

**C–H Bonds Are Not Elongated by Coordination to Lanthanide Metals: Single-Crystal Neutron Diffraction Structures of  $(C_5Me_5)Y(OC_6H_3^tBu_2)CH(SiMe_3)_2$  at 20 K and  $(C_5Me_5)La\{CH(SiMe_3)_2\}_2$  at 15 K**

Wim T. Klooster,<sup>†</sup> Lee Brammer,<sup>\*‡</sup>  
Colin J. Schaverien,<sup>\*§</sup> and Peter H. M. Budzelaar<sup>¶</sup>

Chemistry Department, Brookhaven National Laboratory  
Upton, New York 11973-5000  
Department of Chemistry, University of Missouri—St. Louis  
St. Louis, Missouri 63121-4499  
Shell Research and Technology Centre Amsterdam  
Postbus 38000, 1030 BN Amsterdam, The Netherlands  
Department of Inorganic Chemistry, University of Nijmegen  
Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

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The sterically hindered  $CH(SiMe_3)_2$  alkyl group is ubiquitous in organolanthanide chemistry.<sup>1</sup> Although close intramolecular contacts between  $CH(SiMe_3)_2$  and a lanthanide have often been characterized by X-ray diffraction,<sup>2</sup> conclusive evidence as to the exact nature of these interactions (i.e.,  $\alpha_{CH}$ ,  $\alpha_{CSi}$ ,  $\beta_{SiC}$ , and  $\gamma_{CH}$ ) requires accurate determination of all atomic coordinates, including those of the hydrogen atoms. The lack of detailed structural information contrasts sharply with the abundance of transition metal complexes showing well-defined agostic interactions.<sup>3</sup> We report the first neutron diffraction studies of such lanthanide complexes on  $(C_5Me_5)Y(OAr)CH(SiMe_3)_2$  ( $OAr = O-2,6-C_6H_3^t-Bu_2$ ) (**1**)<sup>4</sup> and  $(C_5Me_5)La\{CH(SiMe_3)_2\}_2$  (**2**)<sup>5</sup> which clearly show that the  $\beta_{SiC}$  agostic interaction predominates.<sup>6</sup>

The molecular structure of **1** as determined by neutron diffraction<sup>7</sup> at 20 K shows a distorted  $CH(SiMe_3)_2$  group with both  $Y\cdots Si(1)$  [3.281(4) Å] and  $Y\cdots C(2)$  [2.972(3) Å] well within the sum of their van der Waals radii. There are also remote

$C-H\cdots Y$  interactions involving two of the aryloxy <sup>t</sup>Bu hydrogen atoms [ $Y(1)\cdots H(16a)$  2.526(6) Å; [ $Y(1)\cdots H(16e)$  2.935(6) Å]. The overall structure as determined by single-crystal neutron diffraction<sup>8</sup> of **2**<sup>5</sup> at 15 K is in good agreement with that from X-ray diffraction<sup>5</sup> at 200 K. The coordinative unsaturation at La is relieved by interaction with two  $Si_\beta-Me_\gamma$  bonds, one from each  $CH(SiMe_3)_2$  group [La $\cdots Si(2)$  3.346(10) Å, La $\cdots C(17)$  2.964(8) Å, La $\cdots Si(4)$  3.416(13) Å, La $\cdots C(22)$  2.973 (9) Å].

None of the short  $C-H\cdots M$  intramolecular contacts in **1** or **2** show a statistically significant elongation<sup>9</sup> of the  $C-H$  bonds (Table 1). In contrast, the elongation of the agostic  $Si_\beta-C_\gamma$  bonds is significant (0.037 Å average for the three  $CH(SiMe_3)_2$  groups in **1** and **2**). This indicates that the metal center interacts mainly with the  $\beta$ -Si–C bond, not with the  $\gamma$ -C–H bonds. This interpretation is supported by an analysis of the  $M\cdots Si-C-H$  torsion angles of the agostic methyl groups. An average angle of  $\sim 0^\circ$  corresponds to an eclipsed conformation and indicates an attractive  $C-H\cdots M$  interaction; this is only seen in the <sup>t</sup>Bu contacts in **1**. Values near  $\pm 60^\circ$  correspond to a staggered conformation, in which the  $\gamma$ -C–H bonds avoid the metal to let the Si–C bond approach as closely as possible; the three  $CH(SiMe_3)_2$  groups in **1** and **2** all show a staggered geometry (Table 1). This minimizes close secondary contacts with the metal and places two hydrogens from each interacting  $\gamma$ -Me group in **1** and **2** almost equidistant from the metal. Staggered agostic methyl groups have been previously observed,<sup>2b–e</sup> but the inherent inaccuracy of hydrogen atom position by X-ray diffraction made any further analysis difficult.

