Synthesis and Trimethylsilyl C−H Activation Processes of 14-Electron Cp*Hf(2,3-dimethyl-1,3-butadiene)trimethylsilylmethyl Complexes†

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The 14-electron alkyl complexes Cp*Hf(C_6H_{10})R (Cp* = η^5-C_5Me_5, C_6H_{10} = 2,3-dimethyl-1,3-butadiene, R = CH_2SiMe_3, **2**; $CH(SiMe_3)_2$, **3**) were synthesized by reaction of Cp*Hf(C_6H_{10})Cl(THF) (**1**·THF) with the corresponding alkyl-lithium reagents in toluene solvent. Complex **3** consists of a 1:1 mixture of two rotamers with respect to rotation around the Hf−alkyl bond. A crystal structure determination of **3** showed that these two isomers cocrystallize randomly. Warming **3** to 80 °C leads to a rearrangement of the $HfCH(SiMe_3)_2$ group to give the complex Cp*Hf(C_6H_{10})($CH_2SiMe_2CH_2SiMe_3$) (**4**). It is likely that in this rearrangement the diene ligand acts as a reversible proton acceptor for one of the protons of a $SiMe_3$ group of the alkyl. Reaction of **1**·THF with 2 equiv of $LiCH(SiMe_3)_2$ in THF leads to deprotonation of one of the alkyl SiMe groups to give Cp*Hf(C_6H_{10})[$CH(SiMe_3)SiMe_2CH_2$]-Li(THF)$_x$ (**5**·THF$_x$, x = 1 or 2), containing a 1-hafna-3-silacyclobutane ring. A crystal structure determination of **5**·THF showed that the Li-cation is bridging the methylene of the deprotonated alkyl group and one of the diene methylene groups.

Introduction

The trimethylsilyl-substituted alkyl groups CH_2SiMe_3 and $CH(SiMe_3)_2$ are frequently used in the preparation of electron-deficient transition metal and lanthanide alkyl complexes, mainly for two reasons. Their steric demand allows low metal coordination numbers to be reached and prevents coordination of salt or solvent to the metal center or the formation of dimeric complexes.[1,2] In addition, they lack β-H atoms, which leads to relatively high thermal stability of their metal alkyl compounds.

Cp*Hf(diene)X complexes (X = halide, alkyl) are 14-electron species with an extensive reactivity.[3] We are investigating these species as precursors to well-defined polynuclear polyhydride complexes. For the efficient synthesis of alkyl derivatives when the alkyl group is Me or Et,[3b] it is necessary to free the chlorides Cp*Hf(diene)Cl·THF (which are obtained in good yield from the reduction of Cp^*HfCl_3 in the presence of the diene in THF) from coordinated THF by sublimation, lowering the yield substantially. By using silylated alkyls it should be possible to obtain the base-free alkyl complexes directly from the THF adducts. Here we describe the synthesis of base-free trimethylsilyl-alkyl hafnium complexes Cp*Hf(2,3-dimethyl-1,3-butadiene)R with R = CH_2SiMe_3 and $CH(SiMe_3)_2$. It was found that the SiMe groups in the latter are susceptible to C−H activation processes, resulting for example in an unusual rearrangement of Hf-$CH(SiMe_3)_2$ to Hf-$CH_2SiMe_2CH_2SiMe_3$.

Results and Discussion

Synthesis of Cp*Hf(C_6H_{10})R (R = CH_2SiMe_3, $CH(SiMe_3)_2$). The alkyl complexes Cp*Hf(C_6H_{10})R (Cp* = η^5-C_5Me_5, R = CH_2SiMe_3 **2**; $CH(SiMe_3)_2$ **3**) were readily obtained from the reaction of Cp*Hf(C_6H_{10})Cl(THF) (**1**·THF) with 1 equiv of LiR in toluene solvent (Scheme 1), followed by extraction with pentane. Complex **2** is an orange-brown oil at ambient temperature, which was obtained in nearly quantitative yield (with as the only observable impurity some residual pentane), and **3** is an orange-brown crystalline solid, which was obtained in 68% yield.

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† Netherlands Institute for Catalysis Research (NIOK) publication no. RUG 01-4-06.

(1) (a) Lappert, M. F.; Pearce, R. *J. Chem. Soc., Chem. Commun.* **1973**, 126. (b) Manriquez, J. M.; Fagan, P. J.; Marks, T. J.; Vollmer, S. H.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 5075. (c) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091. (d) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103. (e) Edelmann, F. T. *Metallocenes*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH Verlag GmbH: Weinheim, 1998; Vol. 1, Chapter 2, and references therein. (f) Anwander, R. *Topics in Organometallic Chemistry*; Kobayashi, S., Ed.; Springer-Verlag: Berlin, 1999; Vol. 2, Chapter 1, and references therein.

(2) (a) Collier, M. R.; Lappert, M. F.; Truelock, M. M. *J. Organomet. Chem.* **1970**, *25*, C36. (b) Yagupsky, G.; Mowat, W.; Shortland, A.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1970**, 1369. (c) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Acc. Chem. Res.* **1974**, *7*, 209, and references therein. (d) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev.* **1976**, *76*, 219, and references therein.

(3) (a) Blenkers, J.; De Liefde Meijer, H. J.; Teuben, J. H. *Organometallics* **1983**, *2*, 1483. (b) Blenkers, J.; Hessen, B.; van Bolhuis, F.; Wagner, A. J.; Teuben, J. H. *Organometallics* **1987**, *6*, 459. (c) Hessen, B.; van Bolhuis, F.; Teuben, J. H. *Organometallics* **1987**, *6*, 1352. (d) Ausema, J. B.; Hessen, B.; Teuben, J. H. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 465. (e) Hessen, B.; Teuben, J. H. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 208. (f) Hessen, B.; Teuben, J. H. *J. Organomet. Chem.* **1988**, *358*, 135. (g) Hessen, B.; Blenkers, J.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1989**, *8*, 830. (h) Hessen, B.; Blenkers, J.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1989**, *8*, 2809. (i) Hessen, B.; van der Heijden, H. *J. Am. Chem. Soc.* **1996**, *118*, 11670.

