Ring hydrogen C-H activation in Cp*2LnCH(SiMe3)2 (Ln = yttrium, lanthanum, cerium): x-ray crystal structures of [Cp*3(.mu.3-.eta.5,.eta.1,.eta.1-C5Me3(CH2)2)Ce2]2 and Cp*2CeCH2C6H5

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Ring Hydrogen C–H Activation in $Cp^*_2LnCH(SiMe_3)_2$ (Ln = Y, La, Ce): X-ray Crystal Structures of $[Cp^*_3(\mu_3\text{-}\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2)Ce_2]_2$ and $Cp^*_2CeCH_2C_6H_5$

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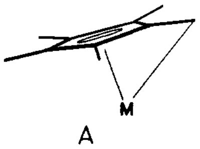
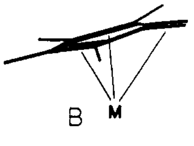
Thermolysis of complexes $Cp^*_2LnCH(SiMe_3)_2$ (**1**, Ln = Y; **2**, Ln = La; **3**, Ln = Ce) in cyclohexane leads to extrusion of $CH_2(SiMe_3)_2$ by hydrogen abstraction from a Cp* ligand and postulated formation of a pentamethylcyclopentadienyl fulvene species Cp*FvLn. For yttrium thermolysis occurs under conditions where Cp*FvY reacts further, e.g. with solvent and $CH_2(SiMe_3)_2$, to produce a complicated mixture. In cyclohexane-d_{12} extensive H/D scrambling between organometallic species and solvent is observed. For lanthanum and cerium secondary reactions take place between molecules of Cp*FvLn, but solvent and $CH_2(SiMe_3)_2$ are not involved. The stable end product for these metals is a tetranuclear complex $[Cp^*_3(\mu_3\text{-}\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2)Ln_2]_2$ (**4**, Ln = La; **5**, Ln = Ce), formed by intermolecular hydrogen transfer. For **5** the molecular structure was determined by X-ray diffraction. The compound crystallizes in the monoclinic space group $C2/c$ (No. 15) with a = 23.849 (9) Å, b = 10.846 (4) Å, c = 30.11 (1) Å, and β = 104.29 (3)°. The unit cell contains four molecules of **5** and two cyclohexane-d_{12} solvate molecules (Z = 4). Compound **5** contains a novel type of bridging ligand, a doubly metalated pentamethylcyclopentadienyl group, $\eta^5,\eta^1,\eta^1\text{-}C_5(CH_2)_2Me_3$, bridging three cerium atoms in a unique manner. The tetranuclear complex is essentially a tightly fitting assembly of four units Cp^*_2LnR. Thermolysis of **2** and **3** or heating of tetranuclear compounds **4** and **5** in toluene leads to the formation of the benzyl compounds $Cp^*_2LnCH_2Ph$ (**6**, Ln = La; **7**, Ln = Ce). Thermolysis of **3** in toluene-d_8 shows that the alkane $CH_2(SiMe_3)_2$ has no deuterium built-in, indicating that **6** and **7** are formed through hydrogen abstraction from a pentamethylcyclopentadienyl ligand and that the solvent is not involved here. Compound **7** crystallizes in the orthorhombic space group $Pna2_1$ with a = 16.730 (4) Å, b = 11.387 (3) Å, c = 12.506 (3) Å, and Z = 4. The bonding of the benzyl group is best described as a benzyl anion with regular sp^2 hybridization of the methylene group η^3-bonded to a $Cp^*_2Ce^+$ cation. The metal has a strong interaction with the methylene, the ipso, and an ortho carbon atom of the benzyl ligand.

Introduction

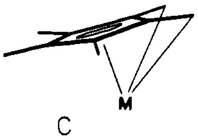
Cyclopentadienyl and substituted cyclopentadienyl groups are among the most widely used ancillary ligands in organometallic chemistry. The pentamethylcyclopentadienyl ligand, Cp*,[1] has found wide application both in late- but especially in early-transition-metal and lanthanide chemistry. The reason is partially that Cp* complexes are more soluble and frequently have higher thermal stability than their Cp analogues. Scientifically more important, however, is that Cp* ligands are excellent in the stabilization of coordinatively unsaturated species, as is clearly demonstrated in group 3 and lanthanide chemistry.[2] Usually, Cp* groups in $Cp^*_nMR_m$ compounds are considered to be spectator ligands which do not participate in reactions. Nevertheless, involvement of Cp* ligands in reactions is well-known.[3] The best documented is abstraction of a hydrogen atom from a methyl group of a Cp* ligand in transition-metal complexes, generating a 2,3,4,5-tetramethylfulvene (Fv) ligand.[3b–j] The bonding of this ligand to an early-transition-metal center may range from η^5,η^1-cyclopentadienyl alkyl (A) to η^6-fulvene (B).



A



B



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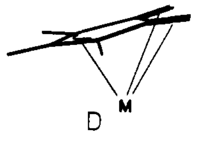

D

Coordination of a fulvene by the *exo*-olefin functionality only has been reported for late transition metals.[4] Abstraction of two hydrogen atoms from adjacent methyl groups of a Cp* ligand leads to the formation of a 1,2-dimethylene-3,4,5-trimethylcyclopentenyl (Ad, allyl diene)[1] ligand. The bonding possibilities lie between η^5,η^1,η^1-cyclopentadienyl dialkyl (C) and η^3,η^4-allyl diene (D). The different bonding modes allow accommodation of formal charges ranging from 0 to -2 (fulvene) or -1 to -3 (allyl diene), and this makes these ligands attractive for the stabilization of metal systems over a range of formal oxidation states, which otherwise are different to attain.

Fulvene-containing lanthanoid systems are particularly

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(1) In this article the following abbreviations are used: Cp = $\eta^5\text{-}C_5H_5$, Cp* = $\eta^5\text{-}C_5Me_5$, Fv = $C_5Me_4CH_2$, Ad = $C_5Me_3(CH_2)_2$, and Ct = ring centroid.

(2) Extensive literature is available to illustrate this. Typical examples can be found in the following. (a) for group 4 metals: Teuben, J. H. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragalà, I. L., Eds., D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1985; p 195. (b) For scandium: 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. (c) For group 3 and lanthanides: Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131.

(3) (a) Wochner, F.; Brintzinger, H. H. *J. Organomet. Chem.* **1986**, *309*, 65. (b) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* **1987**, *6*, 232. (c) Haan, K. H. den; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1986**, 682. (d) Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1219. (e) Cloke, F. G. N.; Green, J. C.; Green, M. L. H.; Morley, C. P. *J. Chem. Soc., Chem. Commun.* **1985**, 945. (f) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21. (g) Pattiasina, J. W.; Hissink, C. E.; Boer, J. L. de; Meetsma, A.; Teuben, J. H.; Spek, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 7758. (h) Carter, S. T.; Clegg, W.; Gibson, V. C.; Kee, T. P.; Sanner, R. D. *Organometallics* **1989**, *8*, 253. (i) Miller, F. D.; Sanner, R. D. *Organometallics* **1988**, *7*, 818. (j) Parkin, G.; Bercaw, J. E. *Organometallics* **1989**, *8*, 1172.