To dispel any remaining doubts concerning C–H bond lengths,<sup>10</sup> a DFT study<sup>11</sup> on the model compound  $(C_5H_5)La\{CH(SiMe_3)_2\}_2$  (**3**) was undertaken. Full geometry optimization resulted in a structure with two agostic  $La\cdots Si_\beta-C_\gamma$  contacts, but in a conformation slightly different from that of **2**; we attribute this to steric effects. Both agostic methyl groups are staggered, like those in **1** and **2**. Because there are no random errors or crystal packing effects in the calculation, the spread in C–H distances is much smaller than in the neutron diffraction results. The difference in bond lengths between agostic and nonagostic C–H bonds is minute (0.005 Å). In contrast, the elongation of the agostic Si–C bonds is significant (0.036 Å), and virtually identical to the experimental value. The agreement of experimental **2** and calculated **3** indicates that the observed geometry is not caused by the bulk of the  $C_5Me_5$  group. The effects are probably electronic, rather than steric, in origin, although this work does not prove this.<sup>12</sup> These results confirm that the dominant agostic interactions in lanthanide– $CH(SiMe_3)_2$  complexes are of the  $M\cdots Si_\beta-C_\gamma$  type,<sup>13</sup> as calculated for  $[Cl_2TiC(SiH_2Me)=CH_2]^+$ ,<sup>6</sup> a model for  $[Cp_2TiC(SiMe_3)=CMePh]AlCl_4$ .<sup>14</sup>

(8) Crystal data for **2**:  $LaSi_4C_{24}H_{53}$ ,  $M = 592.968$ , space group  $P6_3$  (no. 173),  $Z = 6$ ,  $a = 18.458(5)$  Å,  $c = 15.936(5)$  Å,  $V = 4702.0(6)$  Å<sup>3</sup>. Crystal size  $5.3 \times 5.3 \times 3.5$  mm.  $T = 15.0(5)$  K,  $\lambda = 1.15881(15)$  Å (Ge(220) monochromated thermal neutrons).  $R(F^2) 0.221$ ,  $wR(F^2) 0.101$ ,  $S(F^2) 1.289$  for all 4616 data.

(9) Unequivocal C–H bond elongation has, of course, been observed by neutron diffraction in  $\beta$ -agostic allyls, hydride clusters, and Ta alkylidenes.<sup>3</sup>

(10) For a strong agostic interaction one would expect an elongation of 0.03–0.05 Å. The random errors in the C–H bond lengths are on the order of 0.007 Å for **1** and 0.02 Å for **2**.

(11) Program ADF (Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41. Versluis, L.; Ziegler, T. H. *Chem. Phys.* **1988**, *88*, 322. te Velde, G.; Baerends, E. J. *J. Comput. Chem.* **1992**, *99*, 84. Boerrigter, P. M.; te Velde, G.; Baerends, E. J. *Int. J. Quantum Chem.* **1988**, *33*, 87) using quasi-relativistic frozen cores (Boerrigter, P. M. Ph.D. Thesis, Free University, Amsterdam, 1987. Ziegler, T.; Tschinke, V.; Baerends, E. J.; Snijders, J. G.; Ravenek, W. *J. Phys. Chem.* **1989**, *93*, 3050). For further details see Supporting Information.

(12) It is also unlikely that the bulky  $CH(SiMe_3)_2$  group imposes these short contacts; we observed the same kind of alkyl group distortion by DFT calculations on  $(C_5H_5)La(CH_2SiMe_3)_2$ .

(13) The  $C_\alpha-Si_\beta$  bonds are not significantly elongated.

<sup>†</sup> Brookhaven National Laboratory.

<sup>‡</sup> University of Missouri—St. Louis. E-mail: lee.brammer@umsl.edu.

<sup>§</sup> SRTCA. E-mail: Colin.J.Schaverien@opc.shell.com.

<sup>¶</sup> University of Nijmegen. E-mail: budz@sci.kun.nl.

