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Highly Fluxional [Y(C(SiH(CH$_3$)$_2$)$_3$)$_3$]: A DFT Characterization of Structure and NMR Spectra

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Abstract: The structure and NMR spectroscopic properties of [Y(C(SiH(CH$_3$)$_2$)$_3$)$_3$] are investigated with density functional theory calculations. The existence of a C$_3$ principal axis that was found experimentally is reproduced, but the calculations also find that the symmetry of the equilibrium structure of [Y(C(SiH(CH$_3$)$_2$)$_3$)$_3$] has to be reduced from the experimentally suggested C$_{3v}$ or C$_{3h}$ to C$_3$ in order to explain the observed Si*H* NMR chemical shifts. We show that the apparent mirror plane relating two agostic SiH(CH$_3$)$_2$ groups on each ligand is caused by the rapid interchange of the position of the third ligand, which could only be observed at much lower temperatures than used previously in the experiments.

Introduction

Since their discovery in the mid 1960s,[1] various types of agostic interactions have been described for many different systems. However, in some cases, an experimental verification of the presence of an agostic interaction is difficult because either reliable probes such as the characteristically lowered NMR coupling constants are unavailable for a particular compound or available methods such as structural information about CH-bond proximity to a metal center are not very accurate for such a prediction.[2] In these cases, computational inspection of the compound in question can often assist in the determination of the nature of a particular interaction.[3] The methods currently in use for such a computational analysis range from the theoretical reproduction of spectroscopic properties to the discussion of the bonding situation in terms of natural bonding orbitals or the topology of the electron density.[4]

In this study, we examine an yttrium complex with sterically bulky alkyl ligands. The compound was first synthesized by Sadow et al.,[5] who, on the basis of NMR data, described it as having six SiH agostic interactions. The high number of agostic contacts claimed in this molecule warrants a second look and a closer inspection of the situation of the three ligands in relation to the central metal atom.

The SiH agostic interactions reported are not unusual; in fact, several rare-earth complexes with silyl−amido agostic interactions had been reported before.[6] In those, the number of coordinating groups seems to depend on both electronic as well as steric effects. The larger [Eu(N(SiHMe$_2$)tBu)$_3$] complex coordinates through three β-agostic interactions,[6b] while the Me$_2$Si(C$_5$Me$_4$)$_2$YN(SiHMe$_2$)$_2$ ligand coordinates through a bis-β-agostic interaction[6c,e] and the bulkier Cp*$_2$YN(SiHMe$_2$)$_2$ ligand coordinates through a single β-agostic interaction.[6d]

In the initial characterization by Sadow et al., NMR spectroscopy was used as the main analytical tool in the investigation of the agostic nature of the SiH interaction. The authors could show that, in order to obtain sufficient resolution of the spectrum, the sample had to be cooled to approximately 190 K. Above this temperature, the relevant

