. It is likely that oligomeric acetylides supported by two of these bulky ancillary ligands are sterically overcrowded systems which tend to rearrange to the coupled compounds to relieve steric strain.

Reactivity of 6, 7, and 8 toward Protic Reagents. Treatment of 6 and 7 with 2,6-di-*tert*-butyl-4-methylphenol (HOAr) resulted in the quantitative formation of aryl oxides Cp^*_2LnOAr[14] (10, Ln = Ce; 11, Ln = La) and the exclusive formation of (*E*)-2-hexen-4-yne (NMR, GC/MS, eq 6).

Protolysis of the *tert*-butyl analog 8 with HOAr is less selective and resulted in a mixture of three $C_4H_2(t\text{-}Bu)_2$ isomers (GC/MS). The isomers were identified (NMR) as a *trans*-enyne, (*E*)-1,4-di-*tert*-butyl-1-buten-3-yne (60%), the corresponding *cis*-enyne (20%), and a cumulene, 1,4-

---

(9) Neugebauer, W.; Geiger, G. A. P.; Kos, A. J.; Stezowski, J. J.; Schleyer, P. R. *Chem. Ber.* **1985**, *118*, 1504.

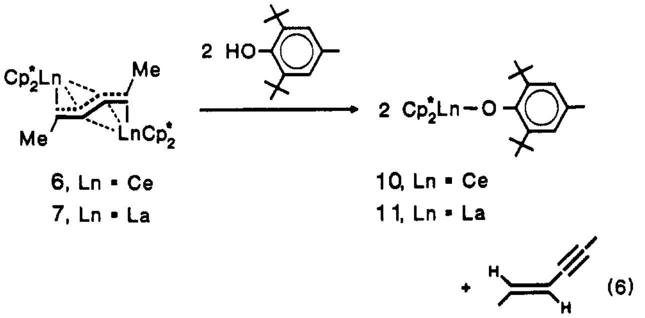
(10) NMR tube studies, aimed at determining the rate of carbon–carbon coupling for 5, revealed the involvement of a second cerium species. If a cold toluene-d_8 solution (−20 °C) of 5 was slowly allowed to warm to room temperature (ca. 1.5 h), the color of the solution gradually changed from purple to red and a new set of NMR resonances appeared (δ 6.41 and −16.3 ppm). Upon cooling to −20 °C, the original NMR resonances from 5 do not reappear. It is very unlikely that these new resonances arise from 8 because this complex is essentially insoluble in toluene. A preparative reaction under identical conditions afforded red-brown crystals which, according to IR, consisted of a mixture of the coupled compound 8 and a second cerium organometallic. The latter was separated from 8 by a benzene extraction. An IR spectrum for this compound is essentially similar to that of 5 and shows a clear band at 2005 cm^{-1}, indicative for the presence of a carbon–carbon triple bond. Thus, it appears that 5 and the unknown species have related molecular structures, and it is well possible that they only differ in degree of association.

(11) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1990**, *9*, 2628.

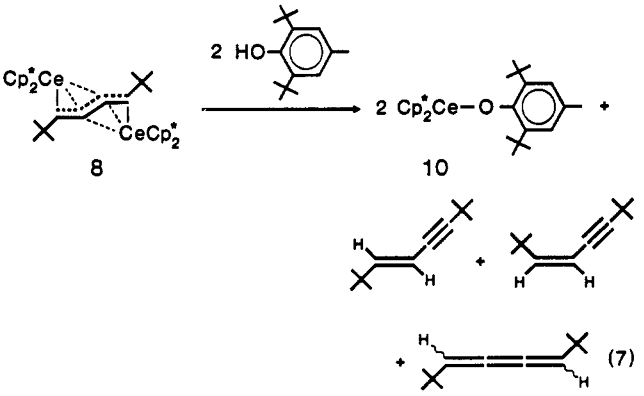
(12) Indirect evidence was obtained by reacting $[Cp^*_2SmH]_2$ with phenylacetylene at low temperatures. Quenching with THF afforded $Cp^*_2SmC{\equiv}CPh{\cdot}THF$ in low yields.

(13) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(14) Heeres, H. J.; Teuben, J. H., Unpublished. Related aryl oxides with a 2,6-di-*tert*-butylphenoxo ligand have been reported: Heeres, H. J.; Teuben, J. H.; Rogers, R. D. *J. Organomet. Chem.* **1989**, *364*, 87.



di-*tert*-butylbutatriene (20%), see eq 7. The stereochemistry of the cumulene could not be established unequivocally.



The predominant formation of enynes instead of the expected cumulenes can be explained by a reaction sequence given in Scheme I. Cerium is primarily bound to the terminal carbons of the C_4 bridge (*vide infra*), and the first protolysis likely produces a metalated butatriene. This species may either react with another proton to form a butatriene or rearrange *via* a 1,3-metal shift to a metalated enyne. 1,3-Metal shifts for lithiated butatrienes are well established[9] and are considered to be low-energy pathways. Theoretical studies[15] for nonmetalated 1,4-dimethylbutatriene and 2-hexen-4-yne indicated that the latter form is ca. 80 kJ/mol lower in energy than the butatriene and thus clearly thermodynamically favored.

The relative rates of the second protolysis and 1,3-metal shift determine the enyne/butatriene ratio. The results obtained so far suggest that rearrangement for the methyl compounds 6 and 7 is much faster than protolysis, resulting in the exclusive formation of enynes. In contrast, protolysis of the *tert*-butyl-substituted compound 8 leads to a mixture of enynes and cumulenes. Assuming that the rate of protolysis is independent on the substituent R, these observations indicate that the rate of 1,3-metal migration is rather sensitive to the steric bulk of the substituent R, with bulky groups having a strong retarding influence.