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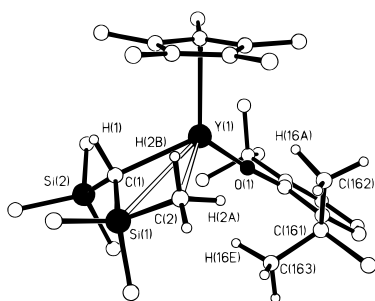
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(7) Crystal data for **1**:  $YSi_2OC_3H_{15}$ ,  $M = 588.881$ , space group  $P2_1/c$  (no. 14),  $Z = 4$ ,  $a = 9.393(1)$  Å,  $b = 22.099(4)$  Å,  $c = 15.768(3)$  Å,  $\beta = 92.52(1)^\circ$ ,  $V = 3269.9(16)$  Å<sup>3</sup>. Crystal size  $2.5 \times 2.8 \times 4.0$  mm.  $T = 20.0(5)$  K,  $\lambda = 1.15863(8)$  Å (Ge(220) monochromated thermal neutrons).  $R(F^2) 0.164$ ,  $wR(F^2) 0.112$ ,  $S(F^2) 1.064$  for all 8852 data. For details of the X-ray structure determination of **1** at 128 K see the Supporting Information.

**Table 1.** Geometrical Details of Interactions in **1**, **2**, and **3**

	C–H		Si <sub>β</sub> –Me <sub>γ</sub>		M···X–C–H torsion angle
	M···H < 3.1 Å	M···H > 3.1 Å	agostic	av nonagostic	
<b>1:</b> <sup>t</sup> Bu					
C(162)–H(16a,b,c)	1.102(6)	1.088(6), 1.092(6)	na	na	–21.0
C(163)–H(16e,d,f)	1.101(6)	1.088(6), 1.093(6)			–23.9
Si <sub>β</sub> –Me <sub>γ</sub> <sup>a</sup>	na	na	1.912(5)	1.876	–45.7
C(1)–H(1) <sup>a</sup>	1.115(5) <sup>a</sup>	na	na	na	na
γ-C(2)–H(2a,b,c)	1.093(7), 1.099(4)	1.081(7)	na	na	na
<b>2:</b> Si <sub>β</sub> –Me <sub>γ</sub> <sup>a</sup>	na	na	1.917(13)	1.881	59.3
Si <sub>β</sub> –Me <sub>γ</sub> <sup>b</sup>	na	na	1.920(15)	1.880	–58.1
C(11)–H(11), <sup>a</sup> C(12)–H(12) <sup>b</sup>	1.120(16), <sup>a</sup> 1.107(15) <sup>b</sup>	na	na	na	na
γ-C(17)–H(17a,c,b) <sup>a</sup>	1.084(24), 1.070(12)	1.048(18)	na	na	na
γ-C(22)–H(22a,c,b) <sup>b</sup>	1.088(18), 1.101(15)	1.082(18)	na	na	na
<b>3:</b> Si <sub>β</sub> –Me <sub>γ</sub> <sup>a</sup>	na	na	1.951	1.906	–58.8
Si <sub>β</sub> –Me <sub>γ</sub> <sup>b</sup>	na	na	1.935	1.908	50.1
α-C–H, <sup>a</sup> α-C–H <sup>b</sup>	1.115, <sup>a</sup> 1.115 <sup>b</sup>	na	na	na	na
γ-C–H <sup>a</sup>	1.107, 1.108	1.103	na	na	na
γ-C–H <sup>b</sup>	1.103, 1.107	1.104	na	na	na

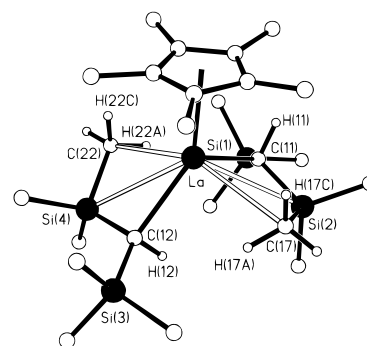
<sup>a</sup> Unit on CH(SiMe<sub>3</sub>)<sub>2</sub> group with methine CH pointing toward Cp. <sup>b</sup> Unit on CH(SiMe<sub>3</sub>)<sub>2</sub> group with methine CH pointing away from Cp.



**Figure 1.** Molecular structure of (C<sub>5</sub>Me<sub>5</sub>)Y(OAr)CH(SiMe<sub>3</sub>)<sub>2</sub> (**1**) at 20 K. Hydrogen atoms omitted except on methine group and on methyl groups in close proximity to the metal. Selected distances (Å) and angles (deg): Y(1)···H(2a,b,c) 2.599(7), 3.029(9), 4.029, Y(1)–H(1) 2.731(6), Y(1)–C(1)–H(1) 94.7(3), Y(1)···H(16a) 2.526(6), Y(1)–H(16e) 2.935(6).