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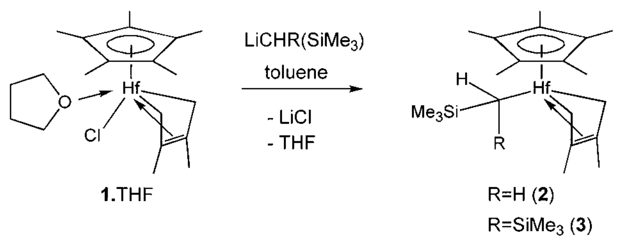
Scheme 1



The ^1H NMR spectrum of **2** is consistent with a symmetrical structure, with a mirror plane through the metal, the alkyl α-carbon, and the central diene C−C bond. The Hf*CH*$_2$SiMe$_3$ resonances are found at −0.68 (^1H) and at 59.20 ppm (^{13}C). The resonances associated with the diene ligand in **2** show all the features expected for a 14-electron Cp*Hf(diene)X complex in which a substantial amount of σ^2,π-metallacyclopentene character is present.[3b] There is a considerable chemical shift difference between the diene methylene *syn* and *anti* protons (Δδ 2.25 ppm; this is usually <1 ppm in the 16-electron Lewis base adducts such as **1**·THF) and a relatively large methylene $^2J_{HH}$ of 11 Hz. Therefore, with the CH$_2$SiMe$_3$ alkyl group it is clearly possible to obtain a base-free 14-electron alkyl complex directly from the THF adduct **1**·THF.

The ^1H NMR spectrum of **3** shows the presence of two isomers in a ratio close to 1:1. Warming a C_6D_6 solution of **3** to 80 °C does not lead to a noticeable difference in isomer ratio or to broadening of any of the resonances. It is likely that these isomers are rotamers associated with hindered rotation around the Hf−C bond to the sterically demanding alkyl group, but at this stage we cannot determine whether slow isomer interconversion does take place; that is, we do not know if the observed isomer ratio is kinetically or thermodynamically determined. The ^1H and ^{13}C NMR resonances of the Hf*CH*(SiMe$_3$)$_2$ group for the two isomers are found at 0.41 (^1H) and 58.25 ppm (^{13}C) and at −0.52 (^1H) and 62.07 ppm (^{13}C). The diene resonances for the two isomers are very similar and characteristic for 14-electron Cp*Hf(C_6H_{10})R species.

Crystals of **3** that were suitable for an X-ray structure determination were obtained by cooling a solution in pentane to −60 °C. The unit cell contains two independent molecules that differ in the rotational orientation of the Cp* ligand. In Figure 1 (pertinent interatomic distances and angles in Table 1) only one of the two independent molecules is shown. The butadiene ligand is bound to Hf in a supine[4] orientation and shows substantial σ^2,π-metallacyclopentene character, i.e., the distances of Hf to the diene CH$_2$ carbons are on average 0.3 Å shorter than those to the diene CMe carbons, and the central diene C−C bond, C(112)−C(113), is noticeably shorter than the two other C−C bonds of the diene backbone. No evidence was found for an asymmetric binding mode of the butadiene, as was suggested earlier from a structure determination of **1**.[3b] The sum of the angles around the Hf-alkyl α-carbon, C(117), is 360°, and this planarity indicates that the two rotational isomers have cocrystallized randomly.

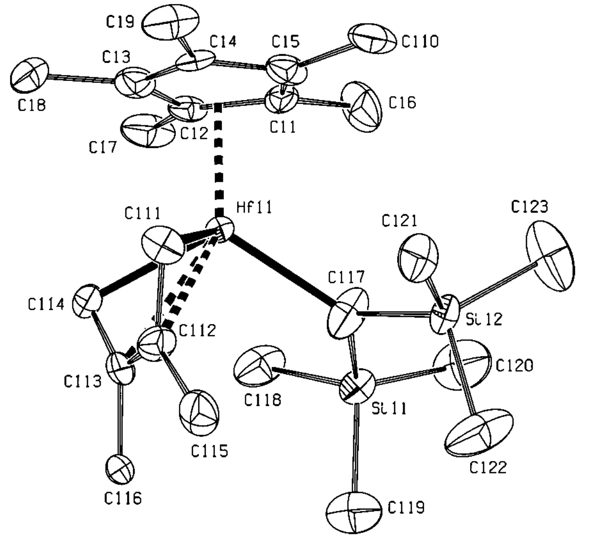


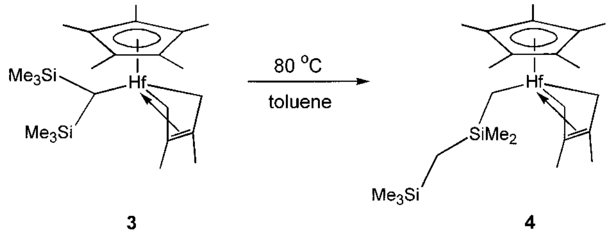
Figure 1. Molecular structure of Cp*Hf(C_6H_{10})[CH(SiMe$_3$)$_2$] (**3**) showing 50% probability ellipsoids.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Cp*Hf(C_6H_{10})[CH(SiMe$_3$)$_2$] (3)

Hf(11)−av C(Cp)	2.221	Hf(11)−C(117)−Si(11)	119.5(6)
Hf(11)−C(111)	2.215(10)	Hf(11)−C(117)−Si(12)	122.6(6)
Hf(11)−C(112)	2.522(8)	Si(11)−C(117)−Si(12)	117.7(5)
Hf(11)−C(113)	2.519(10)	C(11)−Hf(11)−C(117)	91.6(3)
Hf(11)−C(114)	2.220(12)	C(114)−Hf(11)−C(117)	114.8(5)
Hf(11)−C(117)	2.259(9)	Hf(11)−C(111)−C(112)	83.6(6)
C(117)−Si(11)	1.872(13)	Hf(11)−C(114)−C(113)	83.5(6)
C(117)−Si(12)	1.838(12)		
C(111)−C(112)	1.477(16)		
C(112)−C(113)	1.342(14)		
C(113)−C(114)	1.468(15)		
C(112)−C(115)	1.531(11)		
C(113)−C(116)	1.535(14)		

Thermal Stability. Warming a C_6D_6 solution of **2** to 80 °C and monitoring the solution by NMR spectroscopy showed that this compound is stable for at least a week under these conditions. For comparison, it was observed previously that, in C_6D_6 solution, Cp*Hf(C_6H_{10})Me decomposes at 40 °C and Cp*Hf(C_6H_{10})Et even at room temperature.[3b] Thus, when the methyl ligand is substituted with a SiMe$_3$ group, the resulting Hf-alkyl complex is much more stable.