The predominant enyne isomer formed in all reactions was identified spectroscopically as the *trans* isomer. This is not surprising in view of the *trans* orientation of the alkyl substituents in the starting organometallics (Figures 2 and 3). However, significant amounts of the *cis* enyne are formed upon protolysis of the *tert*-butyl derivative 8. This isomerization process is not as yet understood. It is well-established that electrophilic substitution at sp^2 carbon atoms takes place with retention of configuration.[16]

Scheme I

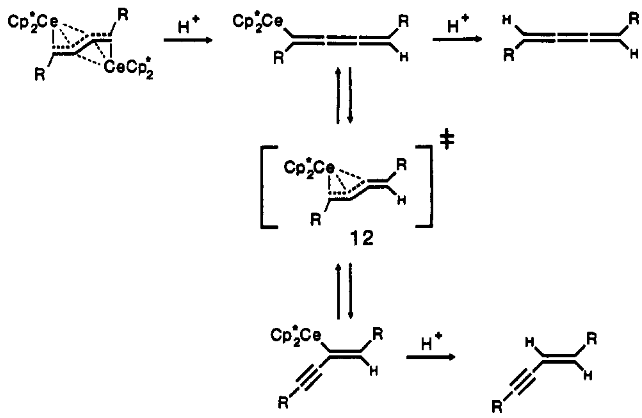


Table II. Selected Bond Distances (Å) and Angles (deg) for 6

Ce(1)–C(1)	2.55(1)	Ce(1)–C(3)	2.789(9)
Ce(1)–C(4)	2.89(1)	Ce(2)–C(3)	2.909(9)
Ce(2)–C(4)	2.779(9)	Ce(2)–C(5)	2.53(1)
C(1)–C(2)	1.54(1)	C(1)–C(3)	1.29(1)
C(3)–C(4)	1.33(1)	C(4)–C(5)	1.31(1)
C(5)–C(6)	1.51(1)	Ce(1)–Cent1[a]	2.52
Ce(1)–Cent2	2.52	Ce(2)–Cent3	2.51
Ce(2)–Cent4	2.52		
C(2)–C(1)–C(3)	127(1)	C(1)–C(3)–C(4)	146.5(9)
C(3)–C(4)–C(5)	147(1)	C(4)–C(5)–C(6)	124(1)
Cent1–Ce(1)–Cent2	134.6	Cent3–Ce(2)–Cent4	134.7

[a] Cent1 is the centroid of the C(7)–C(11) ring; Cent2, C(17)–C(21); Cent3, C(27)–C(31); Cent4, C(37)–C(41).

Hence, isomerization must take place in the starting material or, more likely, in intermediate 12 (Scheme I).

Molecular Structures of 6 and 8. Single-crystal X-ray determinations reveal that the molecular structures of 6 and 8 consist of two $Cp^*{}_2Ce$ units bridged by a R_2C_4 moiety (Figures 2 and 3). The similarities in molecular structures are rather surprising in view of the solubility characteristics. The *tert*-butyl derivative is essentially insoluble in hydrocarbon solvents whereas the methyl analog readily dissolves in these solvents. The poor solubility of the former could be the result of strong intermolecular interactions. However, inspection of intermolecular distances did not reveal extremely close contacts, the closest distance of a *tert*-butyl group with a neighboring molecule being 3.786(7) Å. Similar intermolecular distances were found for the methyl derivative (ca. 3.8 Å).

Of particular interest is the bonding of the newly formed R_2C_4 bridge. Inspection of the atomic distances and angles reveals that the four bridging carbon atoms are coplanar and form a fully conjugated bridge. The C–C bond distances in the C_4 core are identical within the estimated standard deviations (average 1.31(2) Å for 6 and 1.315(6) Å for 8 (see Tables II and III) and close to those found for the related samarium compound (1.33(3) Å)[11] and dilithiated 1,4-di-*tert*-butylbutatriene (1.292(5)–1.321(5) Å).[9] For comparison, the usual carbon–carbon distances in alkenes and alkynes are 1.34 and 1.20 Å, respectively.[17]

Cerium is primarily bound to the terminal carbon atoms of the C_4 bridge. For 6, the two different Ce–C σ-bonds are 2.55(1) Å (Ce1–C1) and 2.53(1) Å (Ce2–C5). The corresponding Ce–C σ-bonds in centrosymmetric 8 are somewhat longer (2.607(4) Å), likely the result of repulsions

---

(15) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604.

(16) Nesmeyanov, A. N.; Borisov, A. E. *Tetrahedron* **1957**, *1*, 158.

(17) *Handbook of Chemistry and Physics*, 67th ed.; CRC Press: Boca Raton, FL, 1986; table F-158.

Table III. Selected Bond Distances (Å) and Angles (deg) for 8

Ce–C(1)	2.813(4)	Ce–C(2)	2.796(4)
Ce–C(3)	2.837(4)	Ce–C(4)	2.856(4)
Ce–C(5)	2.825(4)	Ce–C(21)	2.748(4)
Ce–C(21[a])	2.940(4)	Ce–C(22)	2.607(4)
C(21)–C(22)	1.312(5)	C(21)–C(21[a])	1.324(8)
C(22)–C(23)	1.534(5)	Ce–Cent1[b]	2.56
Ce–Cent2	2.56		
C(22)–C(21)–C(21[a])	154.7(5)	C(21)–C(22)–C(23)	122.9(4)
C(22)–C(23)–C(24)	111.0(3)	Cent1–Ce–Cent2	131.7

[a] Atom related to that in Table VI by crystallographic center of inversion. [b] Cent1 is the centroid of the C(1)–C(5) ring; Cent2, C(11)–C(15).

Figure 4. Possible bonding mode of the coupled acetylide ligands.

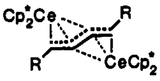


Figure 5. Actual bonding mode of the coupled acetylide ligands.

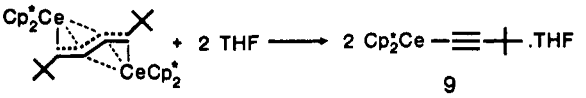
between the *t*-Bu and Cp* methyl groups (*vide infra*). The values for the Ce–C σ-bonds, especially those for 6, are close to those found for $Cp^*_2CeCH(SiMe_3)_2$ (2.535(5) Å)[18] and $Cp^*Ce[CH(SiMe_3)_2]_2$ (2.556(5) and 2.508(6) Å).[19] The metal–carbon bond distances in combination with the carbon–carbon distances in the C_4 bridge indicate that the bonding of the bridging C_4 ligands is best described as a 1,4-dimetalated butatriene (Figure 4).

However, the carbon atoms of the C_4 bridge are, in contrast to dilithiated butatriene,[9] not linear. The C1–C3–C4 and C3–C4–C5 angles for 6 are 146.5(9)° and 147(1)°, respectively. For the centrosymmetric *tert*-butyl derivative 8, these angles are somewhat larger (154.7(5) Å), but still far from linear. This deviation is likely the result of secondary interactions between cerium and the internal carbon atoms of the bridge (Figure 5). For 6, the Ce1–C3 and Ce1–C4 distances are 2.789(9) and 2.89(1) Å, respectively, which are well within the sum of the cerium and carbon contact radii.[20] Similar interactions of cerium with the carbon atoms of the $C_4(t\text{-Bu})_2$ bridge are present in 8.