(4) (a) Werner, H.; Crisp, G. T.; Jolly, P. W.; Kraus, H. J.; Krüger, C. *Organometallics* **1983**, *2*, 1369. (b) Parkin, G.; Bercaw, J. E. *Polyhedron* **1988**, *7*, 2053.

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interesting, since they have been postulated as key intermediates in C–H activation reactions of Cp^*_2LnR complexes.[2b,5] Furthermore, early-transition-metal complexes containing fulvene and allyldiene ligands display very interesting reactivity and are valuable starting materials for the synthesis of compounds with modified Cp* ligands,[3g,6] which are of growing interest for application in catalysis and selective organic synthesis. To explore a potential route to fulvene and allyldiene compounds of lanthanoid elements Y, La, and Ce, thermolysis of $Cp^*_2LnCH(SiMe_3)_2$ was studied. The results are described in this paper.

Results and Discussion

Thermolysis of $Cp^*_2LnCH(SiMe_3)_2$ (1, Ln = Y; 2, Ln = La; 3; Ln = Ce) in Cyclohexane. Compounds Cp^*_2LnR (Ln = group 3 or lanthanide) readily attack solvent or other substrates to give metalation, ether splitting, or other reactions but toward cyclohexane they appear relatively inert.[2b,7] Therefore, we started our study by monitoring the thermolysis of **1**–**3** in cyclohexane-d_{12} by ^1H NMR spectroscopy. Complex **1** ($t_{1/2}$ = 30 h at 425 K) is thermally quite stable, while **2** ($t_{1/2}$ = 3.5 h at 400 K) and **3** ($t_{1/2}$ = 4 h at 400 K) decompose much easier. For **1**, H/D exchange between the ligands on the metal and solvent was observed concurrent with the thermolysis. Initially, liberation of exclusively $CH_2(SiMe_3)_2$ was observed, but during the course of the reaction several other resonances around δ = 0 ppm appeared in the spectrum. This suggests attack on $SiMe_3$ C–H bonds and formation of $Y–CH_2–SiMe_2–R$ moieties at this stage. In addition, a substantial increase of the intensity of residual protons of the solvent was observed, together with a corresponding decrease in the remainder of the signals in the Cp* and $CH_2(SiMe_3)_2$ area. It is clear that organoyttrium species present in the mixture activate C–D bonds and cyclohexane-d_{12} and probably form metalated cyclohexyl derivatives. For this reason a detailed investigation of the thermolysis of **1** was not attempted. In contrast, compounds **2** and **3** showed no H/D scrambling and $CH_2(SiMe_3)_2$ was formed exclusively, indicating hydrogen abstraction from a Cp* ligand only (eq 1). The products **4** and **5** are poorly soluble in cyclohexane and crystallize during the reaction. It appeared very difficult to characterize and identify these complexes (NMR), because they immediately react with solvents such as benzene, toluene, Et_2O, and THF. The IR spectra of **4** and **5** are superimposable and indicate very similar product formation for both metals, but they are not very informative with respect to the identity of the complexes. Fortunately, X-ray-quality crystals were obtained of **5**, which allowed structural identification of the product.

$$\underset{\substack{\mathbf{2},\ Ln = La\\ \mathbf{3},\ Ln = Ce}}{Cp^*_2LnCH(SiMe_3)_2} \xrightarrow[\text{cyclohexane-}d_{12}]{\Delta} \underset{\substack{\mathbf{4},\ Ln = La\\ \mathbf{5},\ Ln = Ce}}{C_{20}H_{29}Ln} + CH_2(SiMe_3)_2 \quad (1)$$

Crystal Structure of $[Cp^*_3(\mu_3\text{-}\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2)Ce_2]_2$ (5). Rectangular brown-red platelets of **5** were obtained from a thermolyzed solution of **3** in cyclohexane-d_{12}. The structure determination revealed that **5** is an intriguing tetranuclear complex (Figure 1; distances and angles in Table I), which crystallizes in the monoclinic space group $C2/c$. The unit cell contains four tetranuclear molecules of **5** and two additional cyclohexane-d_{12} solvate molecules. The molecule has a crystallographic center of inversion (primed atoms are symmetry-related, -x, -y, -z). The asymmetric unit consists of a Cp^*_2Ce group and a Cp*Ce moiety bonded to another Cp* ligand, which is doubly metalated at two adjacent methyl substituents. This ligand bridges three cerium atoms, acting as an η^5,η^1,η^1-cyclopentadienyl dialkyl. The metal atoms are in the usual tervalent oxidation state, and the tetranuclear complex can be seen as four units of Cp^*_2CeR intimately interlocked through metalation of two adjacent methyl groups on a pentamethylcyclopentadienyl ligand. The Cp*

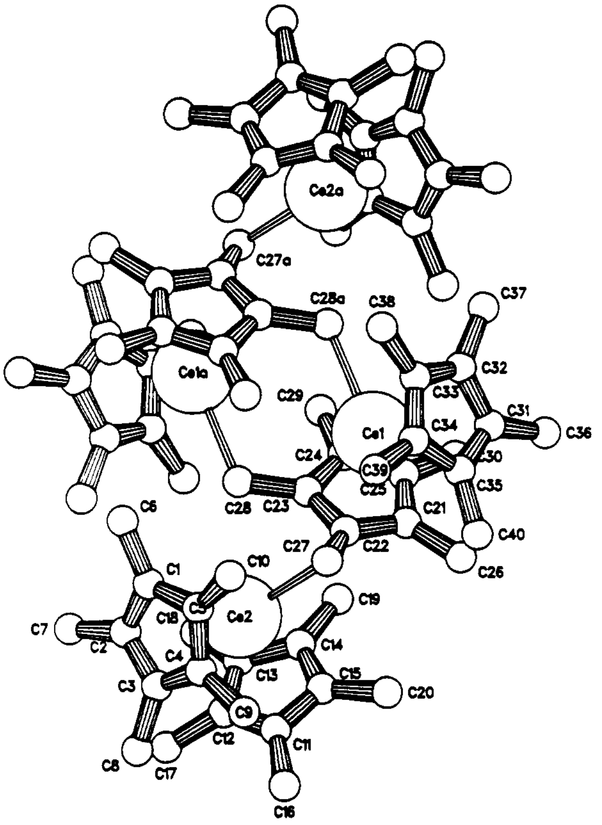

Figure 1. Molecular structure of $[Cp^*_3(\mu_3\text{-}\eta^5,\eta^1,\eta^1\text{-}C_5Me(CH_2)_2)Ce_2]_2$ (5) with the adopted numbering scheme (hydrogen atoms omitted for clarity).