Scheme 2



Upon warming a solution of **3** (a 1:1 mixture of the rotamers) in C_6D_6 to 80 °C, within a few hours the gradual formation of a single new compound can be observed, eventually leading to full conversion of **3** in 24 h. The NMR spectra of this new species are consistent with a symmetrical 14-electron Cp*Hf(C_6H_{10})R complex. It was identified, on the basis of its ^1H, ^{13}C, and ^{29}Si NMR spectra and its reaction with methanol-d_4, as Cp*Hf(C_6H_{10})(CH$_2$SiMe$_2$CH$_2$SiMe$_3$) (**4**, Scheme 2). The reaction of **4** with CD$_3$OD resulted in liberation of CH$_2$DSiMe$_2$CH$_2$SiMe$_3$, as identified by ^1H NMR and GC/MS, indicating that the metal center in **4** is bound to

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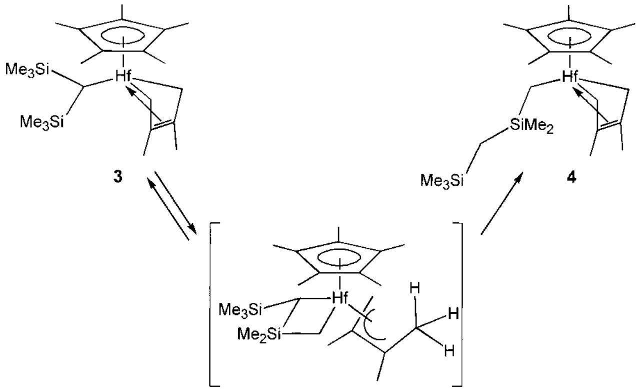
(4) Nakamura, A.; Mashima, K. *J. Organomet. Chem.* **2001**, *621*, 224.

Scheme 3



one of the terminal rather than to the central carbon atom of the alkyl group.

The HfCH_2SiMe$_2$ resonances of **4** are found at −0.60 (^{1}H) and 60.90 ppm (^{13}C), very similar to the HfCH_2-SiMe$_3$ resonances found in **2**, −0.68 (^{1}H) and 59.20 ppm (^{13}C), respectively. In the ^{29}Si NMR spectrum of **4**, two resonances are observed, at −0.12 and −3.87 ppm. These are assigned to the CH$_2$*Si*Me$_3$ and HfCH$_2$*Si*Me$_2$ groups, respectively, by comparison with the HfCH$_2$*Si*Me$_3$ ^{29}Si resonance of **2** that is found at −4.98 ppm.

Formation of the M-CH$_2$SiMe$_2$CH$_2$SiMe$_3$ moiety has been observed before in reactions of M(CH$_2$SiMe$_3$)$_2$ dialkyl compounds, viz., in thermolysis of (Ph$_3$P)$_2$Pt-(CH$_2$SiMe$_3$)$_2$ to give L$_2$Pt(CH$_3$)(CH$_2$SiMe$_2$CH$_2$SiMe$_3$)[5] and in the sequential reaction of [η^5:η^1-C$_5$Me$_4$(CH$_2$)$_3$O]-Ti(CH$_2$SiMe$_3$)$_2$ first with B(C$_6$F$_5$)$_3$ and then with THF to give {[η^5:η^1-C$_5$Me$_4$(CH$_2$)$_3$O]Ti(CH$_2$SiMe$_2$CH$_2$SiMe$_3$)-(THF)}[MeB(C$_6$F$_5$)$_3$].[6] To our knowledge, it is the first time that it has been observed as the product of a rearrangement of a M-CH(SiMe$_3$)$_2$ species.

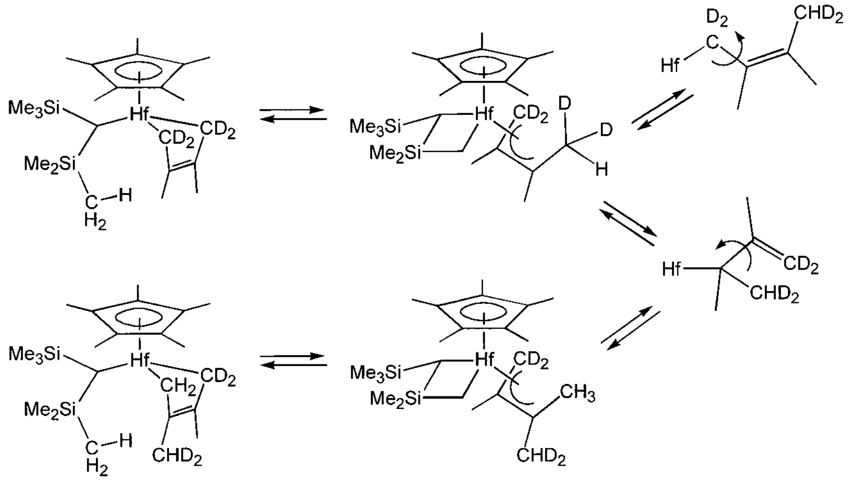
A possible route of formation of **4** could involve proton transfer from a methyl group of one of the SiMe$_3$ substituents of the alkyl to one of the methylene groups of the butadiene, thereby yielding an intermediate that contains a 1-hafna-3-silacyclobutane moiety and a 1,1,2-trimethylallyl group (Scheme 3). In principle this reaction is reversible, regenerating **3**, but transfer of a proton to the Hf*C*H(SiMe$_3$) carbon, rather than to the Hf*C*H$_2$SiMe$_2$ carbon, would result in formation of **4**.

To test the viability of this proposal, we performed the rearrangement reaction with **3**-*d*$_4$, in which the diene methylene groups are deuterated, at 80 °C in C$_6$D$_6$/C$_6$H$_6$ solvent. Monitoring the reaction with both ^{1}H and ^{2}H NMR spectroscopy revealed that, already after 1.5 h, substantial H/D exchange between the diene methylene and methyl positions of **3**-*d*$_4$ can be observed. In the ^{2}H NMR spectrum a broadened resonance at 2.19 ppm is growing in for D atoms on the diene methyl position, while in the ^{1}H NMR spectrum doublet resonances appear for the diene CH$_2$ group of **3**. These resonances are also observed for **4** that is formed more slowly over several hours. No evidence for significant formation of SiCH$_2$D or diene CHD groups could be observed. This suggests that the process involves the transfer of H atoms, which is expected to be significantly faster than that of D atoms in a process with C−H/D cleavage in the rate-determining step. As a similar exchange was not observed upon warming of a C$_6$D$_6$ solution of the corresponding chloride complex **1**-*d*$_4$, it is likely that the bis(trimethylsilyl)methyl group in **3** is involved in the exchange process. A proposed reaction sequence is shown in Scheme 4.