The alkyl substituents for both 6 and 8 are arranged in a *trans*-configuration. Interestingly, MNDO calculation by Schleyer[9] on monomeric dilithiated butatriene, (THF)-$LiC(t\text{-Bu}){=}C{=}C{=}C(t\text{-Bu})Li(THF)$ predicted that a *trans*-configuration is thermodynamically favored.

The Cp* rings in both compounds are η^5-coordinated to cerium with all internal C–C bond distances equal within the estimated standard deviation. A remarkable difference in the molecular structures of 6 and 8 is the conformation of the five-membered rings. For the methyl derivative, these are staggered, as found for most bis(pentamethylcyclopentadienyl) lanthanide compounds.[21] In contrast, the Cp* rings for the *tert*-butyl derivative 8 are eclipsed. Such a conformation is only observed for sterically very congested molecules.[21,22] Indeed, there appears to be strong steric repulsions between the *tert*-butyl groups and the two pentamethylcyclopentadienyl ligands. The *tert*-butyl substituents are oriented in such a way that one of the methyl groups (C24) lies in the plane formed by the bridging carbon atoms (C21–C22–C23–C24 = 0.2°). This results in rather close contacts of C24 with the Cp* rings (C9′···C24 = 3.626(8) Å and C17′···C24 = 3.594(9) Å), and as a consequence C9 and C17 are significantly bent out of the cyclopentadienyl ring plane (0.23 Å for C19 and 0.27 Å for C17). Steric strain is further relieved by narrowing the Cent–Ce–Cent angle to 131.7°. This value is at the short end of the range found for bis(pentamethylcyclopentadienyl) complexes of the early lanthanides La–Nd (129.6–136°)[23] and also smaller than for the methyl derivative 6 (average 134.6°). The eclipsed conformation of the rings in combination with a narrowing of the Cent–Ce–Cent angle results in short interatomic distances for the Cp* methyls opposite of the coordination wedge (C6···C20 = 3.196(1) Å). The deviations of C6 and C20 methyl groups out of the cyclopentadienyl ring plane are also exceptionally large: 0.34 Å for C20 and 0.37 Å for C6.

Kinetics and Thermodynamics of Acetylide Carbon–Carbon Bond Formation. The first indication for acetylide carbon–carbon coupling being a reversible process was obtained from the reactions of 8 with THF. Instead of the formation of a stable and soluble 8·THF adduct, carbon–carbon bond cleavage occurred and $Cp^*_2CeC{\equiv}C$-*t*-Bu·THF (9) was formed (eq 8). The reaction is rather slow, and conversion was complete after 14 days at room temperature (NMR). Thus, carbon–carbon bond breakage for these compounds is a thermodynamically feasible process although the kinetic barriers are rather high.



8 9 (8)

Adduct 9 was characterized by ^{1}H-NMR (δ 3.94 (Cp*) and −1.90 (*t*-Bu) ppm).[24] These values are identical with those reported for a sample prepared by reacting 1 with *tert*-butylacetylene in THF.[5]

Surprisingly, carbon–carbon bond cleavage in the absence of a Lewis base is a reversible process. Thermodynamic data for the coupling reaction were obtained from an NMR study on the thermolysis of pure, diamagnetic 4 (benzene-d_6, 298 K). The conversion of 4 to the coupled compound 7 is not quantitative, and an equilibrium mixture with 4 and 7 is formed (eq 9). At 298 K, this mixture consists of 86 ± 2% of 7 and 14 ± 2% of 4. In accordance, dissolving pure 7 in benzene-d_6 also results in an equilibrium mixture with 4 and 7 present in the expected quantities. Thus, the coupled form is thermodynamically favored. This could either be the result of diminished steric repulsion between the Cp* methyl groups and the substituents R compared to the corresponding acetylide and/or stabilization by electron delocalization in the C_4 bridge.

---

(18) (a) Heeres, H. J.; Renkema, J.; Booij, M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1988**, *7*, 2495.

(19) Heeres, H. J.; Meetsma, A.; Teuben, J. H.; Rogers, R. D. *Organometallics* **1989**, *8*, 2637.

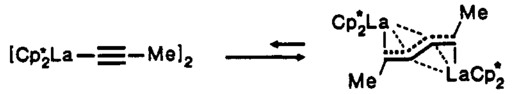
(20) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(21) Evans, W. J.; Ulibarri, T. A.; Chamberlain, L. R.; Ziller, J. W.; Alvarez, D. *Organometallics* **1990**, *9*, 2124 and references cited herein.

(22) (a) Evans, W. J.; Keyer, R. A.; Zhang, H.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1987**, 837. (b) Watson, P. L.; Whitney, J. F.; Harlow, R. L. *Inorg. Chem.* **1981**, *20*, 3271.

(23) Evans, W. J.; Foster, S. E. *J. Organomet. Chem.* **1992**, *433*, 79.

(24) The chemical shifts of the THF protons are somewhat broadened and low-field shifted compared to that of pure 9. This effect is caused by the presence of a small excess of THF which rapidly exchanges with coordinated THF on the NMR time scale.



4 7 (9)

Assuming that acetylide 4 is a dimer, the difference in free energy, $\Delta G°$, between 4 and 7 is 4.5 ± 0.4 kJ/mol at 298 K. At 323 K, the equilibrium mixture consists of 84 ± 2% of 7 and 16 ± 2% of 4, which is not significantly different from the values found at 298 K.[25] Hence, the equilibrium constant appears to be essentially independent of the temperature. This implies that $\Delta S°$ for the reaction is rather small, which although not conclusive, supports that 4 is a dimer.

Kinetic measurements were carried out at 298 ± 1 K in benzene-d_6. The ratio 4 to 7 was determined by integration of the ^{1}H-NMR spectra. The rate constants were determined by fitting plots of $[4]_t/[4)]_0$ versus time according to $[4]_t/[4]_0 = A\exp^{[-Bt]} + C$ with $A = k_1/(k_1 + k_{-1})$, $B = (-k_1 + k_{-1})$, and $C = k_{-1}/(k_1 + k_{-1})$.[26] Solving these equations leads to values of k_1 and k_{-1} of $8.3(\pm 0.4) \times 10^{-5}$ s^{-1} and $1.1(\pm 0.7) \times 10^{-5}$ s^{-1}, respectively. The free energy of activation for the conversion of 4 to 7, $\Delta G^‡$, was calculated to be 96.3 (±0.1) kJ/mol.