Table I. Selected Distances and Angles for $[Cp^*_3(\mu_3\text{-}\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2)Ce_2]_2$ (5)[a]

	Distances (Å)		
Ce1–Ct3	2.540 (9)	Ce2–Ct1	2.54 (3)
Ce1–Ct(Ad)	2.46 (1)	Ce2–Ct2	2.53 (2)
$Cp^*3(C–C)_{int,av}$	1.42 (2)	$Cp^*1(C–C)_{int,av}$	1.41 (2)
$Ad(C–C)_{int,av}$	1.43 (1)	$Cp^*_2(C–C)_{int,av}$	1.41 (2)
$Cp^*3(C–C)_{ext,av}$	1.50 (1)	$Cp^*1(C–C)_{ext,av}$	1.50 (1)
$Ad(C–C)_{ext,av}$	1.49 (2)	$Cp^*2(C–C)_{ext,av}$	1.51 (1)
Ce1–C28a	2.670 (9)	Ce2–C28	3.011 (9)
Ce1–C27	2.981 (8)	Ce2–C27	2.60 (1)
Ce1–C21	2.685 (9)	Ce2–C22	2.989 (7)
Ce1–C22	2.522 (7)	Ce2–C23	3.200 (7)
Ce1–C23	2.708 (7)	$Ce2–C(ring\ 1)_{av}$	2.81 (3)
Ce1–C24	2.881 (7)	$Ce2–C(ring\ 2)_{av}$	2.80 (2)
Ce1–C25	2.878 (7)	$Ce1–C(ring\ 3)_{av}$	2.81 (2)
C22–C27	1.44 (8)	C23–C28	1.53 (1)
	Angles (deg)		
Ce1–C22–C27	93.5 (5)	Ce2–C27–C22	90.6 (5)
Ce1–C23–C28	113.4 (4)	Ce1a–C28–C23	117.9 (5)

[a] Label a refers to position $-x$, $-y$, $-z$.

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(5) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491.

(6) (a) Pattiasina, J. W. Thesis, Groningen, 1987. (b) Fandos, R.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1991**, *10*, 1637. (c) Fandos, R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 2665.

(7) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276.

rings are dish shaped (average out of plane deviation for the methyl groups: 0.19 Å (Cp*1), 0.13 Å (Cp*2), and 0.17 Å (Cp*3),[8] directed away from the metal) and bonded to Ce in a normal η^5-fashion. The Ce–Ct[1] and average Ce–C(ring) distances are similar to those found in $Cp^*_2CeCH(SiMe_3)_2$,[9] $Cp^*_2CeCl_2Li(Et_2O)_2$,[10] and $Cp^*CeI_2{\cdot}3THF$.[11] The C–C distances and angles within the Cp* ligands are also normal. The triply bridging cyclopentadienyl dialkyl ligand, when considered as a modified Cp* ligand, is strongly distorted and shows some interesting features. The Ad ring carbon atoms are coplanar within 0.05 Å and their C–C distances are identical within error limits, indicating full delocalization of the π system. However, the ring slippage[12] of the cyclopentadienyl part of the ligand (0.43 Å) is considerably larger than in the Cp* groups (0.08 Å or less). As a result, Ce1–C22 (2.522 (7) Å) is very short and the distances Ce1–C24 (2.881 (7) Å) and Ce(1)–C25 (2.878 (7) Å) are quite long. After Ce1–C22, the shortest cerium–carbon distances are Ce2–C27 (2.60 (1) Å) and Ce1a–C28 (2.670 (9) Å). Primarily they can be interpreted as regular cerium–carbon σ bonds.[9] At the same time C27 and C28 seem to be bridging to Ce1 and Ce2, respectively. This is indicated by the short distances Ce1··C27 (2.981 (8) Å) and Ce2··C28 (3.011 (9) Å). The difference found in the metal–carbon distances between C27 and C28 is also reflected in the angles and other bond distances around these atoms. The distance C22–C27 (1.44 (1) Å) is much shorter than the C23–C28 distance (1.53 (1) Å). This indicates a considerable double-bond character in the C22–C27 bond.[13] Furthermore, the C27 methylene carbon atom (0.39 (2) Å out of the C_5 ring plane) is clearly bent toward Ce1. This endo orientation has been found in other fulvene and cyclopentadienyl dialkyl complexes as well.[3,6a] In contrast, C28 is coplanar with the ring carbon atoms. Thus, if one examines the geometry of the carbon skeleton, the bonding of the doubly metalated Cp* ligand is best described as that of a μ_3-η^3,η^1,η^1-cyclopentadienyl dialkyl with some η^6,η^1-fulvene alkyl contribution.

Because both metal centers are coordinatively extremely unsaturated, their coordination spheres are completed by secondary interactions, as is clear from several extremely short intramolecular distances. The distance Ce2··C22 (2.989 (7) Å) is significantly shorter than the sum of the van der Waals radii,[14] and the acute Ce2–C27–C22 angle (90.6 (5)°) indicates a strong interaction. Cerium–hydrogen close contacts, accompanied by small Ce–C–H angles (Ce2··H271 = 2.78 (9) Å, Ce2–C27–H271 = 90 (6)°; Ce1a··H282 = (2.82 (9) Å, Ce1a–C28–H282 = 91 (6)°) indicate α-agostic interactions.[15] The distances Ce2··H272 (2.98 (7) Å) and Ce2··H281 (2.80 (6) Å) are also short, but this can equally well be the result of the aforementioned Ce2··C27 and Ce1a··C28 interactions. It is clear that the combination of a flexible ligand with an electronically and sterically unsaturated metal center in this case leads to a number of unique structural features.

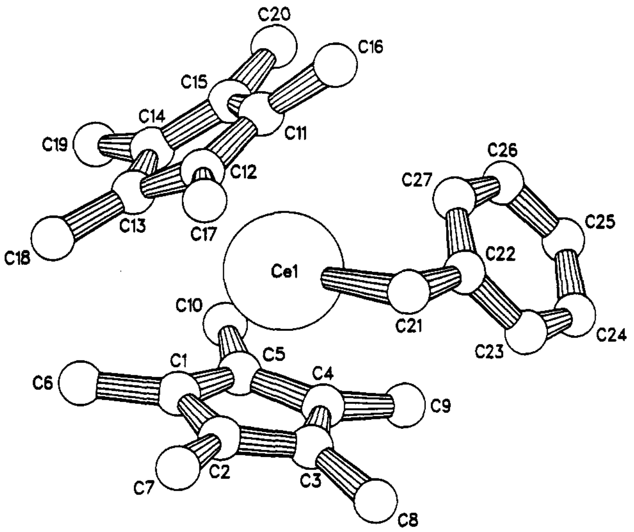

Figure 2. Molecular structure of $Cp^*_2CeCH_2C_6H_5$ (7) with the adopted numbering scheme (hydrogen atoms omitted for clarity).