In this scheme, transfer of one H atom from one of the trimethylsilyl methyl groups in **3**-*d*$_4$ to one of the diene CD$_2$ groups results in the *d*$_4$-analogue of the 1-hafna-3-silacyclobutane 1,1,2-trimethylallyl intermediate proposed in Scheme 3 for the rearrangement of **3** to **4**. Exchange of the dideuterated *anti*- and nondeuterated *syn*-methyl groups can take place through transient η^1-bonding of the allyl group and rotation around the C−C bond. Opening the hafnasilacyclobutane ring by H-transfer from the *anti*-CH$_3$ group of the rearranged trimethylallyl regenerates **3**-*d*$_4$, as the isomer with one dideuterated methylene and one dideuterated methyl group in the diene ligand. This process can explain the observations made on warming a solution of **3**-*d*$_4$ and provides support for the proposed pathway for the rearrangement of **3** to **4**.

SiMe$_3$ Deprotonation with an External Base. The reaction of **1**·THF with (SiMe$_3$)$_2$CHLi was also performed in THF solvent instead of in toluene. In addition to the two isomers of **3**, the formation of another (minor) product was observed. NMR spectroscopy of the product mixture suggested that this additional product has an asymmetric structure. Repeating the reaction with 2 equiv of (SiMe$_3$)$_2$CHLi per hafnium resulted in exclusive formation of this new product. The product was char-

Scheme 4



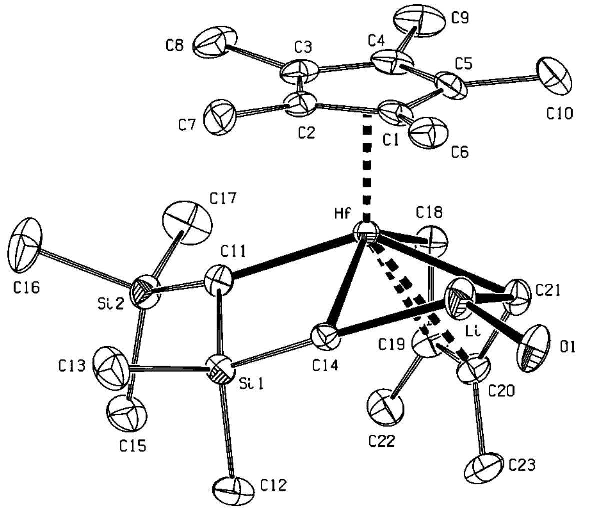
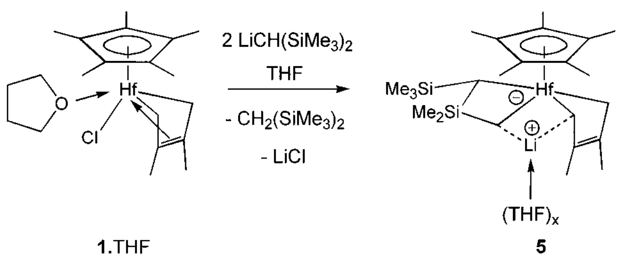


Figure 2. Molecular structure of Cp*Hf(C_6H_{10})[CH($SiMe_3$)$SiMe_2CH_2$]Li(THF) (**5**·THF) showing 50% probability ellipsoids. The carbon atoms of the THF molecule have been omitted for clarity.

acterized by NMR spectroscopy, elemental analysis, and a single-crystal X-ray structure determination, as Cp*Hf(C_6H_{10})[CH($SiMe_3$)$SiMe_2CH_2$]Li(THF)$_x$ (**5**·THF$_x$; $x = 1$, 2). It is derived from a deprotonation of one of the trimethylsilyl methyl groups in **3** by the second equivalent of $(SiMe_3)_2CHLi$, which acts as a Brønsted base (Scheme 5). Performing the reaction in THF-d_8 in an NMR tube indeed revealed the concomitant formation of 1 equiv of $(SiMe_3)_2CH_2$.

Scheme 5



Extraction of the reaction mixture with pentane, followed by crystallization, yielded **5**·THF$_2$ in 64% isolated yield. The product contains two molecules of THF per formula unit, as seen by NMR spectroscopy and elemental analysis. Recrystallization of this material from benzene, yielding crystals suitable for single-crystal X-ray crystallography, resulted in loss of one THF molecule to give the product **5**·THF.

The crystal structure of **5**·THF (Figure 2, pertinent interatomic distances and angles in Table 2) shows a molecule with a 1-hafna-3-silacyclobutane ring, a diene ligand in a σ^2,π-metallacyclopentene coordination mode, and a Li atom (with one coordinated THF molecule) bridging the hafnasilacyclobutane methylene, C(14), and one of the diene methylene groups, C(21). The Hf−C distances are all more or less elongated relative to related distances in **3**, in response to the increased coordination number of the metal center. The diene methylene carbon attached to Li is somewhat more distant from Hf than the other diene methylene: Hf−C(21) = 2.382(7) Å vs Hf−C(18) = 2.307(10) Å. A comparable difference can be observed for the two Hf−C distances in the 1-hafna-3-silacyclobutane. The hafnasilacyclobutane ring is essentially planar, as can be seen, for example, from the torsion angles in the ring, which are all around 8−11°. The $SiMe_3$ substituent, Si(2), takes up an equatorial position relative to the four-membered ring, with the axial hydrogen on C(11) pointing away from the diene ligand. This isomer is likely to be produced by deprotonation of the alkyl group in the rotational isomer of **3** that has the alkyl α-CH bond also pointing away from the diene ligand. Interestingly, only one of the possible isomers of **5** is observed, even when a preformed mixture of the two isomers of **3** is reacted with one additional equivalent of alkyllithium, and the ratio of the two isomers of **3** was observed by NMR to remain constant during the reaction. This may suggest that rotation around the Hf−alkyl bond in **3** (or other rearrangements around the metal center) may still be possible, despite the steric encumbrance of the complex, albeit on a time scale that is inaccessible by conventional NMR spectroscopy.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Cp*Hf(C_6H_{10})[CH($SiMe_3$)$SiMe_2CH_2$]-Li(THF) (5·THF)