Implications for Catalysis. The role of the oligomeric acetylides and the carbon–carbon coupled compounds 6 and 8 in the catalytic oligomerization of terminal alkynes was investigated by a study on the reactions of the *tert*-butyl-substituted compounds 5 and 8 with an excess of *tert*-butylacetylene (NMR tube reactions, benzene-d_6). In accordance with our earlier proposed mechanism,[5] acetylide 5 selectively catalyzes the dimerization of *tert*-butylacetylene to the head to tail dimer 2,4-di-*tert*-butyl-1-buten-3-yne. The minimal turnover frequency for the dimerization was calculated to be 1900 h^{-1}.[27] Acetylide carbon–carbon coupling in 5 is much slower and therefore not expected to interfere with the catalytic cycle. In accordance, *cis*/*trans*-1,4-di-*tert*-butyl-1-buten-3-yne and 1,4-di-*tert*-butylbutatriene, formed by acetylide coupling and subsequent metathesis with another alkyne (Scheme II), could not be detected.

The active species in the catalytic cycle is expected to be a coordinatively unsaturated *monomeric* acetylide, formed by dissociation of an oligomer. So far, we have not been able to isolate or identify spectroscopically such a species. However, as described earlier, monomeric acetylides can be trapped by a Lewis base such as THF. Another indication that monomeric, unsaturated acetylides are involved was obtained by studying the reactivity of 5 with an excess of propyne. Based on our oligomerization mechanism,[5] two different types of dimers are expected. Insertion of propyne in the M–C bond of 5 followed by CH bond activation with another propyne molecule produces a mixed dimer, 2-methyl-4-*tert*-butyl-1-buten-3-yne and the methylacetylide Cp*$_2$CeC≡CMe. The latter catalyzes the dimerization of the excess propyne to 2-methyl-1-penten-3-yne (eq 10).[28] However, GC/MS analysis reveals, besides these dimers, the presence of two others, i.e. 2,4-di-*tert*-butyl-1-buten-3-yne, a *tert*-butylacetylene dimer, and a second mixed dimer, tentatively identified as 2-*tert*-butyl-1-penten-3-yne (eq 10).

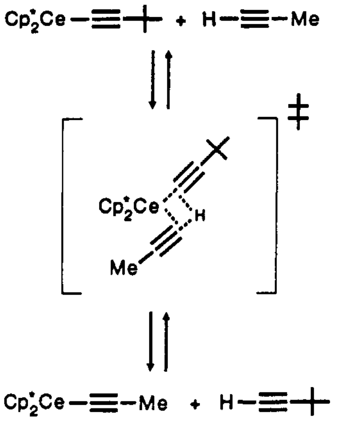
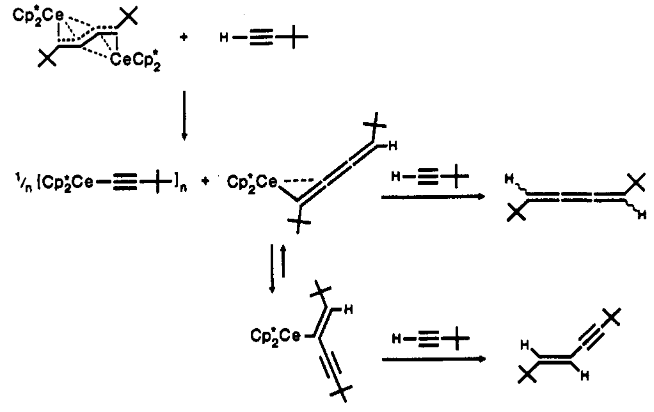
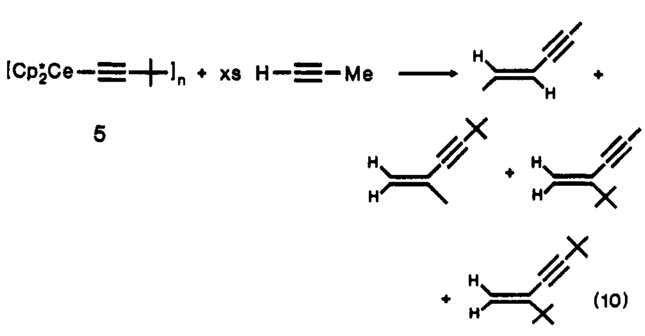


Figure 6. σ-Bond metathesis between a metal–acetylide and a free acetylene.

Scheme II





5 (10)

The presence of the latter two organics indicates that free *tert*-butylacetylene must be formed in the course of the reaction, likely by σ-bond metathesis[29] between acetylide 5 and free propyne (Figure 6). Reaction of *tert*-butylacetylene with remaining 5 produces 2,4-di-*tert*-butyl-1-buten-3-yne; insertion of *tert*-butylacetylene into

---

[25] Attempts to determine the equilibrium constants at higher temperatures were hampered due to the interference of other unidentified organocerium species, presumably decomposition products of 4 and/or 7.

[26] Again, the assumption was made that one molecule of 4 produces one molecule of 7. The following expression is valid for such an equilibrium: $d([4])/dt = -k_1[4] + k_{-1}[7]$. Integration gives $[4]_t/[4]_0 = (k_{-1} + k_1)\exp(-k_1t + k_{-1}t)/(k_1 + k_{-1})$.

[27] The turnover frequency for the catalytic dimerization of *tert*-butylacetylene was obtained from the following experiment. A 90-fold excess of *tert*-butylacetylene was syringed into an NMR tube containing a solution of 1 in benzene-d_6 (0.5 mL). Complete conversion of *tert*-butylacetylene was observed within the time required to measure an ^{1}H-NMR spectrum (2 min and 50 s), giving a turnover frequency of minimal 1900 h^{-1}.

[28] In analogy with the Cp*$_2$CeCH(SiMe$_3$)$_2$-catalyzed oligomerization of propyne,[5] small amounts of a propyne trimer are formed as well.

[29] (a) Watson, P. L. *J. Am. Chem. Soc.* 1983, *105*, 6491. (b) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. L.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* 1987, *109*, 203. (c) Rabaa, H.; Saillaed, J. Y.; Hoffman, R. *J. Am. Chem. Soc.* 1986, *108*, 4327.

the Ce–C bond of $Cp^*_2CeC{\equiv}CMe$ gives 2-*tert*-butyl-1-penten-3-yne. σ-Bond metathesis requires a coordinatively very unsaturated metal center[29] and is therefore expected to take place on monomeric $Cp^*_2CeC{\equiv}C$-*t*-Bu. The observed product distribution suggests that propyne may either insert into a lanthanide acetylide bond or react *via* σ-bond metathesis to liberate an acetylene and form a new lanthanide methylacetylide. Thus, insertion and σ-bond metathesis are competing in these systems and have comparable activation energies.