Table II. Selected Distances and Angles for $Cp^*_2CeCH_2C_6H_5$ (7)

	Distances (Å)		
Ce–Ct1	2.48 (1)	Ce–Ct2	2.53 (2)
Ce–C(ring 1)$_{av}$	2.76 (3)	Ce–C(ring 2)$_{av}$	2.80 (3)
Cp*1(C–C)$_{int,av}$	1.41 (1)	Cp*2(C–C)$_{int,av}$	1.42 (1)
Cp*1(C–C)$_{ext,av}$	1.50 (2)	Cp*2(C–C)$_{ext,av}$	1.51 (1)
Ce–C21	2.596 (5)	C21–C22	1.451 (7)
Ce–C22	2.885 (5)	C22–C27	1.39 (1)
Ce–C27	2.882 (6)	C22–C23	1.425 (7)
	Angles (deg)		
Ct1–Ce–Ct2	137.5 (2)	Ce–C21–C22	86.0 (3)

Thermolysis in Toluene. Alkyl complexes of scandium and yttrium like Cp^*_2LnR are known to metalate toluene to yield mixtures of $Cp^*_2Ln(o,m,p\text{-tolyl})$ and -(benzyl) compounds.[2b,16] Clearly, the reaction is not selective for these metals. Surprisingly, the thermolysis of 2 and 3 in toluene gave $CH_2(SiMe_3)_2$ and a single organometallic product, identified as the benzyl derivatives 6 and 7 (eq 2). When the reaction was monitored by ^1H NMR

$$\underset{\substack{\mathbf{2},\ Ln = La\\ \mathbf{3},\ Ln = Ce}}{Cp^*_2LnCH(SiMe_3)_2} + C_6H_5CH_3 \rightarrow \underset{\substack{\mathbf{6},\ Ln = La\\ \mathbf{7},\ Ln = Ce}}{Cp^*_2LnCH_2C_6H_5} + CH_2(SiMe_3)_2 \quad (2)$$

spectroscopy in toluene-d_8, the only identifiable complexes were the starting materials and the final products. The half-life time was, due to H/D scrambling, difficult to establish accurately. For Ln = La $t_{1/2}$ is about 3 h at 385 K; for Ce the reaction is slower ($t_{1/2} \approx 6$ h). For both metals the reaction is of about the same rate as in cyclohexane, which indicates that also in toluene the abstraction of hydrogen from a pentamethylcyclopentadienyl ligand is the first step. The product formation confirms this as, initially, only $CH_2(SiMe_3)_2$ and no $CHD(SiMe_3)_2$ was formed. At longer reaction times extensive H/D scram-

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[8] Cp*1 = C1–C5, Cp*2 = C11–C15, Cp*3 = C31–C35.

[9] Heeres, H. J.; Renkema, J.; Booij, M.; Meetsma, A.; Teuben, J. H. *Organometallics* 1988, *7*, 2495.

[10] Rausch, M. D.; Moriarty, K. J.; Atwood, J. L.; Weeks, J. A.; Hunter, W. E.; Brittain, H. G. *Organometallics* 1986, *5*, 1281.

[11] Hazin, P. N.; Huffman, J. C.; Bruno, J. W. *Organometallics* 1987, *6*, 23.

[12] Ring slippage is defined as the distance between the center of gravity of the five ring carbon atoms and the perpendicular projection of the metal on the ring plane.

[13] Typical values for C–C single and double bonds are 1.54 and 1.34 Å, respectively. Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper & Row: New York, 1983; p A37.

[14] (a) The distances Ce1a··H291 (2.841 (7) Å) and Ce1a··H293 (2.884 (7) Å) are also very short, but these atoms have been included in a rigid methyl group in the refinement of the structure determination. This makes their interaction with cerium less certain. Nevertheless, Ce1a··C29 (3.254 (7) Å) is short as well. (b) van der Waals radii: r_H = 1.20 Å, r_C = 1.70 Å, r_{Ce} = 2.63 Å.[14c] (c) Bondi, A. *J. Phys. Chem.* 1964, *68*, 441 (or covalent radius + 0.8 Å when not given).

[15] Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* 1983, *250*, 395.

[16] Haan, K. H. den; Wielstra, Y.; Teuben, J. H. *Organometallics* 1987, *6*, 2053.

bling between organometallic product and solvent was observed. For **2** the relative rates for deuteration of various C–H bonds are $C_5(CH_3)_5 > Si(CH_3) >>> Si(CH_2)$; the hydrogen exchange rate of toluene-d_8 is in the order CD_3 > aryl CD. For **3** the behavior is similar, only the latter two hydrogen exchange rates are roughly the same. This shows that all C–H bonds in the reaction mixture, even the sterically very shielded methylene group in $CH_2(SiMe_3)_2$, are susceptible to attack by organolanthanoid species. Consequently, the formation of one single product must be thermodynamically determined, since kinetically all bonds appear roughly equally reactive. The reason for this might be a specially stable metal–ligand bonding in the benzyl complexes **6** and **7**. That this indeed is the case follows from the molecular structure of the cerium compound **7**.

Molecular Structure of $Cp^*_2CeCH_2C_6H_5$ (7). Compound **7** crystallizes as dark green needles from pentane in the orthorhombic space group $Pna2_1$ with four molecules in the unit cell. The molecule has the usual bent metallocene configuration with an essentially planar benzyl ligand (Figure 2; Table II). The methylene carbon C21 is shifted 0.11 (2) Å out of the phenyl ring plane toward the metal. The Cp* ligands exhibit no special features. The Ce–Ct distances of 2.48 (1) and 2.53 (2) Å, the dish-shaped conformation of the methyl groups (average out of plant bending 0.08 Å (Cp*1[17]) and 0.12 Å (Cp*2[17]) exo from the metal), and the C–C distances in the cyclopentadienyl ligands are normal. In contrast, the bonding of the benzyl ligand is quite unusual. It is located roughly perpendicular to the *xz* plane (deviation 13°) and inclined toward the metal, forming an angle of 54° with the *yz* plane (the *xz* plane contains Ct1, Ce, and Ct2; the z axis bisects the angle Ct1–Ce–Ct2). The carbon atoms C21, C22, and C25 are approximately in the *yz* plane. The Ce–C21 distance is 2.596 (5) Å, somewhat longer than found in $Cp^*_2CeCH(SiMe_3)_2$,[9] and the angle Ce–C21–C22 is 86.0 (3)°. This indicates that the main interaction of the benzyl ligand with the metal takes place on C21. There is also a strong interaction of the metal with C22 and C27, as follows from the distances of Ce to these carbon atoms (2.885 (5) and 2.882 (6) Å, respectively). These distances are practically identical with those found between the metal and the pentamethylcyclopentadienyl ring carbon atoms. The internal C–C distances within the phenyl ring are virtually identical (1.39 (2) Å). This indicates full delocalization of the π electrons over the phenyl ring and makes a build up of negative charge at the ortho position unlikely. This metal–ligand interaction can best be compared with that in very polar benzyl complexes of Li and d^0 transition metals.[18] In these compounds the metal also interacts with C(ipso) and C(ortho) of the benzyl. However, in these complexes the M–C(ortho) is at least 0.2 Å longer than the M–C(ipso) distance, whereas they are the same in this structure. This indicates that the cerium–benzyl interaction in **7** must be very strong. In complexes where the benzyl ligand is bonded as an η^3-allyl, the metal–C(α) and metal–C(ortho) distances are roughly equal and the C–C bonds in the aryl ring alternate.[19] The latter indicates delocalization of the π system in the allylic part only, but this is certainly not found for **7**. Other special structural aspects are the very short Ce··H27 and Ce··H211 close contacts of 2.71 (6) and 2.91 (5) Å, respectively. The latter can be seen as an α-agostic interaction,[15] although the angle Ce–C21–H211 (101 (3)°) is not exceptionally small. The former most probably results from the Ce–C(ortho) interaction.

