Angewandte Chemie

DOI: 10.1002/anie.200701565

Unusual Bond Activations

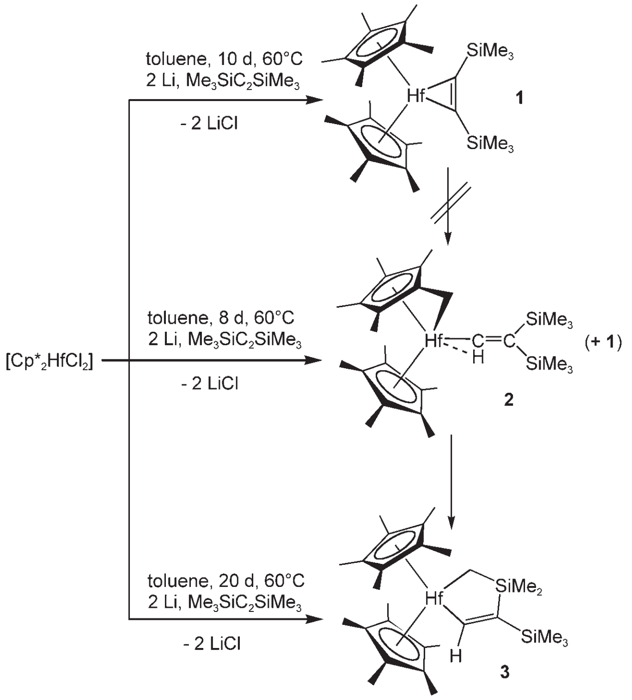
# Tandem Si–C and C–H Activation for Decamethylhafnocene and Bis(trimethylsilyl)acetylene[**]

*Torsten Beweries, Vladimir V. Burlakov, Marc A. Bach, Stephan Peitz, Perdita Arndt, Wolfgang Baumann, Anke Spannenberg, Uwe Rosenthal,* Biswarup Pathak, and Eluvathingal D. Jemmis**

The unusual reactivity of hafnocene complexes in comparison to their titanium and zirconium analogues was dramatically demonstrated in the recent functionalization of coordinated $N_2$ and the coupling of $CO_2$ and $N_2$ to a substituted hydrazine product.[1,2] The differences in their structure and bonding were also noticed;[3] for example, the $\sigma$ and $\pi$ ratio of the diene bonding in (s-*cis*-$\eta^4$-diene) metallocene complexes is shifted to larger $\sigma$ character for Hf compared to Zr, thus giving shorter Hf–C than Zr–C bonds. Herein, we report the unusual tandem Si–C and C–H bond activation of decamethylhafnocene and bis(trimethylsilyl)acetylene, which could not be carried out using titanium and zirconium congeners.

The complexation of bis(trimethylsilyl)acetylene by decamethylhafnocene leads to the three-membered hafnacyclopropene $[Cp^*_2Hf(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ (**1**; $Cp^* = \eta^5\text{-}C_5Me_5$).[4a] Surprisingly, until very recently only Ti and Zr analogues were known, and these show a very multifaceted chemistry.[5] Our first reduction experiments with $[Cp^*_2HfCl_2]$ and $Me_3SiC{\equiv}CSiMe_3$ with magnesium in THF showed that the method used for the successful preparation of titanium and zirconium alkyne complexes failed for hafnocene alkyne complexes. The preferred ring opening of THF was found to be the reason for this failure.[4b] However, the reaction of $[Cp^*_2HfCl_2]$ with $Me_3SiC{\equiv}CSiMe_3$ and lithium in toluene resulted in the formation of the desired complex **1**, which can be isolated in an optimized yield of 45% (Scheme 1).[4a] Apparently, the competition between THF and alkyne coordination to the metal causes the attempted synthesis of the hafnium complexes using magnesium in THF to fail.