Acute M–C<sub>α</sub>–H angles,<sup>15</sup> as determined by X-ray diffraction, and small <sup>1</sup>J<sub>CH</sub> couplings have often been cited as evidence for an α<sub>CH</sub> agostic interaction. However, the present work does *not* support this interpretation (Table 1). The three M–C<sub>α</sub>–H angles in **1** and **2** are >90°, and the elongation of the methine C–H bonds is not statistically significant.<sup>16</sup> The calculated structure of **3** shows the same features, with an α-C–H bond elongation of only 0.01 Å.

Interestingly, the interacting γ-methyl groups are “tilted” away from the metal.<sup>17</sup> This could be due to repulsion; however, an alternative description is that interaction with La moves C toward five-coordination, or at least toward the transition state for β-elimination. In contrast to agostic β- and γ-C–H interactions,<sup>3</sup> in **1** and **2** the γ-methyl hydrogens avoid the metal. The activation energy difference required to achieve the appropriate conformational minimum may be insignificant compared with thermal



**Figure 2.** Molecular structure of (C<sub>5</sub>Me<sub>5</sub>)La{CH(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub> (**2**) at 15 K. Hydrogen atoms omitted except on methine groups and on methyl groups in close proximity to the metal. Selected distances (Å) and angles (deg): La···H(17a) 2.731(17), La···H(17c) 2.820(17), La···H(22a) 2.818(16), La···H(22c) 2.768(16), La–C(11)–H(11) 95.7(8), La–C(12)–H(12) 94.0(13), La···H(11) 2.87(2), La···H(12) 2.88(2).

energies, even at 15–20 K. DFT calculations<sup>18</sup> show that this conformational preference is, indeed, rather soft.

Although previously postulated, and supported by theoretical studies,<sup>6</sup> we provide unequivocal evidence that a polarized, high-energy, spatially diffuse Si–Me σ-bond clearly takes precedence over α-C–H···Ln and γ-C–H···Ln interactions in stabilizing the lanthanide center.

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**Supporting Information Available:** Full tables of crystallographic data for X-ray and neutron diffraction of **1** and neutron diffraction of **2**; displacement ellipsoid plots of **1** and **2**; and Cartesian coordinates for the optimized structure of **3** (33 pages, print/PDF). Crystallographic data are also available in CIF format on the Internet only. See any current masthead page for ordering information and Web access instructions.

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(18) See Supporting Information.

(14) This structure, however, refined poorly. Eisch, J. J.; Pitrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219. Cf. the eclipsed γ-Me conformation in [C<sub>2</sub>H<sub>4</sub>(indenyl)<sub>2</sub>Zr–C(SiMe<sub>3</sub>)=CMe<sub>2</sub>]<sup>+</sup>. Horton, A. D.; Orpen, A. G. *Organometallics* **1991**, *10*, 3910.

(15) The esd's were, however, large: (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>YCH(SiMe<sub>3</sub>)<sub>2</sub>, 84(3)<sup>o</sup>; <sup>2f</sup> Me<sub>2</sub>Ge(C<sub>5</sub>Me<sub>4</sub>)<sub>2</sub>HoCH(SiMe<sub>3</sub>)<sub>2</sub>, 80(6)<sup>o</sup>; <sup>2d</sup> Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)(C<sub>5</sub>H<sub>4</sub>)LuCH(SiMe<sub>3</sub>)<sub>2</sub>, 96(4)<sup>o</sup>; <sup>2e</sup> (C<sub>5</sub>Me<sub>5</sub>)Ce{CH(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>, 90(3)<sup>o</sup>, 93(3)<sup>o</sup>. Cf. **2** by X-ray diffraction: 86(3)<sup>o</sup>, 85(3)<sup>o</sup>.

(16) Neutron diffraction studies of Mg{CH(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub> also provided little evidence for α-agostic interactions. Hitchcock, P. B.; Howard, J. A. K.; Lappert, M. F.; Leung, W.-P.; Mason, S. A. *J. Chem. Soc., Chem. Commun.* **1990**, 847.

(17) Examination of the Si<sub>β</sub>–C<sub>γ</sub>–H angles in the agostic methyl groups of **2** reveal that they, in contrast to all their nonagostic Si–Me counterparts, are distorted, i.e., Si(2)–C(17)–H(17a,b,c) = 112.3(10)<sup>o</sup>, 107.4(12)<sup>o</sup>, 117.7(12)<sup>o</sup> (in **3**: 114.93<sup>o</sup>, 108.29<sup>o</sup>, 114.79<sup>o</sup>) and Si(4)–C(22)–H(22a,b,c) = 114.9(11)<sup>o</sup>, 109.7(15)<sup>o</sup>, 113.7(12)<sup>o</sup> (in **3**: 115.03<sup>o</sup>, 109.49<sup>o</sup>, 112.46<sup>o</sup>).