Mechanism of C–H Activation. The formation of $CH_2(SiMe_3)_2$ and not of $CHD(SiMe_3)_2$ as primary product during the thermolysis of **2** and **3** in toluene-d_8 clearly demonstrates that hydrogen abstraction from a Cp* methyl group precedes the activation of the toluene C–H bonds. Initial formation of a fulvene compound Cp*FvLn, which undergoes further C–H activation reactions with solvent or other molecules Cp*FvLn to give **4** and **5**, is the most probable first step. To test whether **4** or **5** can enter C–H activation reactions the cerium compound, **5**, was heated in toluene-d_8. At room temperature, ^1H NMR spectroscopy showed a large number of broad resonances, attributable to various Cp*-containing paramagnetic compounds. At 80 °C these compounds were converted quantitatively to **7**, as was indicated by the appearance of one (broad) singlet at δ 2.63 (eq 3). The reverse reaction (3) will give

$$\underset{\mathbf{5}}{[Cp^*_3(\mu_3\text{-}\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2)Ce_2]_2} \xrightarrow[\text{toluene-}d_8]{} Cp^*(Cp^*\text{-}d_1)CeCD_2C_6D_5 \quad (3)$$

toluene-d_7 and incorporation of deuterium in Cp*, Fv, or Ad ligands, thus explaining the H/D exchange upon heating in deuterated solvents. The reversibility of reaction **3** was demonstrated by heating **7** in cyclohexane-d_{12}, which led to the formation of toluene and **5** (eq 4). These

$$\underset{\mathbf{7}}{Cp^*_2CeCH_2Ph} \xrightarrow[\text{cyclohexane-}d_{12}]{\Delta} \underset{\mathbf{5}}{[Cp^*_3(\mu\text{-}\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2)Ce_2]_2} + PhCH_3 \quad (4)$$

observations show that thermally induced hydrogen abstraction from a Cp* ligand is a kinetically allowed pathway for cerium alkyls **3** and **7**. The question remains whether the first step in the reaction mechanism is *inter*- or *intra*molecular. Although only a detailed mechanistic study, including crossover experiments, can provide conclusive evidence, we favor the intramolecular pathway. An intermolecular pathway would involve coordination of a C–H bond of a methyl group of a Cp* or $-CH(SiMe_3)_2$ group to the sterically congested $Cp^*_2LnCH(SiMe_3)_2$ complexes and is very unlikely. Initially a kinetically determined product like Cp*FvLn will be formed, which reacts further to thermodynamically stable species. In inert media it will react with other molecules Cp*FvLn to give ultimately the isolated tetranuclear complex, but in reactive solvents like THF, benzene, or toluene it will attack solvent molecules producing phenyl or tolyl compounds and as was observed for lanthanum and cerium even lead exclusively to benzyl compounds $Cp^*_2LnCH_2Ph$. Formation of the latter from the tetranuclear complexes **4** and **5** indicates the large kinetic lability of organometallic compounds of group 3 and lanthanides. It is reasonable to assume that in solutions of **4** and **5** these dissociate and recombine and even form mixtures of oligomers $(C_{20}H_{29}Ln)_n$. The kinetic lability of yttrium compounds appears to be smaller than for lanthanum or cerium. This is indicated by the formation of mixtures of products on thermolysis of **1**, both in cyclohexane and in aromatic solvents, although it is also possible that for yttrium the energetic difference between tolyl and benzyl compounds Cp^*_2YR is quite small. Additionally, the formation of the benzyl complexes **6** and **7** from **2** and **3** in toluene seems

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[17] Cp*1 = C1–C5 and Cp*2 = C11–C15.

[18] (a) Patterman, S. P.; Karle, I. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 1150. (b) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902. (c) Edwards, P. G.; Andersen, R. A.; Zalkin, A. *Organometallics* **1984**, *3*, 293 and references cited therein.

[19] (a) Cotton, F. A.; LaPrade, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 5418. (b) Roberts, J. S.; Klabunde, K. J. *J. Am. Chem. Soc.* **1977**, *99*, 2509.

Table III. Details on the Structure Determinations of [Cp*$_3$(μ_3-η^5,η^1,η^1-C$_5$Me$_3$(CH$_2$)$_2$Ce$_2$]$_2$ (5) and Cp*$_2$CeCH$_2$C$_6$H$_5$ (7)

a. Crystal Data		
chem formula	$(C_{40}H_{58}Ce_2)_2 \cdot 0.5C_6D_{12}$	$C_{27}H_{37}Ce$
mol wt	1734.52	501.74
cryst system	monoclinic	orthorombic
space group	*C*2/*c*	*Pna*2_1
a, Å	23.849 (9)	16.730 (4)
b, Å	10.846 (4)	11.387 (3)
c, Å	30.11 (1)	12.506 (3)
β, deg	104.29 (3)	
V, Å^3	7547 (5)	2382 (1)
Z	4	4
D_{calc}, g·gm^{-3}	1.516	1.399
F(000), electrons	3504	1028
μ(Mo K$\bar{\alpha}$), cm^{-1}	24.5	19.5
approx cryst dimens, mm	0.11 × 0.35 × 0.37	0.15 × 0.18 × 0.30
b. Data Collection		
diffractometer	Enraf-Nonius CAD-4F	Enraf-Nonius CAD-4F
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
monochromator	graphite	graphite
temp, K	130	130
θ range, deg min; max	1.40, 27.0	1.22, 30.0
$\omega/2\theta$ scan, deg	$\Delta\omega = 0.80 + 0.35 \tan\theta$	$\Delta\omega = 0.85 + 0.35 \tan\theta$
data set	h, $-1 \rightarrow +30$ k, $-1 \rightarrow +13$ l, $-38 \rightarrow +37$	h, $-1 \rightarrow +23$ h, $-1 \rightarrow +15$; l, $-38 \rightarrow +37$ l, $-1 \rightarrow +17$
cryst to receiving aperture dist, mm	173	173
horizontal, vertical aperture, mm	$3.2 + \tan\theta$, 4.0	$3.2 + \tan\theta$, 4.0
ref reflcns, rms dev in %	825, 4.4 $3\bar{1}\bar{6}$, 4.4 $\bar{3}\bar{1}\bar{4}$, 3.8	$\bar{6}31$, 2.2 $63\bar{1}$, 1.9 631, 1.9
drift corr	1.00–1.024	1.00–1.067
*R*1 ($=\sum(I - \bar{I})/\sum I$)	0.087	0.025
*R*2 ($=\sum\sigma/\sum I$)	0.118	0.049
min/max abs corr fac	0.796–1.462	
X-ray exposure time, h	222.4	111.8
tot. no. of data	10239	4884
no. of unique data	8216	3605
no. of obsd data, $F > 4.0\sigma(F)$	5027	
no. of obsd data $I > 2.5\sigma(I)$		2845
c. Refinement		
no. of reflcns	5025	2845
no. of refined params	437	365
final R_F ($=\sum(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/\sum\lvert F_o\rvert$)	0.049	0.029
final R_w ($=[\sum(w(\lvert F_o\rvert - \lvert F_c\rvert))/\sum\lvert wF_o\rvert^2]^{1/2}$)	0.033	0.029
weighting scheme	$1/\sigma^2(F)$	
S ($=(\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(m - n))^{1/2}$)[a]	1.879	1.266
resid electron density in final diff Fourier map, e/Å^3	−1.40, 1.42	−0.84, 0.87
max shift/σ, final cycle	0.365	0.347
av shift/σ, final cycle	0.020	0.035