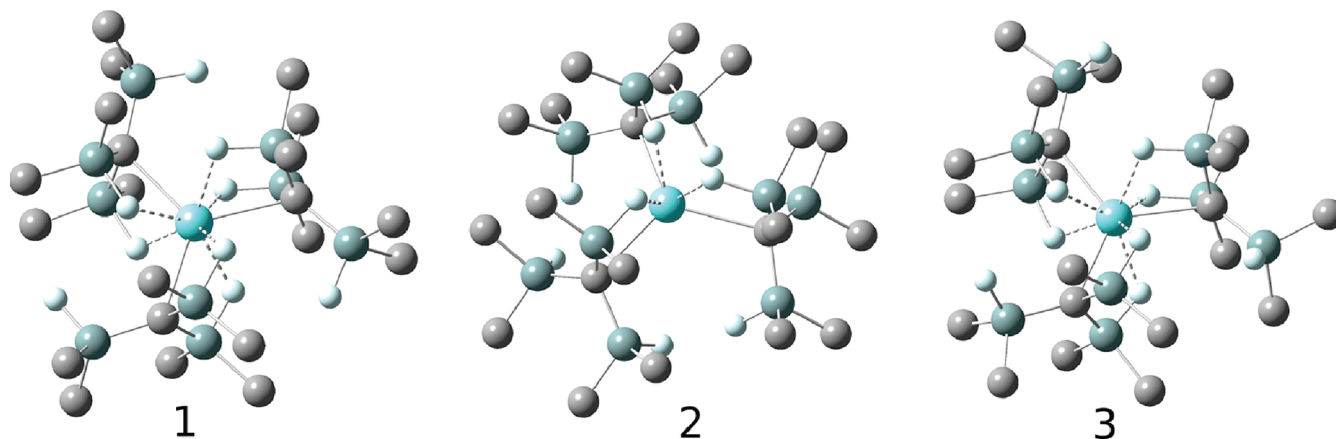* To whom correspondence should be addressed. E-mail: matthias.lein@vuw.ac.nz.
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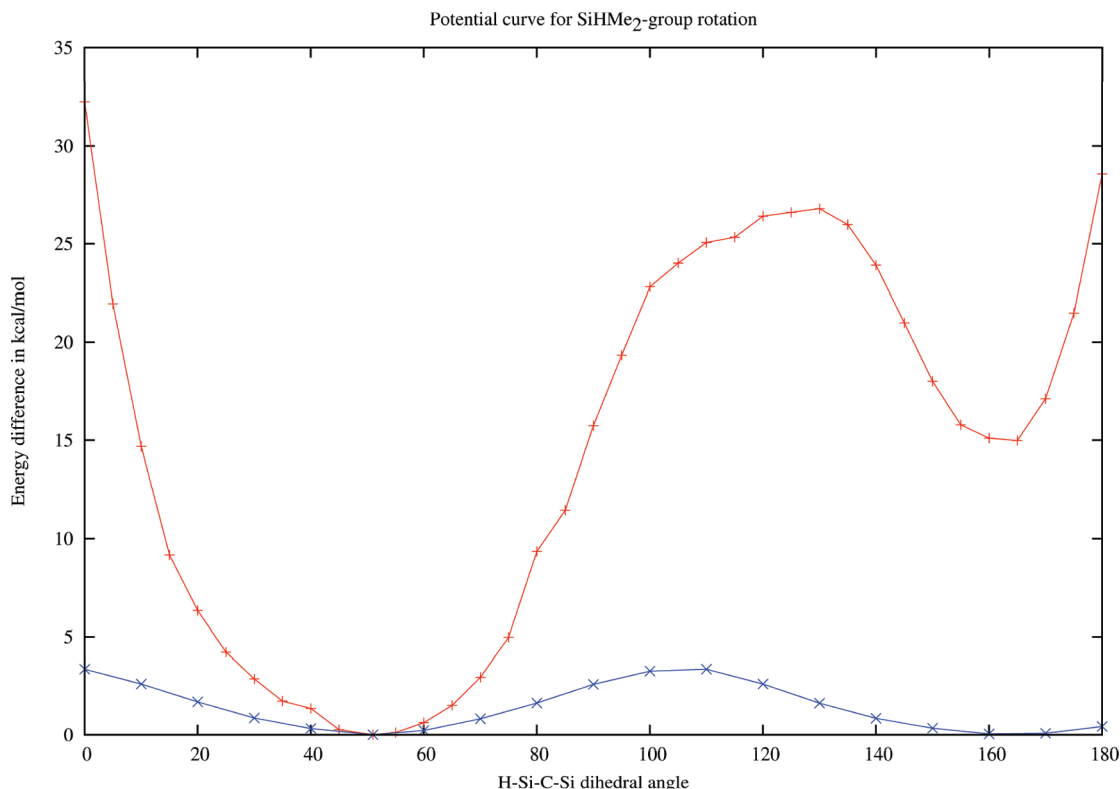
Figure 1. Energetic profile for the internal rotation of the noncoordinating SiHMe$_2$ group in **3**.

Figure 2. Structures of **1**, **2**, and **3** (only SiH hydrogen atoms are shown; all other hydrogen atoms are omitted for clarity). Bonds are shown as solid lines; Si—H···Y agostic interactions are shown as dashed lines.