Hf−av C(Cp)	2.238	Hf−C(11)−Si(1)	90.6(3)
Hf−C(11)	2.325(6)	Hf−C(11)−Si(2)	139.5(4)
Hf−C(14)	2.380(8)	Hf−C(14)−Si(1)	88.6(3)
Hf−C(18)	2.307(10)	Hf−C(14)−Li	79.2(5)
Hf−C(19)	2.556(12)	Hf−C(21)−Li	76.4(4)
Hf−C(20)	2.585(8)	C(11)−Si(1)−C(14)	102.6(3)
Hf−C(21)	2.382(7)	C(14)−Li−C(21)	94.6(7)
C(18)−C(19)	1.463(12)	C(14)−Li−O	128.5(9)
C(19)−C(20)	1.391(15)	C(21)−Li−O	119.8(8)
C(20)−C(21)	1.479(11)		
C(11)−Si(2)	1.842(8)		
Si(1)−C(11)	1.863(8)		
Si(1)−C(14)	1.877(7)		
Si(1)−C(12)	1.879(8)		
Si(1)−C(13)	1.887(12)		
C(14)−Li	2.109(15)		
C(21)−Li	2.27(3)		
Li−O	1.90(3)		
C(18)−C(19)	1.44(2)		
C(19)−C(20)	1.37(2)		
C(19)−C(22)	1.50(2)		
C(20)−C(21)	1.478(19)		
C(20)−C(23)	1.512(16)		

The ^1H NMR spectrum of **5** shows two sets of resonances for the butadiene CH_2 protons, at 1.06 and −0.21 ppm ($^2J_{HH} = 7.2$ Hz) and at −0.39 and −0.48 ppm ($^2J_{HH} = 9.6$ Hz). Seen from the pronounced upfield shift, the latter can probably be attributed to the methylene group that is in contact with the Li-ion. The $SiCH_2$ resonances are found even further upfield at −0.87 and −1.15 ppm ($^2J_{HH} = 9.8$ Hz).

Deprotonation of the $CH(SiMe_3)_2$ group by alkyl-lithium reagents has been observed previously, e.g., in the reaction of $Me_2Si(\eta^5\text{-}C_5Me_4)_2LuCH(SiMe_3)_2$ with ^tBuLi/TMEDA (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine) to give the ionic compound $[Li(TMEDA)_3]^+[Me_2SiCp_2LuCH_2SiMe_2C(H)SiMe_3]^-$,[1d] with a 1-lutetia-3-silacyclobutane moiety, or in a related reaction be-

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tween Al[CH$(SiMe_3)_2$]$_3$ and ^{t}BuLi/TMEDA.[7] The interesting feature of complex **5** is that the lithium ion is still associated with the alkyl group that was deprotonated and that it is additionally stabilized by an interaction with one of the diene methylene groups. This might be considered as a model for the "frozen" transition state of a H-transfer reaction from one of the trimethylsilyl groups in **3** to the diene, but with the H replaced by Li. This H-transfer is the process that was proposed to lead to the 1-hafna-3-silacyclobutane 1,1,2-trimethylallyl intermediate invoked in the pathway for the observed rearrangement of **3** to **4** and the H/D scrambling in **3**-d_4.

Conclusions

The mono- and bis-trimethylsilyl-substituted methyl groups can be used for the direct synthesis of 14-electron alkyl complexes Cp*Hf(C_6H_{10})R (C_6H_{10} = 2,3-dimethyl-1,3-butadiene; R = CH_2SiMe_3, **2**; CH$(SiMe_3)_2$, **3**) from the 16-electron complex Cp*Hf(C_6H_{10})Cl·THF. The steric hindrance imparted by the alkyl groups is sufficient to disfavor interaction of the metal center with the Lewis base THF. Trimethylsilyl substitution of the alkyl also leads to a greatly improved thermal stability of the alkyl compounds, but the CH$(SiMe_3)_2$ group is susceptible to intramolecular and intermolecular C−H activation of the trimethylsilyl substituents. Reversible intramolecular H-transfer from these groups to the coordinated diene ligand leads at elevated temperatures to the rearrangement of the Hf-CH$(SiMe_3)_2$ moiety in **3** to the less sterically encumbered Hf-$CH_2SiMe_2CH_2$-$SiMe_3$ unit. Deprotonation of the CH$(SiMe_3)_2$ group in **3** by added alkyllithium reagents leads to a compound in which the Li-ion bridges the $SiCH_2$ group and one of the diene methylene groups. This structure mimics the proposed transition state for the process of intramolecular H-transfer from one of the trimethylsilyl groups to the coordinated diene.

Experimental Section

General Considerations. All manipulations were carried out under nitrogen atmosphere using standard glovebox, Schlenk, and vacuum-line techniques. Toluene, pentane, and hexane (Aldrich, anhydrous, 99.8%) were passed over columns of Al_2O_3 (Fluka), BASF R3-11-supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å). Diethyl ether and THF (Aldrich, anhydrous, 99.8%) were dried over Al_2O_3 (Fluka). All solvents were degassed prior to use and stored under nitrogen. Deuterated solvents (C_6D_6, C_7D_8, C_4D_8O; Aldrich) were vacuum transferred from Na/K alloy. Cp*Hf(C_6H_{10})Cl(THF) (**1**·THF),[3b] LiCH$(SiMe_3)_2$[8], $LiCH_2SiMe_3$,[9] and 1,1,4,4-tetradeutero-2,3-dimethyl-1,3-butadiene[10] were synthesized according to published procedures, and **1**-d_4 was prepared following the reported procedure for **1** but using 1,1,4,4-tetradeutero-2,3-dimethyl-1,3-butadiene.[3b,11] NMR spectra were recorded on Varian VXR 300 or Varian Inova 500 spectrometers. The ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances and reported in ppm relative to TMS (δ 0 ppm); J is reported in Hz. The ^{29}Si-DEPT NMR spectra were referenced to TMS. Elemental analyses were performed at the Microanalytical Department of the University of Groningen. Found values are the average of at least two independent determinations.