Surprisingly, suspensions of the coupled species **8** also catalyze the dimerization of *tert*-butylacetylene. The reaction is again remarkably selective, and the head to tail dimer, 2,4-di-*tert*-butyl-1-buten-3-yne, is formed exclusively. The selective formation of the latter indicates that the actual active species in the reaction is not **8** but the acetylide $Cp^*_2CeC{\equiv}C$-*t*-Bu. This species could either be formed by σ-bond metathesis of the coupled product with free *tert*-butylacetylene or by carbon–carbon bond clevage, which is, as discussed earlier, a reversible process. It is very difficult to discriminate between both possibilities. Catalytic oligomerization is very rapid, and only trace amounts of acetylides have to be present. The first mechanism, i.e. a proton-transfer reaction, is expected to produce a mixture of *cis*- and *trans*-1,4-di-*tert*-butyl-1-buten-3-yne and 1,4-di-*tert*-butylbutatriene, analogous to the reaction of **8** with 2,6-di-*tert*-butyl-4-methylphenol. However, these could not be detected by NMR or GC/MS, which suggests that only very minor amounts of **8** are protonated to the active catalyst or that this mechanism is not valid under these conditions.

Experimental Section

General Considerations. All compounds described here are extremely air-sensitive, and manipulations were carried out by using Schlenk, vacuum-line, or glovebox techniques under nitrogen or argon. Toluene, benzene, pentane, and NMR solvents (benzene-d_6 and toluene-d_8) were distilled from Na or Na/K alloy. Carbyls $Cp^*_2LnCH(SiMe_3)_2$ (**1**, Ln = Ce; **2**, Ln = La) were prepared according to published procedures.[18,30] Propyne (Matheson, C.P.) was used as purchased, *tert*-butylacetylene was distilled and stored on molecular sieves (4 Å). IR spectra were recorded on a Mattson-4020 Galaxy FT-IR spectrophotometer using Nujol mulls between KBr disks. NMR spectra were recorded on a Brucker WH-90 or Varian VXR-300 spectrometer. Proton spectra are referenced to residual protons in deuterated solvents (benzene-d_6, δ 7.15 ppm; toluene-d_8, δ 7.02 ppm). NMR data are given in Table I. Elemental analyses were performed at the Microanalytical Department of the Department of Chemistry. All percentages given are the average of at least two independent determinations.

Preparation of $[Cp^*_2CeC{\equiv}CMe]_n$ (3). A 1.274-g (2.24-mmol) portion of **1** was dissolved in 80 mL of pentane. The solution was cooled to 0 °C, and the nitrogen was replaced by propyne (1 atm). The color of the solution instantaneously changed from red to purple, and a pink-purple solid was deposited. After the mixture was stirred about 5 min at 0 °C, propyne was replaced by nitrogen. The solution was decanted, and the remaining solid was washed with cold pentane (−50 °C) and subsequently dried *in vacuo* at −20 °C. Isolation gave 628 mg (68%) of **3** as a purple solid which was stored at −30 °C to prevent thermal decomposition. IR (cm^{-1}): 2720 (w), 2365 (w), 2140 (w), 2035 (w, sharp), 1370 (m), 1165 (vw), 1065 (w), 1020 (m), 945 (w), 935 (m), 860 (w), 800 (w), 725 (w), 595 (w). Anal. Calcd for $C_{23}H_{33}Ce$: C, 61.44; H, 7.40; Ce, 31.2. Found: C, 61.03; H, 7.29; Ce, 30.7.

Preparation of $[Cp^*_2LaC{\equiv}CMe]_n$ (4). A synthetic procedure analogous to that for **3** was followed. A 1.215-g (2.14-mmol) portion of **2**, dissolved in 80 mL of pentane, was placed under 1 atm of propyne. Workup afforded 870 mg (1.94 mmol, 91%) of **4** as a white powder. IR (cm^{-1}): 2725 (w), 2035 (sharp, w), 1165 (vw), 1080 (vw), 1055 (vw), 1020 (m), 945 (w), 930 (m), 800 (w), 720 (w), 595 (m), 575 (m), 438 (w). Anal. Calcd. for $C_{23}H_{33}La$: C, 61.60; H, 7.42; La, 31.0. Found: C, 61.55; H, 7.50; La, 31.0.

Preparation of $[Cp^*_2CeC{\equiv}C$-*t*-Bu$]_n$ (5). An aliquot of 150 μL (1.22 mmol) of *tert*-butylacetylene was syringed into a cooled pentane solution (−60 °C, 30 mL) of **1** (457 mg, 0.80 mmol). Upon addition the color of the solution rapidly changed from red to purple, and a pink-purple solid was deposited. This solid was washed with two portions of cold pentane (−50 °C). Subsequent drying *in vacuo* at −20 °C afforded **5** as a purple powder in 89% yield (352 mg). The compound was stored at −30 °C to prevent decomposition. IR (cm^{-1}): 2720 (w), 2005 (m, sharp), 1360 (m), 1235 (m), 1200 (m), 1060 (vw), 1020 (w), 845 (vw), 805 (vw), 725 (w), 700 (w), 600 (w). Anal. Calcd for $C_{26}H_{39}Ce$: C, 63.51; H, 8.00; Ce, 28.5. Found: C, 63.51; H, 7.94; Ce, 28.4.

Preparation of $[Cp^*_2Ce]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}MeC_4Me)$ (6). A 578-mg (1.29-mmol) aliquot of **3** was dissolved in 30 mL of benzene. The solvent was slowly evaporated (room temperature, ca. 3 d), resulting in well-formed dark crystals. These were washed with cold pentane and dried *in vacuo*, producing red-brown crystals of **6** in 81% yield (471 mg). IR (cm^{-1}): 2710 (w), 2120 (w), 1600 (m), 1030 (m), 940 (m), 800 (w), 730 (w), 450 (m). Anal. Calcd for $C_{46}H_{66}Ce_2$: C, 61.44; H, 7.40; Ce, 31.16. Found: C, 61.59; H, 7.34; Ce, 31.25.