SiH signals in the ^{1}H NMR spectrum coalesced into a single peak at 3.85 ppm.

Results and Discussion

Structures. In order to get a first insight into the structural properties of the yttrium compound in question, geometry optimizations were performed for both structures that had been previously suggested.[5] Those suggestions were based on the assumption of a pyramidalized structure (**1**), where the three −C(Si(CH$_3$)$_2$H)$_3$ ligands all coordinate from one side of the central yttrium atom, and a planar structure (**2**), where the coordinating carbon atoms of all three ligands and the central yttrium atom are in the same plane (see Figure 2). It was previously suggested[5] that a pyramidal structure

might be the more likely one because [Y(CH(SiMe$_3$)$_2$)$_3$], a similar compound, had been shown to be pyramidal.[7]

Both optimizations lead to stationary points on the potential energy hyper surface, but both structures, **2** with C$_{3v}$ symmetry and structure **1** with C$_{3h}$ symmetry, were calculated to be transition states. Unfortunately, it was also found that the C$_{3v}$ structure is almost 70 kcal/mol higher in energy than the transition structure with C$_{3h}$ symmetry and, in addition, has only three Si−H units coordinated to the central yttrium atom because of steric constraints, as opposed to six Si−H units, which had been suggested when this compound had been characterized for the first time (see Table 1). Consequently, the C$_{3h}$ symmetric structure, **1**, was then used as a starting point for the search for the lowest energy

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Table 1. Symmetries, Relative Energies (in kcal/mol), Number of Imaginary Modes (i), and ^{1}H NMR Chemical Shifts (in ppm) for Coordinating and Noncoordinating Si−H Protons

|	symm	ΔE	i	δ_{coord}	$\delta_{noncoord}$
1	C_{3h}	10.6	3	6×3.45	3×5.26
1a	C_{3h}	14.0	3	6×3.43	3×5.13
2	C_{3v}	80.2	10	3×4.48	6×5.97
2a	C_s	45.9	4	$2 \times 4.01, 2 \times 4.56$	$2 \times 4.97, 2 \times 4.84, 5.00$
2b	C_s	13.3	2	$2 \times 5.12, 2 \times 4.72, 4.23$	$2 \times 5.03, 2 \times 5.16$
2c	C_3	8.9	0	3×3.70	$3 \times 4.97, 3 \times 5.10$
3	C_3	0.0	0	$3 \times 3.28, 3 \times 3.70$	3×4.75
3a	C_1	0.0	0	$3.38, 3.45, 3.47, 3.52, 3.57, 3.62$	$4.76, 4.79, 4.80$
3b	C_1	3.4	1		
exp[5]				6×3.40	3×4.71

conformation. In order to find such a structure, the coordinates of the transition state with C_{3h} symmetry were displaced according to the vibrational modes corresponding to imaginary frequencies, and the resulting initial structure with C_3 symmetry was again optimized. This resulted in a true minimum structure (**3**) with C_3 symmetry, which is 10.6 kcal/mol lower in energy than the previously obtained transition state (Figure 2). The retention of the C_3 axis is consistent with the spectral data obtained by Sadow and co-workers. In the energetic minimum, the three Si−H units that used to be coplanar with the horizontal mirror plane in the transition structure are now rotated out of the Y−C−Si plane by 52.7°. This leads to the observed lowering of symmetry by removal of the horizontal mirror plane. The other two Si(CH₃)₂H units of each of the three ligands are mostly unaffected by this internal rotation, and their mode of coordination to the central yttrium atom through their SiH groups does not change considerably, although a significant lengthening of the Y−H distances is noted. Furthermore, the loss of the horizontal mirror plane in **3** also makes the Si(CH₃)₂H units that used to be above the mirror plane different from the Si(CH₃)₂H units that used to be below the mirror plane. Those had been identical in the C_{3h} symmetrical transition structure, **1**, because of the σ_h-mirror symmetry between them. While the noncoordinating Si−H units showed a Y−H distance of 2.36 Å in the transition structure **1** and a much longer Y−H distance of 4.36 Å in the minimum structure **3** with C_3 symmetry, the corresponding changes in the groups with the coordinating Si−H units were much smaller. In those groups, the Y−H distances increased from 2.27 Å in the transition structure **1** to 2.30 Å and 2.36 Å in the minimum energy structure **3** for the groups that used to be above and below the mirror plane, respectively.