Cp*Hf(C_6H_{10})(CH_2SiMe_3) (2). At 0 °C, 20 mL of toluene was added to a solid mixture of **1**·THF (1.33 g, 2.47 mmol) and $LiCH_2(SiMe_3)$ (0.23 g, 2.47 mmol). After 3 h of stirring at 0 °C, the orange-brown solution was allowed to warm to room temperature and stirred overnight. The solvent was removed in vacuo. Residual solvent was removed by stirring the mixture in 7 mL of pentane, which was subsequently pumped off. The orange mixture was extracted twice with 20 mL of pentane. Evaporation of pentane yielded **2** as a brown oil, the ^{1}H NMR spectrum of which showed some residual pentane. Attempts to recrystallize **2** at −60 °C did not succeed, as the solid deposited at that temperature readily melted again upon workup. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 2.23 (s, 6H, CMe), 1.95 (s, 15H, C_5Me_5), 1.91 (d, 2H, J = 11.0, CH_2), 0.034 (s, 9H, $SiMe_3$), −0.34 (d, 2H, J = 11.0, CH_2), −0.68 (s, 2H, C$H_2$$SiMe_3$). ^{13}C NMR (125.89 MHz, C_6D_6, 25 °C): δ 125.87 (s, *C*Me), 117.91 (s, Cp* C), 68.80 (dd, J = 129.4 and 145.1, CH_2), 59.20 (t, J = 104.1, *C*H_2SiMe_3), 24.44 (q, J = 126.3, C*Me*), 11.64 (q, J = 128.1, Cp* Me), 4.47 (q, J = 117.1, $SiMe_3$). ^{29}Si NMR (99.45 MHz, C_6D_6, 25 °C): δ −4.98 ($SiMe_3$).

An aliquot of **2** was reacted with an excess of methanol-d_4, and the Si-containing product was characterized by ^{1}H NMR and ^{29}Si NMR as $(CH_3)_3SiCH_2D$. ^{1}H NMR: −0.022 (s, 9H, $SiMe_3$), −0.04 (t, 2H, $^2J_{HD}$ = 2.0, CH_2D). ^{29}Si NMR: δ −0.12.

Cp*Hf(C_6H_{10})[CH$(SiMe_3)_2$] (3). At 0 °C, 10 mL of toluene was added to a solid mixture of **1**·THF (0.56 g, 1.04 mmol) and LiCH$(SiMe_3)_2$ (0.18 g, 1.08 mmol). After 3 h of stirring at 0 °C, the orange-brown solution was allowed to warm to room temperature and was stirred overnight. The solvent was removed in vacuo. Residual solvent was removed by stirring the mixture in 7 mL of pentane, which was subsequently pumped off. The orange mixture was extracted twice with 30 mL of pentane. Concentrating the extract and cooling to −80 °C yielded 0.39 g (0.70 mmol, 68%) of orange-brown crystalline **3**. The compound is obtained as a 1:1 mixture of two isomers, the NMR resonances of which have not been assigned to the specific isomer. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 2.35 (s, 6H, CMe), 2.20 (s, 6H, CMe), 1.96 (s, 15H, C_5Me_5), 1.91 (s, 15H, C_5Me_5), 1.89 (d, 2H, J = 11.6, CH_2), 1.64 (d, 2H, J = 11.6, CH_2), 0.41 (s, 1H, C*H*$(SiMe_3)_2$), 0.10 (s, 18H, $SiMe_3$), 0.076 (s, 18H, $SiMe_3$), −0.057 (d, 2H, J = 11.6, CH_2), −0.22 (d, 2H, J = 11.6, CH_2), −0.52 (s, 1H, C*H*$(SiMe_3)_2$). ^{13}C NMR (125.89 MHz, C_6D_6, 25 °C): δ 125.86 (s, *C*Me), 125.71 (s, *C*Me), 118.61 (s, Cp* C), 118.06 (s, Cp* C), 70.74 (dd, J = 130.7 and 142.6, CH_2), 70.13 (dd, J = 130.0 and 144.7, CH_2), 62.07 (d, J = 82.7, *C*H$(SiMe_3)_2$), 58.25 (d, J = 87.7, *C*H$(SiMe_3)_2$), 25.58 (q, J = 126.1, C*Me*), 24.10 (q, J = 126.1, C*Me*), 12.09 (q, J = 126.2, Cp* Me), 11.83 (q, J = 126.2, Cp* Me), 5.73 (q, J = 118.4, $SiMe_3$), 5.57 (q, J = 118.4, $SiMe_3$). ^{29}Si NMR (99.45 MHz, C_6D_6, 25 °C): δ −8.67 ($SiMe_3$), −9.10 ($SiMe_3$). ^{1}H and ^{13}C NMR assignments were aided by ^{1}H,^{13}C-HSQC 2D NMR spectra. Anal. Calcd for $C_{23}H_{44}Si_2Hf$: C, 49.75; H, 7.99; Hf, 32.14. Found: C, 50.11; H, 7.91; Hf, 32.02.

An aliquot of **3** was reacted with an excess of methanol-d_4, and the products were analyzed by ^{1}H NMR, ^{29}Si NMR, and GC/MS. ^{1}H NMR: 0.028 (s, 18H, $SiMe_3$), −0.41 (t, 1H, $^2J_{HD}$ = 2.0, CHD). ^{29}Si NMR: δ 0.39. GC/MS (EI): m/z 146 (M − CH_3) ($Me_3SiCHDSiMe_3$), 137 (1,2,3,4,5-pentamethylcyclopentadiene-d_1), 86 (2,3-dimethyl-2-butene-d_2).

Cp*Hf(C_6H_{10})($CH_2SiMe_2CH_2SiMe_3$) (4). A solution of **3** (0.21 g, 0.38 mmol) in 10 mL of toluene was heated for 24 h at 80 °C. After removal of the solvent in vacuo and removing the residual solvent by stirring in 7 mL of pentane. which subsequently was pumped off, **4** was obtained as a brown oil in quantitative yield and pure by NMR spectroscopy. ^{1}H NMR

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(500 MHz, C_6D_6, 25 °C): δ 2.27 (s, 6H, CMe), 1.96 (s, 15H, C_5Me_5), 1.94 (d, 2H, *J* = 10.8, CH_2), 0.14 (s, 9H, $SiMe_3$), 0.078 (s, 6H, $SiMe_2$), −0.23 (s, 2H, $SiCH_2Si$), −0.29 (d, 2H, *J* = 10.8, CH_2), −0.60 (s, 2H, $HfCH_2Si$). ^{13}C NMR (125.89 MHz, C_6D_6, 25 °C): δ 125.87 (s, *C*Me), 117.93 (s, Cp* C), 68.78 (dd, *J* = 130.5 and 145.6, CH_2), 60.90 (t, *J* = 103.6, $HfCH_2Si$), 24.53 (q, *J* = 126.2, C*Me*), 11.62 (q, *J* = 125.6, Cp* Me), 8.87 (t, 107.8, $SiCH_2Si$), 5.26 (q, *J* = 118.3, $SiMe_2$), 1.85 (q, *J* = 118.3, $SiMe_3$). ^{29}Si NMR (99.45 MHz, C_6D_6, 25 °C): δ −0.12 ($SiMe_3$), −3.87 ($SiMe_2$). ^1H and ^{13}C NMR assignments were aided by ^1H,^{13}C-HSQC 2D NMR spectra.