Preparation of $[Cp^*_2La]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}MeC_4Me)$ (7). A cooled solution (−60 °C) of **2** (770 mg, 1.36 mmol) in pentane (30 mL) was placed under 1 atm of propyne for 10 min. The resulting suspension was allowed to warm to room temperature, and the pentane was removed *in vacuo*. The pink solid was dissolved in toluene (15 mL), and the mixture was stirred for 72 h at room temperature. Concentration of the deep-red solution and cooling to −80 °C afforded **7** as red crystals in 46% yield (282 mg, 0.31 mmol). IR (cm^{-1}): 2725 (w), 1605 (m), 1280 (w), 1165 (w), 1090 (vw), 1065 (vw), 1020 (m), 925 (s), 895 (vw), 800 (w), 725 (w), 590 (w), 565 (w), 440 (m). Anal. Calcd for $C_{46}H_{66}La_2$: C, 61.60; H, 7.42; La, 31.0. Found: C, 62.05; H, 7.40; La, 30.6.

Preparation of $[Cp^*_2Ce]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}$*t*-BuC$_4$-*t*-Bu$)$ (8). An aliquot of *tert*-butylacetylene (0.40 mL, 3.3 mmol) was syringed into to a cooled toluene solution (20 mL, −60 °C) of **1** (363 mg, 0.64 mmol). After being stirred for 20 min at −60 °C, the resulting pink suspension was allowed to warm to room temperature and subsequently to 40 °C. At this temperature, all solid dissolved and a purple solution formed. On standing at room temperature for 7 days, red-brown crystals deposited. The crystals were washed with benzene (2 × 5 mL) and dried *in vacuo*. Yield: 214 mg (0.22 mmol, 68%). IR (cm^{-1}): 2725 (w), 1560 (m), 1365 (m), 1335 (w), 1210 (w), 1060 (vw), 1020 (m), 955 (vw), 880 (m), 820 (vw), 735 (m), 620 (vw), 590 (w), 550 (m), 420 (m). Compound **8** is essentially insoluble in hydrocarbon solvents and in THF, and suitable NMR spectra could not be obtained. Anal. Calcd for $C_{52}H_{78}Ce_2$: C, 63.51; H, 8.00; Ce, 28.5. Found: C, 63.19; H, 7.88; Ce, 28.9.

NMR Tube reaction of $[Cp^*_2Ce]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}$*t*-BuC$_4$-*t*-Bu$)$ (8) with THF. THF (10 μL, 123 μmol) was syringed into an NMR tube containing a suspension of **8** (32 mg, 33 μmol) in benzene-d_8. The tube was sealed, and the reaction was monitored by NMR at room temperature. After several days, the solution gradually turned red. After 2 weeks, no solid remained and a red solution

---

[30] Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.

[31] Sheldrick, G. M. SHELX76, a system of computer programs for X-ray structure determination as locally modified, University of Cambridge, England, 1976.

[32] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

[33] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; pp 4, 72, 99, 149. (present distributor: Kluwer, Academic Publishers, Dordrecht).

Table IV. Crystal Data, Summary of Data Collection, and Structure Refinement for 6 and 8

	6	**8**
color/shape	red/parallelepiped	red/parallelepiped
FW	899.27	983.44
space group	$P2_1/n$	$P2_1/n$
temp, °C	18	20
cell constants[a]		
a, Å	10.670(8)	11.376(6)
b, Å	25.081(9)	14.151(5)
c, Å	16.706(9)	15.541(4)
β, deg	102.41(7)	103.92(4)
cell vol, $Å^3$	4366.3	2428.3
formula units/unit cell	4	2
D_{calc}, $g \cdot cm^{-3}$	1.37	1.34
μ_{calc}, cm^{-1}	21.96	19.05
diffractometer, scan	Enraf-Nonius CAD-4/ω–2θ	Enraf-Nonius CAD-4/ω–2θ
radiation, graphite monochromator	Mo Kα ($\lambda = 0.710\,73$)	Mo Kα ($\lambda = 0.710\,73$)
max crystal dimensions, mm	$0.10 \times 0.17 \times 0.40$	$0.13 \times 0.20 \times 0.70$
scan width	$0.80 + 0.35 \tan \theta$	$0.80 + 0.35 \tan \theta$
standard reflections	800; 0,10,0; 004	10,0,0; 0,12,0; 0,0,12
decay of standards, %	±2	±2.5
no. of reflections measured	8294	4693
2θ range, deg	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$
range of *hkl*	+12,+29,±19	+13,+16,±18
no. of reflections observed ($F_o \geq 5\sigma(F_o)$)[b]	4179	3502
computer programs[c]	SHELX[31] and SHELXS[32]	SHELX[31] and SHELXS[32]
no. of parameters varied	433	283
weights	$[\sigma(F_o)^2 + 0.0003(F_o)^2]^{-1}$	$[\sigma(F_o)^2 + 0.0004(F_o)^2]^{-1}$
$R = \Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert$	0.046	0.031
R_w	0.053	0.040
GOF	1.46	0.58
largest feature final diff map, e $Å^{-3}$	0.6	0.6

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections with $\theta > 15°$ for **6** and $\theta > 23°$ for **8**. [b] Corrections: Lorentz-polarization and absorption (emperical, psi scan). [c] Neutral scattering factors and anomalous dispersion corrections from ref 33.

was formed. NMR shows the quantitative formation of $Cp^*_2CeC{\equiv}C$-*t*-Bu·THF.

Kinetic and Thermodynamic Measurements for Acetylide Coupling. The kinetics of acetylide coupling for **4** were measured by ^1H-NMR spectroscopy. Freshly prepared solution samples (28 μM, benzene-d_6) in sealed 5-mm NMR tubes were immediately placed in a temperature-controlled probe of an NMR spectrometer. Approximately 20 FT-NMR spectra were recorded automatically at preset intervals (30 min). Rate constants were determined by fitting plots of $[4]_t/[4]_0$ versus time according to $[4]_t/[4]_0 = A \exp^{[-Bt]} + C$ with $A = k_1/(k_1 + k_{-1})$, $B = (-k_1 + k_{-1})$, and $C = k_{-1}/(k_1 + k_{-1})$.[26] Equilibrium constants at different temperatures were obtained by ^1H-NMR spectroscopy. Solution samples of **4** were placed in an oven and maintained at constant temperature (±1 °C). NMR spectra were recorded at regular intervals. The concentration of **4** and **7** were measured by integration of the well-separated Cp* resonances.