In an attempt to gain further insight into the hafnocene chemistry, the reaction of $[Cp^*_2HfCl_2]$ with Li and $Me_3SiC{\equiv}CSiMe_3$ in toluene was studied. By shortening the reaction time, we were able to isolate (in addition to the alkyne complex **1**) a light green crystalline solid consisting of complex **2**, in which one of the C–H bonds of a methyl group of a Cp* ligand has reacted with the metal to form a Hf–C bond (Scheme 1). The vinyl ligand is obtained from $Me_3SiC{\equiv}CSiMe_3$ by the formal migration of a $Me_3Si$ group from one carbon atom to the other (perhaps via vinylidene complex **B**, Scheme 2). This is a tandem activation of a C–H bond of one Cp* methyl group and a Si–C bond of the alkyne by the Hf center.



***Scheme 1.*** Synthesis of complexes **1**, **2**, and **3**.

---

[*] T. Beweries, M. A. Bach, S. Peitz, Dr. P. Arndt, Dr. W. Baumann, Dr. A. Spannenberg, Prof. Dr. U. Rosenthal
Leibniz-Institut für Katalyse e. V.
an der Universität Rostock
Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)
Fax: (+49) 381-1281-51176
E-mail: uwe.rosenthal@catalysis.de
Homepage: http://www.catalysis.de

B. Pathak, Prof. E. D. Jemmis
Indian Institute of Science
Department of Inorganic and Physical Chemistry
Bangalore-560012 (India)
Fax: (+91) 80-2360-1552
E-mail: jemmis@ipc.iisc.ernet.in

Dr. V. V. Burlakov
A. N. Nesmeyanov Institute of Organoelement Compounds
Russian Academy of Sciences
Vavilov Str. 28, 117813 Moscow (Russia)

[**] We are indebted to Dr. Marko Hapke for many useful suggestions and discussions regarding the manuscript. We thank our technical staff, in particular Regina Jesse and Petra Bartels, for assistance. Support by the DFG (GRK 1213), the DAAD-DST (Indo-German Project Based Personnel Exchange Program), CMSD-University of Hyderabad, and the Russian Foundation for Basic Research (Project code 05-03-32515) is acknowledged.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

Extending the reaction time led to transfer of a hydrogen atom back to the Cp* ligand, but activation of a methyl C–H bond from the $Me_3Si$ group resulted in metallacycle **3**, which was formed from complex **2** by an even more intriguing pathway. The intermediacy of **2** in the formation of **3** was established experimentally by the direct conversion of **2** to **3**.

Upon heating in toluene, isolated complex **2** cleanly gave complex **3**, whereas no conversion of **1** to the other complexes was found. Formation of complexes **1** and **2** (and from this **3**) is simultaneous. Interestingly, the methyl groups of the Cp* ligands compete with those of the $Me_3Si$ groups to interact with the Hf center to form either **2** or **3**.

The near-linear Hf-$C_\alpha$-$C_\beta$ unit (174.8°) and the α-agostic C–H interaction with the hafnium center (Hf1–H1 separation 2.08(5) Å) in complex **2** (Figure 1) are reminiscent of the agostic interaction in the complex $[\{\eta^5\text{-}1,3\text{-}(SiMe_2CH_2P\mathit{i}Pr_2)_2C_5H_3\}Hf{=}CHPh(Cl)]$ (Hf–H 1.93(3) Å, Hf-$C_\alpha$-$C_\beta$ 167.8(4)°).[6]

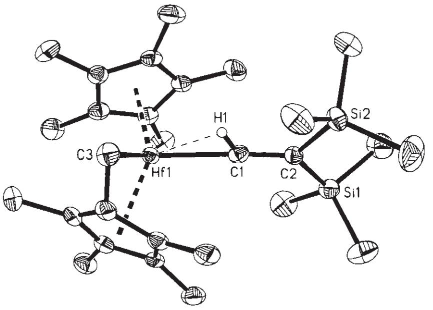


*Figure 1.* Molecular structure of complex **2**. Hydrogen atoms (except H1) are omitted. Thermal ellipsoids are set at 30% probability.

The vinyl hydrogen atom appears as a doublet in the $^1H$ NMR spectrum at 2.51 ppm with a coupling constant of $^3J_{H,H} = 1.7$ Hz. The signal for the $C_\alpha$ atom displays an extreme downfield shift (261.5 ppm), giving a doublet in the $^{13}C$ NMR spectrum with a coupling constant of $J_{C,H} = 62$ Hz.