An aliquot of **4** was reacted with an excess of methanol-d_4, and the products were analyzed by ^1H NMR, ^{29}Si NMR, and GC/MS. ^1H NMR: δ 0.004 (s, 15H, SiMe), −0.014 (t, 2H, $^2J_{HD}$ = 2.0, $SiCH_2D$), −0.40 (s, 2H, $SiCH_2Si$). ^{29}Si NMR: δ 0.44. GC/MS (EI): *m*/*z* 146 (M − CH_3) ($Me_3SiCH_2SiMe_2CH_2D$), 137 (1,2,3,4,5-pentamethylcyclopentadiene-d_1), 86 (2,3-dimethyl-2-butene-d_2).

Cp*Hf(C_6H_{10})[CH($SiMe_3$)$SiMe_2CH_2$]Li($THF)_2$ (5·THF_2). At 0 °C, 10 mL of THF was added to a solid mixture of **1**·THF (0.48 g, 0.89 mmol) and 2 equiv of $LiCH(SiMe_3)_2$ (0.31 g, 1.86 mmol). After 3 h of stirring at 0 °C, the yellow-orange solution was allowed to warm to room temperature and stirred overnight. The solvent was removed in vacuo. Residual solvent was removed by stirring the mixture in 7 mL of pentane, which was subsequently pumped off. The orange mixture was extracted twice with 30 mL of pentane. Concentrating the extract and cooling to −80 °C yielded 0.40 g (0.57 mmol, 64%) of yellow-orange crystalline **5**·THF_2. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ 3.36 (ps t, 8H, THF), 2.57 (s, 3H, CMe), 2.30 (s, 3H, CMe), 2.10 (s, 15H, C_5Me_5), 1.29 (ps t, 8H, THF), 1.06 (d, 1H, *J* = 7.2, C*H*$_2$−CMe), 0.64 (s, 3H, $SiMe_2$), 0.42 (s, 9H, $SiMe_3$), 0.36 (s, 3H, $SiMe_2$), −0.21 (d, 1H, *J* = 7.2, C*H*$_2$−CMe), −0.39 (d, 1H, *J* = 9.6, C*H*$_2$−CMe), −0.48 (d, 1H, *J* = 9.6, C*H*$_2$−CMe), −0.87 (d, 1H, *J* = 9.8, C*H*$_2$−$SiMe_2$), −0.91 (s, 1H, C*H*$SiMe_3$), −1.15 (d, 1H, *J* = 9.8, C*H*$_2$−$SiMe_2$). ^{13}C NMR (125.89 MHz, C_6D_6, 25 °C): δ 121.52 (s, *C*Me), 116.19 (s, *C*Me), 115.64 (s, Cp* C), 68.11 (t, *J* = 145.4, THF), 60.29 (t, *J* = 137.1, *C*H_2−CMe), 44.51 (dd, *J* = 119.3 and 134.4, Li···*C*H_2−CMe), 35.35 (d, *J* = 85.7, *C*H$SiMe_3$), 25.51 (t, *J* = 132.5, THF), 23.86 (q, *J* = 125.7, C*Me*), 23.26 (q, *J* = 123.7, C*Me*), 17.65 (t, *J* = 109.2, *C*H_2−$SiMe_2$), 12.24 (q, *J* = 125.7, Cp* Me), 7.05 (q, *J* = 117.0, $SiMe_3$), 6.33 (q, *J* = 115.6, $SiMe_2$), 3.76 (q, *J* = 115.6, $SiMe_2$). ^{29}Si NMR (99.45 MHz, C_6D_6, 25 °C): δ −3.93 ($SiMe_3$), −27.54 ($SiMe_2$). ^1H and ^{13}C NMR assignments were aided by ^1H,^{13}C-HSQC 2D NMR spectra. Anal. Calcd for $C_{31}H_{59}Si_2O_2HfLi$: C, 52.78; H, 8.43; Hf, 25.30. Found: C, 52.70; H, 8.61; Hf, 25.11.

Recrystallization from benzene resulted in loss of one molecule of THF, and suitable crystals of Cp*Hf(C_6H_{10})[CH($SiMe_3$)$SiMe_2CH_2$]Li(THF) (**5**·THF) were obtained. They contain only one molecule of THF, as determined by ^1H NMR, elemental analysis, and X-ray crystallography. The ^1H NMR spectrum is essentially identical to that reported above for **5**·THF_2, apart from the intensity of the THF resonances. Anal. Calcd for $C_{27}H_{51}Si_2OHfLi$: C, 51.21; H, 8.12; Hf, 28.18. Found: C, 51.51; H, 8.22; Hf, 27.86.