Considering the energetic gain of about 11 kcal/mol by the internal rotation of one Si(CH₃)₂H unit at each of the three C(Si(CH₃)₂H)₃ ligands at the same time by going from structure **1** to structure **3**, the question about the size of the energy barrier for the rotation of a single Si(CH₃)₂H unit around the C−Si(CH₃)₂H bond has to be asked. In order to determine this, two sets of surface scans were obtained and evaluated (see Figure 1). In the first scan, the Y−C−Si−H angle was varied from 0° to 180° in 5° increments with all other structural parameters unchanged. This constrained scan showed a large barrier for the rotation of the Si(CH₃)₂H unit of 26.8 kcal/mol into a shallow energetic minimum on the other side. This rotational barrier can be lowered significantly if the remaining structural parameters are allowed to

minimize as well during the scan. This second, relaxed scan shows that the energetic profile of the rotation is much shallower and has a barrier of less than 3.5 kcal/mol between two structures with nearly identical energies. The second minimum in the curve (structure **3a**) at 160° corresponds to a structure where one Si(CH₃)₂H unit of one C(Si(CH₃)₂H)₃ ligand has rotated through to the other side and the other two ligands have been left largely unchanged. This structure has been confirmed to be an energetic minimum that shows the same energy as structure **3** within numerical accuracy but is completely unsymmetrical (point group C_1). The transition structure **3b** that connects **3** and **3a** has also been identified and is calculated to be 3.4 kcal/mol higher in energy than **3** (and **3a**).

Because of the large number of internal rotations that are possible in this compound, a number of alternative structures can be imagined. For example, in the "planar" structure **1**, the noncoordinating Si−H groups are all pointing in the same direction in the horizontal mirror plane. It can be imagined that the particular Si(CH₃)₂H groups those Si−H groups belong to might be rotated by 180° in such a way that all Si−H groups point in the opposite direction of structure **1** but still coplanar with the horizontal mirror plane. This new structure (**1a**) also has C_{3h} symmetry and has been calculated to be a transition state like structure **1** but lies 3.4 kcal/mol above the previously considered structure, **1**.