Complex **2** must reorganize by reconstitution of the free methyl group at the Cp* ligand to form **3**, thus requiring C–H activation of a methyl substituent of the $Me_3Si$ group in β-position to the metal. With respect to the starting alkyne, one of the $Me_3Si$ groups has migrated from one alkyne C atom to the other, and one of the corresponding methyl groups shows a C–H activation. The resulting $CH_2$ group bonds to the Hf center, thus forming the five-membered ring (Figure 2). In brief, Hf has activated a Si–C bond and a C–H bond in the formation of **2** and has activated another C–H bond in the formation of **3**. Similar reactions are not observed with Ti or Zr.

Metallacycle **3** was obtained as a pale yellow crystalline solid in 64% yield, accompanied by the alkyne complex **1**. The $^1H$ NMR spectrum shows three singlets, one each for the $Me_3Si$ (0.27 ppm), $SiMe_2$ (0.45 ppm), and $CH_2$ groups (0.41 ppm). The signal for the C–H group is found to be shifted downfield to 8.43 ppm. The observed wavenumber $\tilde{\nu}(C{=}C) = 1461\ cm^{-1}$ clearly shows the double-bond character of the C12–C13 bond in the five-membered ring, which is also indicated by the bond length of 1.381(15) Å (Figure 2).

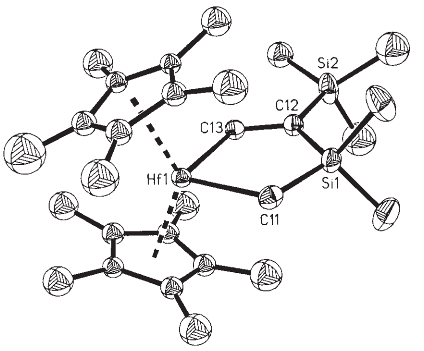


*Figure 2.* Molecular structure of complex **3**. Hydrogen atoms and one position of the disordered groups are omitted. Thermal ellipsoids are set at 30% probability.

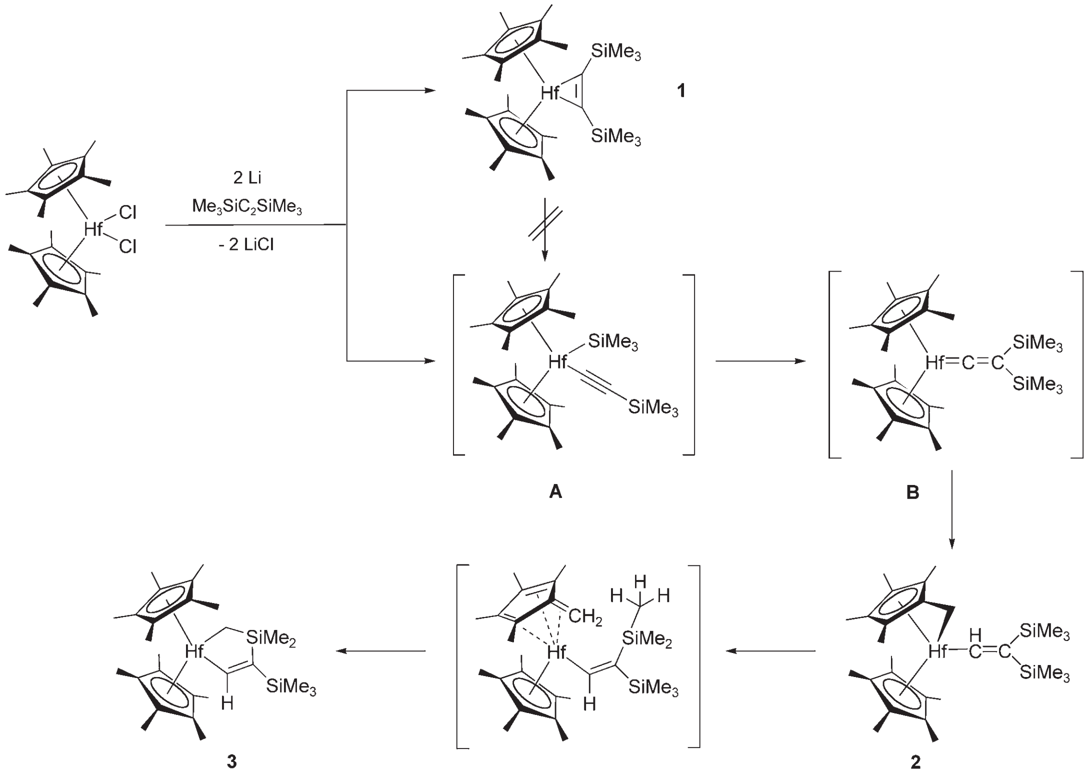
How can the reaction to form complexes **2** and **3**, which was observed exclusively for Hf and never for Ti and Zr, be rationalized? Most likely during the synthesis of **1**, and alternatively to its formation, a C–Si bond is cleaved to form the acetylide complex $[Cp^*_2Hf(SiMe_3)(C{\equiv}CSiMe_3)]$ (**A**) with subsequent silyl-group migration to form the vinylidene complex $[Cp^*_2Hf{=}C{=}C(SiMe_3)_2]$ (**B**; Scheme 2). We have no experimental hints for the formation of these intermediates, but similar reactions are well-known in transition-metal chemistry. For example, Jones and co-workers published such a Si–C bond cleavage reaction for Pt and Ni.[7] Schneider and Werner found the formation of vinylidene complexes starting from bis(trimethylsilyl)acetylene complexes of Rh.[8]