[a] *m* = number of observations; *n* = number of variables.

both thermodynamically and kinetically favored. In particular for lanthanum the hydrogen–deuterium exchange rate of the toluene C*D*$_3$ group was higher than that of the aryl C*D* group. This possibility was recently suggested for the reaction of Cp*$_2$SmMe·THF with toluene as well.[20]

Experimental Section

General Considerations. All experiments were carried out under nitrogen by using standard Schlenk, glovebox (Braun MB200), and vacuum-line techniques. The compounds Cp*$_2$LnCH(SiMe$_3$)$_2$ (Ln = Y (1),[21] La (2),[22] Ce (3)[9]) were prepared according to published procedures. Cyclohexane and cyclohexane-d_{12} were stored over molecular sieves (4 Å). Toluene, toluene-d_8, and benzene-d_6 were distilled from Na/K alloy. Solvents were degassed prior to use. IR spectra were obtained from Nujol mulls between KBr disks on a Pye-Unicam SP3-300 spectrophotometer. NMR spectra were recorded on Bruker WH90 and Varian VXR300 spectrometers. Elemental analyses were performed at the Micro-Analytical Department of the University of Groningen under the supervision of Mr. A. F. Hamminga. The given data are the average of at least two independent determinations.

Thermolysis of Cp*$_2$YCH(SiMe$_3$)$_2$ (1). A solution of 0.57 g (1.1 mmol) of 1 in 10 mL of cyclohexane was sealed in a thick-walled glass ampule under vacuum and stored in an oven at 175 °C for 24 h. The color of the reaction mixture changed from colorless to orange. The ampule was opened in the glovebox, and the contents were transferred into a Schlenk vessel. The solvent was removed in vacuum, and the residual orange oil was stripped with several 10-mL portions of pentane until a foamy, solid residue was obtained; 0.35 g of thermolysis product was isolated as an orange powder. IR (cm^{-1}): 2720 (m), 1490 (sh), 1455 (s), 1380 (s), 1300 (w), 1245 (s), 1165 (m), 1140 (w), 1100 (w), 1030 (s), 920 (w), 855 (s), 830 (sh), 810 (w), 775 (w), 760 (w), 740 (w), 685 (m), 670 (m), 600 (w), 580 (m), 540 (w), 440 (m).

Thermolysis of Cp*$_2$LaCH(SiMe$_3$)$_2$ (2). A solution of 0.68 g (1.2 mmol) of 2 in 10 mL of cyclohexane was sealed in a thick-walled glass ampule under vacuum and stored in an oven

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(20) Evans, W. J.; Chamberlain, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423.

(21) Haan, K. H. den; Boer, J. L. de; Teuben, J. H.; Spek, A. L.; Kojić-Prodić, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726.

(22) (a) Cp*$_2$LaCH(SiMe$_3$)$_2$ was synthesized analogous to Cp*$_2$CeCH(SiMe$_3$)$_2$.[9] (b) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.

Table IV. Final Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Non-H Atoms (with Esd's in Parentheses) for 5 and 7