Starting from structure **2**, where all three C(Si(CH₃)₂H)₃ ligands coordinate through one Si−H group to the yttrium atom in the center of the complex, other modes of coordination can be imagined (see Figure 3). In structure **2a**, with C_s symmetry, one of the ligands is rotated by 180° and now coordinates through two Si−H groups to the central metal atom. This increases the number of coordinating groups from three in **2** to four in **2a**. At the same time, some of the steric strain in **2** is released so that **2a** is 34.3 kcal/mol more stable than **2**. Even more steric strain can be released if not all ligands are aligned in a way where all three Si(CH₃)₂H groups are above or below the plane defined by the central yttrium atom and the three carbon atoms through which the ligands coordinate to the metal. The C(Si(CH₃)₂H)₃ ligands can also rotate around the Y−C bond in a way so that one Si(CH₃)₂H group (more precisely, the C−Si bond of one C−Si(CH₃)₂H group) is coplanar with the plane mentioned above. This is the case in **1**, **1a**, **3**, and **3a**, whereas in **2** and **2a**, the ligands are not in this favorable orientation. An intermediate structure **2b** has been constructed and optimized where two ligands are in the favorable "in-plane" orientation
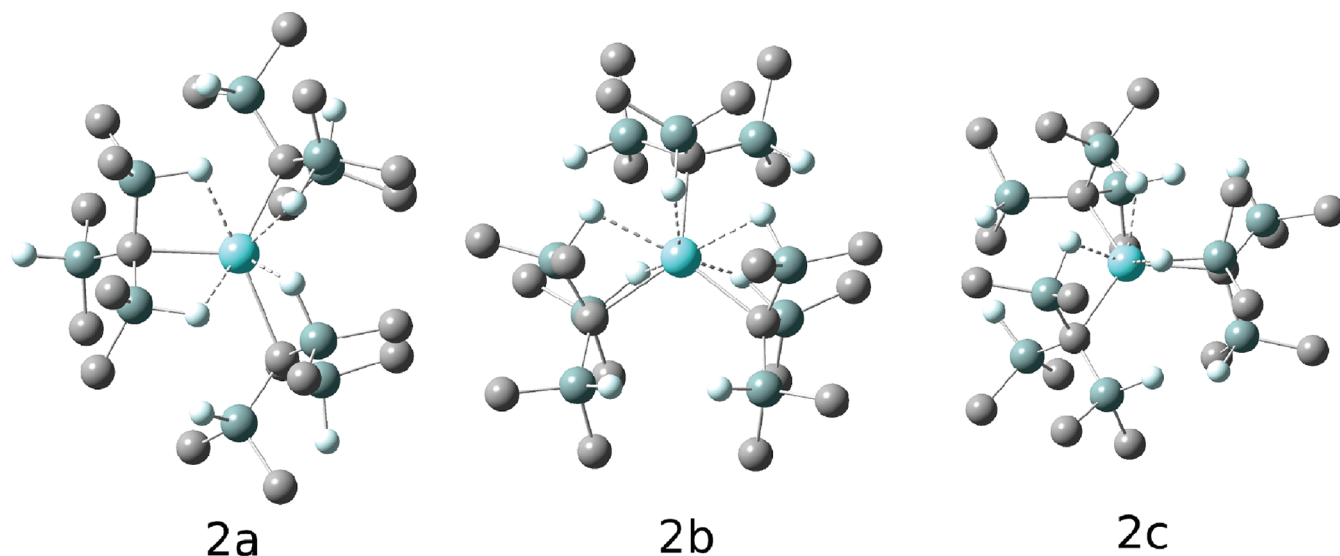
Figure 3. Structures of **2a**, **2b**, and **2c** (only SiH hydrogen atoms are shown; all other hydrogen atoms are omitted for clarity). Bonds are shown as solid lines; Si—H···Y agostic interactions are shown as dashed lines.

and hence coordinate through two Si—H bonds to the metal center each. The remaining third ligand is not in this orientation and coordinates through just one Si—H bond so that the total number of coordinating Si—H bonds in **2b** is five. With most of the steric strain now released, **2b** is only 13.3 kcal/mol less stable than **3**.

Although the comparison of **2**, **2a**, and **2b** seems to suggest that the release of steric strain is coupled to an increasing number of coordinating Si—H bonds, this is not the case. Starting from structure **2**, it is possible to create a structure that releases most steric strain but still coordinates through only three Si—H bonds like **2**. This new structure **2c** is obtained by rotating all three ligands concertedly to one side, thereby reducing the symmetry from C_{3v} to just C_3. This structure is 71.6 kcal/mol more stable than **2** and only 8.9 kcal/mol less stable than the energetic minimum **3** and, by extension, 4.4 kcal/mol more stable than **2b**, which coordinates through five Si—H bonds.

NMR Spectra. While the structural data alone demonstrate convincingly that **3** is indeed the lowest energy structure of the compound in question, it is desirable to corroborate the evidence by looking at the problem from another angle. Because of the availability of experimental ^{1}H NMR data for the system at hand, this was chosen as a basis for comparison to the computationally obtained NMR chemical shifts (see Table 1).

The Si—H protons fall into two distinct groups for all isomers. First, there are those Si—H protons that coordinate to the central metal atom, i.e., those that are in close proximity to the yttrium atom. The ^{1}H NMR signals of these protons are shifted upfield and have been characterized experimentally at 3.40 ppm. Second, there are those Si—H protons that do not coordinate and hence are further away from the central yttrium atom. Those Si—H protons give NMR signals that are shifted downfield, and they appear at 4.71 ppm in the experimental spectrum of the compound in question.