Cleavage of the Si–C bond[9a] in $Me_3SiC{\equiv}CSiMe_3$ by interaction with lithium under formation of $Me_3SiC{\equiv}CLi$ and $LiSiMe_3$ was excluded experimentally. Thus, pathways involving subsequent salt elimination with $[Cp^*_2HfCl_2]$ to form **A** and reactions of $[Cp^*_2HfCl_2]$ with $LiSiMe_3$ and possibly formed $HC{\equiv}CSiMe_3$ to give **3** (in analogy to studies by Mori and co-workers for Zr complexes) can be excluded.[9b]

In the vinylidene intermediate **B**, the methyl groups of the Cp* ligand compete with those of the $Me_3Si$ groups to interact with the Hf center. The C–H bond-activation complex **2** is probably the kinetically favored product, which gives, with time, the thermodynamically more stable complex **3**.

Density functional theory studies (B3LYP/LANL2DZ)[10] on the analogous Hf, Zr, and Ti structures support this mechanistic route (Scheme 2). Frequency calculations confirm the nature of stationary points. The calculated geometrical parameters are in close agreement with the experimental structures (Table 1).

Relative energies (with respect to structure **1′**) show that structure **3′** is lowest in energy for Hf, thus supporting the experimental observations (Figure 3 and Table 1). The high relative energy of structure **A′** (Scheme 2) for Ti and Zr prevents its formation and further reactions. Further studies on the mechanistic details of the conversion of **2** into **3** will be published in due course. We have also studied these reactions while varying the number of methyl substituents on the cyclopentadienyl moiety and at the Si atoms. The results are



*Scheme 2.* C–H and Si–C activation steps during the formation of **2** and **3**.

*Table 1:* Relative energies of the structures given in Scheme 2 for Hf, Ti, and Zr analogues.[a]

| Structures[b] | $\Delta E_0$(ZPE) Ti | Zr | Hf |
|---|---|---|---|
| **A′** | 23.55 | 13.45 | 9.51 |
| **B′** | 1.45 | 11.02 | 12.39 |
| **2′** | 11.69 | 11.14 | 8.81 |
| **3′** | 7.76 | −0.51 | −6.20 |

[a] Values in kcal mol$^{-1}$ with respect to $E_0$(ZPE) = 0 for structure **1′**. [b] The prime symbol (′) indicates the replacement of Hf in the formula with another metal center (M = Ti, Zr, Hf).