NMR Tube Reactions of $[Cp^*_2Ln]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}MeC_4Me)$ (6, Ln = Ce; 7, Ln = La) with 2,6-Di-*tert*-butyl-4-methylphenol. An 18-mg (82-μmol) aliquot of 2,6-di-*tert*-butyl-4-methylphenol was added to an NMR tube containing 37 mg (41 μmol) of **6** in benzene-d_6 (0.5 mL). The resulting red solution was characterized by NMR and was shown to consist of Cp^*_2CeOAr (comparison with an authentic sample[14]) and (*E*)-2-hexen-4-yne. ^1H-NMR data for the latter (benzene-d_6): δ 6.01 (m, $=$C*H*(Me)), 5.45 (d, $J_{HH} = 15.6$ Hz, $=$CH), 1.60 (d, *J* = 1.6 Hz, $\equiv$CMe), 1.40 (d, *J* = 8 Hz, $=$CH(*Me*)), assignment confirmed by ^1H-homonuclear decoupling experiments.

Table V. Final Fractional Coordinates for $[Cp^*_2Ce]_2(C_4Me_2)$ (6)

atom	*x/a*	*y/b*	*z/c*	*B*(equiv),[a] $Å^2$
Ce(1)	0.63181(5)	0.05286(2)	0.76533(3)	2.90
Ce(2)	0.38673(5)	0.24286(2)	0.80029(3)	2.69
C(1)	0.501(1)	0.1232(4)	0.6735(6)	3.70
C(2)	0.442(1)	0.1409(6)	0.5850(6)	5.61
C(3)	0.4935(8)	0.1480(4)	0.7402(5)	2.75
C(4)	0.5264(8)	0.1485(4)	0.8217(6)	2.83
C(5)	0.523(1)	0.1741(4)	0.8895(6)	3.87
C(6)	0.586(1)	0.1544(6)	0.9741(6)	5.66
C(7)	0.578(1)	−0.0556(4)	0.7346(7)	4.11
C(8)	0.562(1)	−0.0462(4)	0.8148(7)	4.12
C(9)	0.451(1)	−0.0153(4)	0.8093(7)	4.13
C(10)	0.4015(9)	−0.0040(4)	0.7296(6)	3.30
C(11)	0.480(1)	−0.0280(4)	0.6819(6)	4.16
C(12)	0.669(1)	−0.0944(5)	0.7065(9)	6.38
C(13)	0.642(1)	−0.0720(6)	0.8902(8)	6.37
C(14)	0.397(1)	−0.0016(5)	0.8853(6)	5.42
C(15)	0.277(1)	0.0246(5)	0.6926(8)	5.38
C(16)	0.451(2)	−0.0278(6)	0.5892(6)	6.99
C(17)	0.854(1)	0.1142(5)	0.795(1)	4.96
C(18)	0.834(1)	0.0985(7)	0.7107(9)	5.79
C(19)	0.858(1)	0.0440(6)	0.7094(7)	4.70
C(20)	0.895(1)	0.0265(5)	0.7927(8)	4.56
C(21)	0.887(1)	0.0690(5)	0.8428(7)	4.29
C(22)	0.849(1)	0.1686(5)	0.828(1)	7.00
C(23)	0.802(1)	0.1366(8)	0.641(1)	9.97
C(24)	0.864(2)	0.0111(8)	0.635(1)	10.24
C(25)	0.948(1)	−0.0283(6)	0.8207(9)	6.28
C(26)	0.917(1)	0.0658(7)	0.9336(7)	6.60
C(27)	0.156(1)	0.2683(5)	0.8497(7)	3.96
C(28)	0.1232(9)	0.2552(5)	0.7658(7)	3.91
C(29)	0.1463(9)	0.2001(5)	0.7567(7)	3.87
C(30)	0.194(1)	0.1797(5)	0.8358(8)	4.17
C(31)	0.200(1)	0.2212(5)	0.8907(7)	4.41
C(32)	0.126(1)	0.3187(6)	0.889(1)	8.18
C(33)	0.061(1)	0.2939(8)	0.6977(9)	7.61
C(34)	0.131(1)	0.1704(8)	0.6784(8)	8.75
C(35)	0.223(1)	0.1225(4)	0.859(1)	6.17
C(36)	0.238(1)	0.2165(7)	0.9837(7)	7.90
C(37)	0.579(1)	0.3016(4)	0.7513(6)	3.45
C(38)	0.465(1)	0.3283(4)	0.7156(6)	3.48
C(39)	0.417(1)	0.3522(4)	0.779(1)	4.88
C(40)	0.505(2)	0.3381(5)	0.8532(9)	5.90
C(41)	0.604(1)	0.3082(4)	0.8366(6)	3.61
C(42)	0.665(1)	0.2753(5)	0.7041(8)	5.30
C(43)	0.407(2)	0.3313(6)	0.6278(7)	7.14
C(44)	0.308(2)	0.3900(6)	0.764(1)	11.76
C(45)	0.503(2)	0.3570(7)	0.9426(9)	12.90
C(46)	0.719(1)	0.2917(5)	0.8976(8)	6.18

[a] $B(\text{equiv}) = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Additional evidence for the presence of (*E*)-2-hexen-4-yne was obtained by vacuum transfer of the volatiles and subsequent analysis of this fraction by GC and GC/MS ($M^{\bullet+} = 80$).

Reaction with the lanthanum analog **7** was performed analogously. NMR showed the quantitative formation of Cp^*_2LaOAr[14] and (*E*)-2-hexen-4-yne.

NMR Tube Reaction of $[Cp^*_2Ce]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}t\text{-}BuC_4\text{-}t\text{-}Bu)$ (8) with 2,6-Di-*tert*-butyl-4-methylphenol. 2,6-Di-*tert*-butyl-4-methylphenol (15 mg, 68 μmol) was added to an NMR tube containing 35 mg (36 μmol) of **8** in benzene-d_6. The reaction was followed by ^1H NMR. After being kept for 8 days at room temperature, all phenol was consumed and Cp^*_2CeOAr[14] was formed quantitatively. The tube was opened in a glovebox, and the volatiles were vacuum transferred under reduced pressure (0.01 mmHg) and analyzed by NMR, GC, and GC/MS. Three $C_4H_2(t\text{-}Bu)_2$ isomers ($M^{\bullet+} = 164$) were present which were characterized by ^1H NMR to be (*E*)-1,4-di-*tert*-butyl-1-buten-3-yne (60%, δ 6.15, d, *J* = 16 Hz, $=$CH; δ 5.50, d, *J* = 16 Hz, $=$CH), (*Z*)-1,4-di-*tert*-butyl-1-buten-3-yne (20%, δ 5.57, d, *J* = 12 Hz, $=$CH; δ 5.47, d, *J* = 12 Hz, $=$CH), and (*Z*)- or (*E*)-1,4-di-*tert*-butylbutatriene (20%, δ 5.55, s, $=$C$=$CH).