The calculated chemical shifts of structures **1** and **1a** appear to be in line with the experimental findings. The six

coordinating Si—H protons are found at 3.45 ppm and 3.43 ppm, respectively. This correlates very well with the experimental finding of 3.40 ppm for those protons. Unfortunately, the agreement is undone by the calculated chemical shifts of the noncoordinating Si—H protons which are found at 5.26 ppm for **1** and 5.13 ppm for **1a**, whereas the experimentally observed chemical shifts for these protons is 4.71 ppm. A comparison to the computed NMR data of structure **2**, the pyramidalized structure favored by the initial experimental assessment, shows even worse agreement with the experimental findings. Because of the high steric strain introduced into the system by the alignment of the ligands in C_{3v}, the six equivalent Si—H protons are too far away from the central yttrium atom to coordinate effectively. Conversely, the other three Si—H protons are pushed into the proximity of the central metal atom and hence can be seen as coordinating. This reverses the experimental findings which indicate that there must be six coordinating Si—H protons and three noncoordinating protons. This clearly eliminates **2** as a possible candidate for the structure of the yttrium compound in this investigation.

Our structural candidate, **3**, is a slightly more complicated case. Instead of six equivalent coordinating Si—H protons, there are two groups of three Si—H protons that coordinate to the central metal atom but give separate signals since they are not equivalent. Those signals are predicted at 3.28 ppm and 3.70 ppm. At first glance, this seems to contradict the experimental observation of a single signal for all six coordinating Si—H protons. However, we have demonstrated above that there is only a very small barrier of 3.4 kcal/mol to the internal rotation that transforms **3** into **3a**. This internal rotation also transforms the two coordinating Si(CH$_3$)$_2$H groups into each other, and hence the two calculated signals at 3.28 ppm and 3.70 ppm will merge at the temperature at which the experiment was performed to an average value of 3.49 ppm, which compares very well with the observed resonance at 3.40 ppm. Because of the extremely low barrier for the internal rotation, it will most probably not be possible to cool the sample below the coalescence point and retain

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the liquid state at the same time. This quick internal rearrangement of **3** through **3b** into **3a**, or possibly from **3** to the mirror image of **3** through **1** if all ligands rotate at the same time, is also the reason why the experiment appears to indicate that all three ligands are equivalent (at all experimental temperatures) and that a mirror plane relates the two coordinating Si(CH$_3$)$_2$H groups.

Conclusions

The main findings of this investigation can be summarized as follows:

Density functional theory calculations have shown that the structure of [Y(C(SiH(CH$_3$)$_2$)$_3$)$_3$] is more complicated than first anticipated. The potential energy surface is very shallow with respect to internal rotations of the three ligands. In fact, the barriers between several low-lying minima are so small that it will be exceedingly difficult to observe the global minimum in an NMR experiment. The fast exchange of position exhibited by some Si(CH$_3$)$_2$H groups in the compound makes them appear equivalent in the experimental NMR spectrum even though our theoretical data shows that the only two possible structures containing a mirror plane which would explain the observation are transition states between the true minimum structure (**3**) or sterically unfavorable high energy structures (**2**).

The findings of the structural analysis are corroborated by the calculation of NMR chemical shifts for the Si−H protons in the compound, which show very good agreement between the experimental findings and our proposed structure of the global minimum and in turn the poor agreement of the calculated chemical shifts of the other structures in consideration of the experimental results.

Computational Details

All calculations were carried out using density functional theory (DFT) with the B3LYP density functional.[8] Correlation consistent basis sets of the Dunning type were used throughout. The yttrium atom is described by a triple-ζ-quality basis set (aug-cc-pVTZ-PP) and the accompanying effective core potential.[9] The inner shell of atoms around the yttrium metal center is described by triple-ζ-quality basis sets[10] (cc-pVTZ); this includes the carbon atoms that coordinate to the metal center, all silicon atoms, and all hydrogen atoms directly bound to a silicon atom. All other carbon and hydrogen atoms are described by a double-ζ-quality basis set[10b] (cc-pVDZ). All calculations were carried out with the Gaussian suite of programs[11] (g03).

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