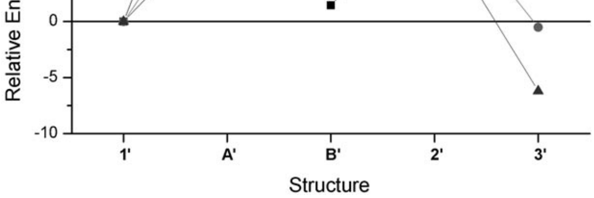
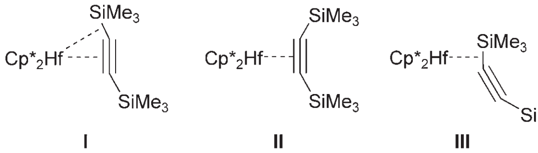


*Figure 3.* Relative energies for the structures **1′**–**3′**, **A′**, and **B′** for Hf (▲), Ti (■), and Zr analogues (●).

comparable to those obtained with the permethylated structures.

The tandem Si–C and C–H bond cleavage reactions of $Me_3SiC{\equiv}CSiMe_3$ by hafnocene described herein are of general importance for Group 4 organometallic chemistry. The {$Cp^*_2Hf$} fragment, as a reactive intermediate, alternatively attacks two different bonds of $Me_3SiC{\equiv}CSiMe_3$: the C–C triple bond and the silicon–carbon bond Si–$C_2$. Concerning the discrimination between these two alternative reactions, it seems reasonable to speculate that the formation of **A** starts from an alkyne ligand in a *trans* conformation. A similar situation was found in the complexes [$Cp_2M(\eta^2$-*trans*-$Me_3SiC_2SiMe_2$-H)] (M = Ti, Zr) in which the C≡C and Si–H bonds compete for coordination to the metal center.[11] In both cases, the use of Cp* ligands prevents *trans* coordination ("and" case **I** for complexation of both functionalities) and favors *cis* coordination ("or" cases **II** and **III** for selective complexation of one of the two functionalities, Scheme 3).

Owing to the stronger interaction of the hafnocene core, unusual bond activations become possible which are not favorable for its titanocene and zirconocene congeners, for



*Scheme 3.* Variable interactions of the Hf center with two functional groups for complexation of $Me_3SiC{\equiv}CSiMe_3$.

example, intermolecular for $N_2$ with aryl isocyanates,[1] $N_2$ with $CO_2$,[2] butadiene,[3] THF,[4] and so forth, or as described herein, intramolecular for the Cp* ligands and the $SiMe_3$ substituents. This enhanced reactivity should always be considered if hafnium complexes are synthesized or applied catalytically.

## Experimental Section

All experiments were conducted under exclusion of oxygen and moisture. All operations were carried out under argon using standard Schlenk techniques. Prior to use, solvents were distilled from sodium tetraethylaluminate and stored under argon. The starting material $[Cp^*_2HfCl_2]$ is commercially available and was provided by MCAT. The following spectrometers were used: Mass spectra MAT 95-XP (Thermo Electron), NMR spectra Bruker AV 400. Chemical shifts ($^1H$, $^{13}C$) are given relative to $SiMe_4$ and are referenced to solvent signals ([$D_6$]benzene, $\delta_H = 7.16$, $\delta_C = 128.0$); the spectra were assigned with the help of DEPT, NOE, and shift correlation experiments. Melting points were measured using sealed capillaries and a Büchi 535 apparatus. Elemental analyses were carried out with a Leco CHNS-932 elemental analyzer.

X-ray crystal structure analyses of **2** and **3**: STOE-IPDS diffractometer, graphite-monochromated $Mo_{K\alpha}$ radiation, structures were solved by direct methods (SIR 2004)[12] and refined by full-matrix least-squares techniques against $F^2$ (SHELXL-97);[13] graphical representations: XP (Bruker AXS). **2**: $C_{28}H_{48}HfSi_2$, $M_r = 619.33$, space group $P2_1/c$, monoclinic, $a = 17.1796(4)$, $b = 9.9693(2)$, $c = 17.1403(4)$ Å, $\beta = 91.496(2)°$, $V = 2934.6(1)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.402$ g cm$^{-3}$, 29101 reflections measured, 4065 were independent of symmetry, of which 3661 were observed ($I > 2\sigma(I)$), $R1 = 0.031$, $wR2$ (all data) = 0.079, 292 parameters. **3**: $C_{28}H_{48}HfSi_2$, $M_r = 619.33$, space group $P2_1/m$, monoclinic, $a = 8.5591(5)$, $b = 14.982(1)$, $c = 12.0572(8)$ Å, $\beta = 107.832(5)°$, $V = 1471.9(2)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.397$ g cm$^{-3}$, 19046 reflections measured, 2700 were independent of symmetry, of which 2553 were observed ($I > 2\sigma(I)$), $R1 = 0.045$, $wR2$ (all data) = 0.118, 99 parameters.