In Situ Preparation and Rearrangement of 3-*d*$_4$. To Cp*Hf($C_6H_6D_4$)Cl (**1**-d_4, 34.1 mg, 72.4 μmol) was added a solution of $LiCH(SiMe_3)_2$ (12.0 mg, 72.4 μmol) in 0.35 mL of C_6D_6. The orange solution was transferred to an NMR tube (equipped with Teflon stopcock) and was monitored by NMR spectroscopy directly after mixing and after standing at 80 °C for 1.5, 3, 6, 10, and 24 h. **3**-d_4: ^1H NMR (500 MHz, C_6D_6, 25 °C): δ 2.34 (s, 6H, CMe), 2.20 (s, 6H, CMe), 1.99 (s, 15H, C_5Me_5), 1.95 (s, 15H, C_5Me_5), 0.41 (s, 1H, C*H*($SiMe_3)_2$), 0.081 (s, 18H, $SiMe_3$), 0.059 (s, 18H, $SiMe_3$), −0.49 (s, 1H, C*H*($SiMe_3)_2$). ^2H NMR (76.73 MHz, C_6D_6, 25 °C): δ 1.80 (br s, 2D, CD_2), 1.55 (br s, 2D, CD_2), −0.05 (br s, 2D, CD_2), −0.26 (d, 2D, CD_2). After 1.5 h, resonances for methylene groups of the butadiene were found in the ^1H NMR spectrum at δ 1.83 (d, *J* = 10.8), 1.59 (d, *J* = 12.1), −0.055 (d, *J* = 10.8), −0.22 (d, *J* = 12.1) for the two isomers of **3** and one at −0.29 (d, *J* = 11.3) for **4**. The other methylene signal for **4** is overlapped by the Cp* resonances of **3**. In the ^2H NMR spectrum a signal for the CD_2H groups of the butadiene was found at δ 2.19. After 24 h: **4**-d_4. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ 2.26 (s, ∼2.2H, CH_3), 2.24 (br, ∼1.5H CD_2H), 1.98 (s, 15H, C_5Me_5), 1.88 (d, ∼1.5H, *J* = 11, C*H*$_2$−CMe), 0.11 (s, 9H, $SiMe_3$), 0.053 (s, 6H, $SiMe_2$), −0.24 (s, 2H, $SiCH_2Si$), −0.29 (d, ∼1.5H, *J* = 11, C*H*$_2$−CMe), −0.65 (s, 2H, $HfCH_2Si$). ^2H NMR (76.73 MHz, C_6D_6, 25 °C): δ 2.19 (s, CD_2H), 1.85 (br s, CD_2), −0.33 (br s, CD_2).

Table 3. Crystallographic Data for Cp*Hf(C_6H_{10})[CH($SiMe_3)_2$] (3) and Cp*Hf(C_6H_{10})[CH($SiMe_3$)$SiMe_2CH_2$]Li(THF) (5·THF)

	3	5
chem formula	$C_{23}H_{44}HfSi_2$	$C_{27}H_{51}HfLiOSi_2$
M_r	555.26	633.30
cryst syst	monoclinic	triclinic
color, habit	white, plate	pale yellow, plate
size (mm)	0.12 × 0.38 × 0.48	0.18 × 0.25 × 0.30
space group	$P2_1/a$	P_1
a (Å)	17.8823(9)	8.6235(7)
b (Å)	17.8144(9)	9.5410(8)
c (Å)	17.8853(9)	11.0841(9)
α (deg)		93.623(1)
β (deg)	117.402(1)	109.404(1)
γ (deg)		115.713(1)
V (Å^3)	5058.3(4)	751.57(11)
Z	8	1
ρ_{calc} (g cm^{-3})	1.458	1.399
μ(Mo Kα) (cm^{-1})	42.25	35.65
F(000)	2256	324
temp (K)	125	130
θ range (deg)	2.19−29.74	2.44−29.63
data collected (*h*,*k*,*l*)	−22:23, −24:21, −24:24	−10:11, −12:13, −15:15
min. and max. transm	0.6311, 0.8492	0.2794, 0.6743
no. of rflns collected	48158	6897
no. of ind rflns	13647	5727
no. of obsd rflns	8905 ($F_o \geq 4\sigma(F_o)$)	5727 ($F_o \geq 4\sigma(F_o)$)
R(*F*) (%)	4.55	3.33
$R_w(F^2)$ (%)	8.50	8.96
GOF	0.950	1.043
weighting *a*,*b*	0.0269,0.0	0.0692,1.3642
no. of params refined	528	301

Warming Cp*Hf($C_6H_6D_4$)Cl (1-*d*$_4$) in C_6D_6. A solution was made of Cp*Hf($C_6H_6D_4$)Cl (23.0 mg, 48.8 μmol) and 0.35 mL of C_6D_6. The orange solution was transferred to an NMR tube (equipped with Teflon stopcock) and warmed to 80 °C. The solution was monitored by ^1H and ^2H NMR after 3, 6, and 24 h. The spectra remained unchanged throughout the experiment. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ 2.07 (s, 6H, CMe), 1.97 (s, 15H, C_5Me_5). ^2H NMR (76.73 MHz, C_6D_6, 25 °C): δ 2.05 (s, 2D, CD_2), −0.05 (s, 2D, CD_2).

X-ray Structures. Suitable crystals of **3** and **5**·THF were mounted on a glass fiber in a drybox and transferred, using inert-atmosphere handling techniques, into the cold nitrogen stream on a Bruker SMART APEX CCD diffractometer. The final unit cell was obtained from the *xyz* centroids of 5956 (**3**) or 6345 (**5**·THF) reflections after integration. Reduced cell calculations did not indicate any higher metric lattice symmetry,[12] and examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements.[13] Crystal data and details on data collection and refinement are presented in Table 3. Intensity data were corrected for Lorentz and polarization effects, scale variation, decay, and absorption. The structures were solved by Patterson methods, and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF.[14] All refinement calculations and graphics were performed with

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the program packages SHELXL[15] (least-squares refinements), PLATON[16] (calculation of geometric data and the ORTEP[16] illustrations), and a locally modified version of the program PLUTO[17] (preparation of illustrations). For **3**, the space group $P2_1/a$ was derived from systematic extinctions, but a number of violations were observed. The structure was successfully solved in this space group after introduction of a twin operation [001 0−10 110], with the major component of the twin model refining to a gof of 0.532(1). Hydrogen atoms were introduced on calculated positions and included in the final refinement riding on their carrier atoms, except for the H atoms on the diene methylene carbons, which were allowed to refine freely. The alkyl α-carbons, C(117) and C(217), are planar and showed in the initial refinement elongated thermal ellipsoids perpendicular to the plane. This suggests that the two possible rotational isomers around the Hf−C bond have cocrystallized randomly. In the final refinement two hydrogen atoms attached to each of these carbons were included, above and below the plane and with a gof of 0.5. For **5**·THF, the space group ($P1$) was identified as non-centrosymmetric by $|E|$ distribution statistics. A final value for Flack's x parameter[18] of 0.008(11) was obtained from the refinement. Hydrogen atoms were included in the final refinement riding on their carrier atoms.

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Supporting Information Available: Tables showing details of the crystal structure determinations, atom coordinates, equivalent isotropic displacement parameters, anisotropic thermal displacement parameters, bond lengths and angles, and hydrogen parameters for **3** and **5**·THF. This material is available free of charge via the Internet at http://pubs.acs.org.

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