	x	y	z	U_{eq},[a] Å^2		x	y	z	U_{eq},[a] Å^2
				Data for 5					
Ce1	−0.06128 (2)	−0.08036 (4)	0.04525 (2)	0.0101 (1)	C20	0.1048 (3)	−0.0007 (8)	0.2334 (3)	0.025 (3)
Ce2	0.15305 (2)	−0.10912 (4)	0.12988 (2)	0.0109 (1)	C21	−0.0124 (3)	0.0404 (7)	0.1230 (3)	0.017 (3)
C1	0.1748 (4)	−0.2958 (7)	0.0706 (2)	0.018 (3)	C22	0.0289 (3)	−0.0321 (7)	0.1067 (2)	0.014 (3)
C2	0.2286 (3)	−0.2600 (7)	0.0984 (3)	0.015 (3)	C23	0.0427 (3)	0.0340 (7)	0.0701 (2)	0.010 (2)
C3	0.2325 (3)	−0.3025 (7)	0.1437 (2)	0.014 (3)	C24	0.0074 (3)	0.1412 (6)	0.0612 (2)	0.008 (2)
C4	0.1809 (3)	−0.3600 (7)	0.1441 (2)	0.015 (3)	C25	−0.0260 (3)	0.1466 (7)	0.0936 (2)	0.013 (2)
C5	0.1435 (3)	−0.3587 (7)	0.0999 (3)	0.015 (3)	C26	−0.0361 (4)	0.0143 (8)	0.1630 (3)	0.020 (3)
C6	0.1562 (4)	−0.2858 (7)	0.0194 (3)	0.024 (3)	C27[b]	0.0434 (4)	−0.1601 (7)	0.1159 (2)	0.016 (3)
C7	0.2775 (3)	−0.2020 (7)	0.0819 (3)	0.023 (3)	C28	0.0840 (3)	−0.0028 (7)	0.0407 (3)	0.015 (3)
C8	0.2869 (3)	−0.3149 (8)	0.1815 (3)	0.023 (3)	C29	0.0111 (3)	0.2401 (7)	0.0279 (2)	0.015 (3)
C9	0.1651 (3)	−0.4231 (8)	0.1833 (2)	0.027 (3)	C30	−0.0611 (3)	0.2548 (7)	0.1021 (3)	0.017 (3)
C10	0.0880 (3)	−0.4297 (8)	0.0842 (3)	0.024 (3)	C31	−0.1635 (4)	−0.1303 (7)	0.0737 (2)	0.017 (3)
C11	0.2067 (3)	−0.0489 (7)	0.2223 (2)	0.016 (3)	C32	−0.1789 (3)	−0.1394 (7)	0.0240 (2)	0.015 (3)
C12	0.2425 (3)	0.0023 (8)	0.1963 (2)	0.016 (3)	C33	−0.1537 (3)	−0.2463 (7)	0.0118 (2)	0.012 (3)
C13	0.2125 (3)	0.0997 (8)	0.1697 (2)	0.018 (3)	C34	−0.1203 (3)	−0.2992 (7)	0.0527 (3)	0.015 (3)
C14	0.1575 (3)	0.1117 (8)	0.1783 (2)	0.017 (3)	C35	0.1258 (3)	−0.2281 (7)	0.0911 (3)	0.016 (3)
C15	0.1544 (4)	0.0156 (8)	0.2113 (3)	0.022 (3)	C36	−0.1870 (4)	−0.0317 (7)	0.1006 (3)	0.023 (3)
C16	0.2212 (4)	−0.1467 (7)	0.2594 (3)	0.024 (3)	C37	−0.2235 (3)	−0.0600 (8)	−0.0060 (3)	0.026 (3)
C17	0.3061 (3)	−0.0176 (8)	0.2020 (3)	0.024 (3)	C38	−0.1675 (3)	−0.3001 (7)	−0.0352 (2)	0.020 (3)
C18	0.2403 (4)	0.1876 (7)	0.1413 (3)	0.024 (3)	C39	−0.0891 (3)	−0.4210 (8)	0.0559 (3)	0.026 (3)
C19	0.1145 (4)	0.2144 (7)	0.1632 (3)	0.024 (3)					
				Hexane Positions					
C40	−0.1047 (3)	−0.2685 (8)	0.1391 (2)	0.023 (3)	C42	0.0203 (4)	0.3700 (9)	0.2339 (3)	0.042 (4)
C41	0.0197 (4)	0.602 (1)	0.2343 (3)	0.050 (4)	C43	0.0109 (5)	0.486 (1)	0.2045 (3)	0.050 (4)
				Data for 7					
Ce1	0.16445 (1)	0.06411 (2)	0.4999 (1)	0.0145 (1)	C14	0.1878 (3)	−0.1342 (4)	0.6235 (4)	0.017 (1)
C1	0.0635 (3)	−0.0532 (4)	0.3652 (4)	0.019 (1)	C15	0.2117 (3)	−0.0395 (4)	0.6895 (4)	0.017 (1)
C2	0.1117 (3)	0.0122 (6)	0.2964 (4)	0.025 (2)	C16	0.3397 (3)	0.0937 (5)	0.7017 (4)	0.021 (1)
C3	0.0914 (3)	0.1324 (5)	0.3089 (4)	0.022 (1)	C17	0.3797 (3)	−0.0496 (4)	0.4881 (7)	0.020 (2)
C4	0.0314 (3)	0.1392 (5)	0.3879 (4)	0.019 (1)	C18	0.2527 (3)	−0.2475 (5)	0.4640 (4)	0.026 (2)
C5	0.0143 (3)	0.0231 (5)	0.4227 (4)	0.022 (2)	C19	0.1173 (3)	−0.2129 (5)	0.6481 (5)	0.027 (2)
C6	0.0553 (4)	−0.1859 (6)	0.3647 (5)	0.036 (2)	C20	0.1665 (4)	0.0045 (5)	0.7856 (4)	0.025 (2)
C7	0.1767 (4)	−0.0359 (7)	0.2236 (5)	0.041 (2)	C21	0.2597 (3)	0.2377 (4)	0.4566 (4)	0.022 (1)
C8	0.1212 (4)	0.2309 (7)	0.2399 (6)	0.041 (2)	C22	0.2036 (2)	0.3103 (4)	0.5154 (7)	0.018 (2)
C9	−0.0131 (4)	0.2479 (5)	0.4221 (5)	0.035 (2)	C23	0.1653 (3)	0.4081 (4)	0.4662 (5)	0.030 (2)
C10	−0.0447 (3)	−0.0075 (5)	0.506 (1)	0.037 (2)	C24	0.1076 (3)	0.4710 (4)	0.5210 (8)	0.036 (3)
C11	0.2853 (3)	0.0049 (4)	0.6486 (4)	0.017 (1)	C25	0.0841 (3)	0.4402 (5)	0.6241 (6)	0.036 (2)
C12	0.3044 (3)	−0.0605 (4)	0.5565 (4)	0.017 (1)	C26	0.1191 (3)	0.3451 (5)	0.6725 (5)	0.031 (2)
C13	0.2447 (3)	−0.1493 (4)	0.5416 (4)	0.017 (1)	C27	0.1781 (3)	0.2806 (5)	0.6178 (5)	0.027 (2)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$. [b] Nonpositive-definite temperature factors.

at 125 °C for 24 h. The color changed from slightly yellow to dark orange-brown. The ampule was opened in the glovebox and the solution transferred into a Schlenk vessel. The solvent was removed in vacuum, and the orange oil was stripped with 10 mL of pentane. The remaining solid was isolated to yield 0.35 g of 4 as an orange powder. IR (cm^{-1}): 2720 (m), 2685 (w), 1560 (w), 1490 (sh), 1445 (s), 1370 (s), 1250 (s), 1155 (m), 1080 (s, br), 1045 (s), 1015 (m), 945 (w), 890 (w), 875 (m), 845 (s), 830 (sh), 800 (w), 785 (w), 770 (w), 720 (w), 685 (w), 570 (m), 505 (w). Anal. Calcd for $C_{20}H_{29}La$: C, 58.83; H, 7.16. Found: C, 58.97; H, 7.74.

Thermolysis of $Cp^*_2CeCH(SiMe_3)_2$ (3). In a procedure similar to that for 2, starting from 0.76 g (1.3 mmol) of 3 in 12 mL of cyclohexane, 0.51 g of 5 was isolated as a brown powder. IR (cm^{-1}): 2720 (m), 2115 (w), 1560 (w), 1490 (sh), 1440 (s), 1370 (s), 1250 (s), 1155 (m), 1110 (m, br), 1050 (s), 1015 (m), 890 (w), 845 (s), 830 (sh), 805 (w), 720 (w), 680 (w), 570 (m), 505 (w). Anal. Calcd for $C_{20}H_{29}Ce$: C, 58.65; H, 7.14. Found: C, 59.41; H, 7.61.

$Cp^*_2LaCD_2C_6D_5$ (6-d_7). An NMR tube was filled with a solution of ca. 20 mg (ca. 0.04 mmol) of 2 in 0.4 mL of toluene-d_8. The solution was cooled to −196 °C, and the tube was sealed under vacuum. The tube was stored in an oven at 120 °C for 1 h. After this, the characteristic resonances of 2 had disappeared and the resonance of the Cp* hydrogens of 6-d_7 appeared at δ 1.82.