Table VI. Final Fractional Coordinates for $[Cp^*_2Ce]_2(C_4\text{-}t\text{-}Bu_2)$ (8)

atom	x/a	y/b	z/c	B(equiv),[a] Å^2
Ce	0.45812(2)	0.49195(1)	0.16807(1)	1.79
C(1)	0.3040(5)	0.5755(4)	0.2633(3)	3.45
C(2)	0.2281(4)	0.5473(3)	0.1834(4)	3.23
C(3)	0.2494(4)	0.6078(3)	0.1167(3)	2.64
C(4)	0.3409(4)	0.6715(3)	0.1567(3)	2.86
C(5)	0.3755(4)	0.6500(4)	0.2478(3)	3.27
C(6)	0.2853(8)	0.5450(6)	0.3531(4)	6.91
C(7)	0.1297(6)	0.4734(5)	0.1721(6)	6.15
C(8)	0.1784(6)	0.6136(5)	0.0217(4)	4.65
C(9)	0.3761(6)	0.7568(4)	0.1116(5)	5.23
C(10)	0.4615(6)	0.7073(5)	0.3177(5)	5.90
C(11)	0.6365(5)	0.4380(3)	0.3225(3)	3.12
C(12)	0.6824(4)	0.4063(3)	0.2523(3)	3.14
C(13)	0.6085(4)	0.3321(3)	0.2098(3)	2.86
C(14)	0.5160(4)	0.3193(3)	0.2551(3)	2.85
C(15)	0.5360(4)	0.3837(4)	0.3250(3)	3.17
C(16)	0.6946(8)	0.5095(4)	0.3934(5)	5.51
C(17)	0.8057(5)	0.4317(6)	0.2364(6)	6.10
C(18)	0.6333(7)	0.2721(4)	0.1363(4)	5.36
C(19)	0.4209(6)	0.2449(4)	0.2372(5)	5.80
C(20)	0.4772(7)	0.3767(6)	0.4016(5)	6.84
C(21)	0.4578(3)	0.4668(3)	−0.0074(2)	1.91
C(22)	0.3787(4)	0.4101(3)	0.0148(3)	2.19
C(23)	0.2994(4)	0.3415(3)	−0.0509(3)	2.31
C(24)	0.3263(4)	0.3492(4)	−0.1433(3)	3.06
C(25)	0.1645(4)	0.3643(4)	−0.0597(4)	4.12
C(26)	0.3220(5)	0.2399(3)	−0.0195(4)	3.83

[a] Cf. footnote *a* in Table V.

NMR Tube Reaction of $[Cp^*_2CeC{\equiv}C\text{-}t\text{-}Bu]_n$ (5) with THF. An aliquot of 5 μL (62 μmol) of THF was syringed into a benzene-d_6 solution of 5 (30 mg, 61 μmol). After the solution stood for 1 day at room temperature, the color of the solution had changed from purple to red. NMR shows that 5 has been converted quantitatively to $Cp^*_2CeC{\equiv}C\text{-}t\text{-}Bu{\cdot}THF$.[5,24]

NMR Tube Reaction of $[Cp^*_2CeC{\equiv}C\text{-}t\text{-}Bu]_n$ (5) with an Excess of *tert*-Butylacetylene. A 100-μL (0.81-mmol) aliquot of *tert*-butylacetylene was added to an NMR tube containing a cooled (5 °C) suspension of 20 mg (0.02 mmol) of 5 in benzene-d_6. After addition the tube was immediately placed in the spectrometer. NMR spectroscopy showed that all *tert*-butylacetylene had selectively been dimerized to 2,4-di-*tert*-butyl-1-buten-3-yne (δ 5.34 and 5.13 ppm (CH_2) and 1.18 and 1.17 ppm (*t*-Bu)).

NMR Tube Reaction of 5 with Propyne. Propyne (42 μmol) was allowed to react with a benzene-d_6 solution of 5 (7 mg, 14 μmol). After being stirred for 10 min at room temperature, the volatiles were vacuum transferred in a cold trap and analyzed by GC and GC/MS. Besides a propyne dimer and traces of a trimer, two mixed dimers with $M^{\cdot+}$ = 122 and 2,4-di-*tert*-butyl-1-buten-3-yne ($M^{\cdot+}$ = 164) could be detected.

NMR Tube Reaction of $[Cp^*_2Ce]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}t\text{-}BuC_4\text{-}t\text{-}Bu)$ (8) with *tert*-Butylacetylene. A 50-μL (0.40-mmol) aliquot of *tert*-butylacetylene was added to an NMR tube containing a suspension of 10 mg (10 μmol) of 8 in benzene-d_6 (0.5 mL). Upon addition the solution turned slightly purple and subsequently red-brown, although most of 8 did not dissolve. NMR analysis showed that all of the *tert*-butylacetylene had selectively been dimerized to 2,4-di-*tert*-butyl-1-buten-3-yne.

X-ray Data Collection, Structure Determination, and Refinement for $[Cp^*_2Ce]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}MeC_4Me)$ (6). A red single crystal of 6, obtained directly from the reaction mixture, was mounted in a thin-walled glass capillary under argon and transferred to the goniometer. The space group was determined to be the centric $P2_1/n$ from the systematic absences. A summary of the data collection parameters is given in Table IV. Least-squares refinement with isotropic thermal parameters led to R = 0.075. The methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atoms (C–H = 0.95 Å, B = 5.5 Å^2). Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of R = 0.046 and R_w = 0.053. The final values of the positional parameters are given in Table V.

X-ray Data Collection, Structure Determination, and Refinement for $[Cp^*_2Ce]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}t\text{-}BuC_4\text{-}t\text{-}Bu)$ (8). A deep red single crystal of 8 was mounted in a thin-walled glass capillary flushed under argon and transferred to the goniometer. The space group was determined to be the centric $P2_1/n$ from the systematic absences. A summary of the data collection parameters is given in Table IV. Least-squares refinement with isotropic thermal parameters led to R = 0.068. The methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atom (C–H = 0.95 Å, B = 5.5 Å^2). Refinement of the non-hydrogen atoms with anistotropic temperature factors led to the final values of R = 0.031 and R_w = 0.040. The final values of the positional parameters are given in Table VI.

Acknowledgment. We thank Shell Research B.V. for financial support for this research and Dr. S. A. Galema for stimulating discussion on the kinetics and thermodynamics of the acetylide coupling reaction.

Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters for 6 and 8 (16 pages). Ordering information is given on any current masthead page.

OM9208376