CCDC-640820 (**2**) and CCDC-640819 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**2**: Bis(trimethylsilyl)acetylene (0.80 mL, 3.6 mmol) was added to a suspension of $[Cp^*_2HfCl_2]$ (1.77 g, 3.4 mmol) and finely cut lithium (0.10 g, 14.8 mmol) in toluene (15 mL). The mixture was stirred for eight days at 60 °C; subsequently, all volatiles were removed in vacuum. The residue was extracted with *n*-hexane (15 mL) at 55 °C. Upon cooling to room temperature, light green crystals of **2** had formed in the filtrate. These were separated, washed with cold *n*-hexane, and dried in vacuum. Optimized yield of isolated product: 0.34 g (16 %); m.p. 145 °C (dec) under Ar. Elemental analysis (%) for $C_{28}H_{48}HfSi_2$ calcd: C 54.30, H 7.81; found: C 53.30, H 7.66 (due to formation of SiC, no better values for C were obtained). IR (KBr): $\tilde{\nu} = 1240$ (m, $SiMe_3$), 1503 cm$^{-1}$ (m, $C{=}C$). $^1H$ NMR (400 MHz, [$D_6$]benzene, 297 K): $\delta = 0.19$ (s, 9H, $SiMe_3$), 0.32 (s, 9H, $SiMe_3$), 1.47, 1.68, 1.70, 1.87 (each s, each 3H, $CH_3$), 1.84 (s, 15H, Cp*), 1.97 (d, $^2J_{H,H} = 6.8$ Hz, 1H, $CH_2$), 2.51 (d, $^3J_{H,H} = 1.7$ Hz, 1H, CH), 2.56 ppm (dd, $^2J_{H,H} = 6.8$ Hz, $^3J_{H,H} = 1.7$ Hz, 1H, $CH_2$). $^{13}C$ NMR: $\delta = 0.8$ ($SiMe_3$), 1.4 ($SiMe_3$), 10.4, 10.4, 12.9, 13.3 ($C_5\mathit{Me_4}$), 11.9 ($C_5\mathit{Me_4}$), 55.7 ($^1J_{C,H} = 143$ Hz, $CH_2$), 114.0 ($\mathit{C_5}Me_4$), 114.8, 116.3, 116.7, 117.5, 122.2 ($\mathit{C_5}Me_4$), 160.1 ($C_{quart}$), 261.5 ppm ($^1J_{C,H} = 62$ Hz, CH). $^{29}Si$ NMR: $\delta = -9.2$ ($SiMe_3$), $-5.8$ ($SiMe_3$). MS (70 eV, EI-MS): *m*/*z* 620 [*M*]$^+$.

**3**: Bis(trimethylsilyl)acetylene (1.02 mL, 4.5 mmol) was added to a suspension of $[Cp^*_2HfCl_2]$ (2.26 g, 4.4 mmol) and finely cut lithium (0.15 g, 21.6 mmol) in toluene (30 mL). The mixture was stirred for 20 days at 60 °C; subsequently, all volatiles were removed in vacuum. The residue was extracted with *n*-hexane (3 × 15 mL). The filtrate was concentrated to half its volume and stored at −78 °C. After 24 h, pale yellow crystals had formed. These were isolated by decanting the mother liquor, washed with cold *n*-hexane, and dried in vacuum. Optimized yield of isolated product: 1.72 g (64 %); m.p. 215 °C under Ar. Elemental analysis (%) for $C_{28}H_{48}HfSi_2$ calcd: C 54.30, H 7.81; found: C 54.22, H 7.71. IR (nujol mull): $\tilde{\nu} = 1461$ cm$^{-1}$ (m, $C{=}C$). $^1H$ NMR (400 MHz, [$D_6$]benzene, 297 K): $\delta = 0.27$ (s, 9H, $SiMe_3$), 0.41 (s, 2H, $CH_2$), 0.45 (s, 6H, $SiMe_2$), 1.80 (s, 30H, Cp*), 8.43 ppm (s, 1H, CH). $^{13}C$ NMR: $\delta = 0.7$ ($SiMe_3$), 5.9 ($SiMe_2$), 11.7 ($C_5\mathit{Me_5}$), 48.2 ($CH_2$), 117.1 ($\mathit{C_5}Me_5$), 164.7 ($C_{quart}$), 242.7 ppm (CH). $^{29}Si$ NMR: $\delta = -29.2$ ($SiMe_2$), $-11.6$ ppm ($SiMe_3$). MS (CI-MS, isobutane): *m*/*z* 621 [*M*]$^+$.