$Cp^*_2CeCH_2C_6H_5$ (7). A solution of 4.80 g (8.4 mmol) of 3 in 150 mL of toluene was refluxed for 48 h, during which the color changed from red to dark green. The solvent was removed in vacuum, and the residue was stripped with 50 mL of pentane and subsequently dissolved in 50 mL of pentane. Slow cooling to −80 °C afforded 2.67 g (5.3 mmol) of 7 as dark green needles. Concentration of the mother liquor yielded a second crop of 0.48 g (1.0 mmol) of 7. Total yield: 74%. IR (cm^{-1}): 2720 (w), 1590 (s), 1540 (w), 1360 (sh), 1320 (w), 1290 (w), 1235 (m), 1175 (m), 1020 (m, br), 985 (w), 870 (m), 835 (w), 805 (w), 765 (s), 730 (m), 715 (m), 705 (s), 530 (m, br). ^{1}H NMR (benzene-d_6, 30 °C): δ 2.90 (s, $C_5(CH_3)_5$, 30 H), 1.29, 0.88, −2.83, −3.03, −3.64 (all s, signals overlap, 7 H, CH_2Ph and aryl C–H). ^{13}C NMR (benzene-d_6, 30 °C): δ 284.0 (br, no coupling observed, CH$_2$Ph), 201.0 (s, C_5Me$_5$), 113.0, 112.1, 111.0, 109.6 (signals overlap, all aryl C), 8.1 (q, $^1J_{CH}$ = 124.4 Hz, $C_5(CH_3)_5$). Anal. Calcd for $C_{27}H_{37}Ce$: C, 64.64; H, 7.43; Ce, 27.93. Found: C, 64.64; H, 7.50; Ce, 27.87.

Structure Determination of $[Cp^*_3(\mu_3\text{-}\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2)Ce_2]_2\cdot 0.5C_6D_{12}$ (5). An NMR tube, containing a solution of thermolyzed 3 in cyclohexane-d_{12}, was allowed to stand at room temperature for several weeks. During this period brown-red crystals of $[Cp^*_3(\mu_3\text{-}\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2)Ce_2]_2$ formed. The NMR tube was opened in the glovebox. A thin, rectangular plate was cut in its longest dimension, glued on a glass fiber, and transferred directly into the cold nitrogen stream of the low-temperature unit mounted on an Enraf-Nonius CAD-4F diffractometer interfaced to a PDP-11/23 computer. Automatic centering and at least-squares fit were carried out on 25 reflections in the range 8.68° < θ < 14.49° to obtain the cell dimensions and their standard deviations. The monoclinic unit cell was checked for the presence of higher lattice symmetry.[23] Three reference reflections were measured every 3 h during data collection; these exhibited no significant decay. A 360° ψ scan for a close to axial reflection $(0\bar{2}\bar{1})$ showed a variation in intensity up to 43% about the mean value. The net intensities of the data were corrected for the scale variation and Lorentz and polarization effects. Crystal data and

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experimental details of the structure determination are compiled in Table III. The Ce atoms were found with Patterson methods (SHELXS86).[24] The remaining non-H atoms were located from the subsequent difference Fourier maps. After completion of the isotropic refinement, empirical absorption corrections based on $F_0 - F_c$ differences were applied with the program DIFABS[25] (R_F dropped from 0.105 to 0.063). At this stage of the refinement some hydrogen atoms could be located on a difference Fourier map. The positions of the remaining methyl hydrogens were calculated from an idealized sp^3 hybridization at C, thereby served the found hydrogen atoms to determine the conformation of the methyl groups. The hydrogen atoms of the methyl groups were refined in the riding mode with a fixed C–H bond length of 1.0 Å. Refinement on F by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms and one overall isotropic temperature factor for the hydrogen atoms converged at $R_F = 0.049$ ($R_w = 0.033$). Weights were introduced in the final refinement cycles. Two reflections (204 and 802) with a $w\Delta F/\sigma(F)$ ratio greater then 20 were excluded from the final refinement (probably severe secondary extinction). The final difference map was essentially featureless with a few peaks in the vicinity of the Ce atoms. Table IV gives the final fractional atomic coordinates for 5.

Structure Determination of $Cp^*_2CeCH_2C_6H_5$ (7). A dark green, needle-shaped crystal, obtained by crystallization from pentane, was glued on the top of a glass fiber and transferred into the cold nitrogen stream of the low-temperature unit mounted on an Enraf-Nonius CAD-4F diffractometer interfaced to a PDP-11/23 computer. Precise lattice parameters and their standard deviations were derived from the angular settings of 25 reflections in the range $9.23° < \theta < 17.03°$. The space group $Pna2_1$ was determined from the following systematic extinctions: $0kl$, $k + l = 2n + 1$; $h0l$, $h = 2n + 1$; $00l$, $l = 2n + 1$. This choice was confirmed by the solution and refinement of the structure. Reduced cell calculations did not indicate any higher lattice symmetry.[23] Crystal and/or instrumental instability was monitored by measurement of the intensities of three reflections that were collected after every 3 h of X-ray exposure time; they showed a decay of 7%. A 360° ψ scan for a close to axial reflection (022) showed a variation in intensity of 6.5% about the mean value. The net intensities of the data were corrected for the decay and Lorentz and polarization effects but not for absorption. Standard deviations in the intensities were increased according to an analysis of the excess variance of the reference reflection: Standard deviation $\sigma(I)$ was calculated on the basis of counting statistics and the term P^2I^2, where P (=0.034) is the instability constant[25] as derived from the excess variance in the reference reflections. Crystal data and experimental details of the structure determination are compiled in Table III. The structure was solved by Patterson methods and partial structure expansion (SHELXS86).[24] The three remaining non-hydrogen atoms were located from the subsequent difference Fourier map. Refinement using anisotropic thermal parameters followed by difference Fourier synthesis resulted in the location of 25 hydrogen atoms; the remaining hydrogen atoms were initially placed at calculated positions, and all hydrogen atoms subsequently refined satisfactorily. The alternative absolute structure was rejected on the basis of the resulting higher R values ($R_F = 0.031$; $R_{wF} = 0.031$), obtained by refinement with negative anomalous-dispersion factors (negative if''). Refinement on F by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms and one overall temperature factor for the hydrogen atoms converged at $R_F = 0.029$ ($R_w = 0.029$). A final difference Fourier map did not show any significant residual features. Table IV gives the final fractional atomic coordinates for 7.

Computational Data. Scattering factors are those given by Cromer and Mann.[27] Anomalous dispersion factors were taken from Cromer and Liberman.[28] All calculations were carried out on the CDC-Cyber 170/760 computer of the University of Groningen with the program packages XTAL,[29] EUCLID[30] (calculation of geometric data), ORTEP,[31] and a locally modified version of the program PLUTO[32] (preparation of illustrations).

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Supplementary Material Available: ORTEP drawings of 5 and 7 and tables of all atomic coordinates, thermal parameters, bond distances, bond angles, and torsion angles (34 pages); listings of observed and calculated structure factors (45 pages). Ordering information is given on any current masthead page.

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