Received: April 10, 2007

**Keywords:** C−H activation · density functional calculations · hafnium · metallacycles · Si−C activation

---

[1] a) W. H. Bernskoetter, A. V. Olmos, J. A. Pool, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2006**, *128*, 10696–10697; b) P. J. Chirik, *Dalton Trans.* **2007**, 16–25, and references therein.

[2] W. H. Bernskoetter, E. Lobkovsky, P. J. Chirik, *Angew. Chem.* **2007**, *119*, 2916–2919; *Angew. Chem. Int. Ed.* **2007**, *46*, 2858–2861.

[3] a) C. Krüger, G. Müller, G. Erker, U. Dorf, K. Engel, *Organometallics* **1985**, *4*, 215–223; b) G. Erker, C. Krüger, G. Müller, *Adv. Organomet. Chem.* **1985**, *24*, 1–39.

[4] a) T. Beweries, V. V. Burlakov, M. A. Bach, P. Arndt, W. Baumann, A. Spannenberg, U. Rosenthal, *Organometallics* **2007**, *26*, 247–249; b) T. Beweries, U. Jäger-Fiedler, V. V. Burlakov, M. A. Bach, P. Arndt, W. Baumann, A. Spannenberg, U. Rosenthal, *Organometallics* **2007**, *26*, 3000–3004.

[5] U. Rosenthal, V. V. Burlakov in *Titanium and Zirconium in Organic Synthesis* (Ed.: I. Marek), Wiley-VCH, Weinheim, **2002**, pp. 355–389.

[6] M. D. Fryzuk, P. B. Duval, B. O. Patrick, S. J. Rettig, *Organometallics* **2001**, *20*, 1608–1613.

[7] a) B. L. Edelbach, R. J. Lachicotte, W. D. Jones, *Organometallics* **1999**, *18*, 4660–4668; b) C. Müller, R. J. Lachicotte, W. D. Jones, *Organometallics* **2002**, *21*, 1190–1196, and references therein.

[8] D. Schneider, H. Werner, *Angew. Chem.* **1991**, *103*, 710–712; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 700–702.

[9] a) M. Saito, M. Nakamura, T. Tajima, M. Yoshioka, *Angew. Chem.* **2007**, *119*, 1526–1529; *Angew. Chem. Int. Ed.* **2007**, *46*, 1504–1507; b) S. Kuroda, F. Dekura, Y. Sato, M. Mori, *J. Am. Chem. Soc.* **2001**, *123*, 4139–4146.

[10] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789; d) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299–310; e) Gaussian 03, Revision B.03, M. J. Frisch, et al., Gaussian, Inc., Pittsburgh, PA, **2003**.

[11] a) A. Ohff, P. Kosse, W. Baumann, A. Tillack, R. Kempe, H. Görls, V. V. Burlakov, U. Rosenthal, *J. Am. Chem. Soc.* **1995**, *117*, 10399–10400; b) M.-F. Fan, Z. Lin, *Organometallics* **1997**, *16*, 494–496; c) N. Peulecke, A. Ohff, P. Kosse, W. Baumann, A. Tillack, A. Spannenberg, R. Kempe, V. V. Burlakov, U. Rosenthal, *Chem. Eur. J.* **1998**, *4*, 1852–1861.

[12] M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **2005**, *38*, 381.

[13] G. M. Sheldrick, SHELXL-97, Program of Crystal Structure Refinement, University Göttingen, Germany, **1997**.