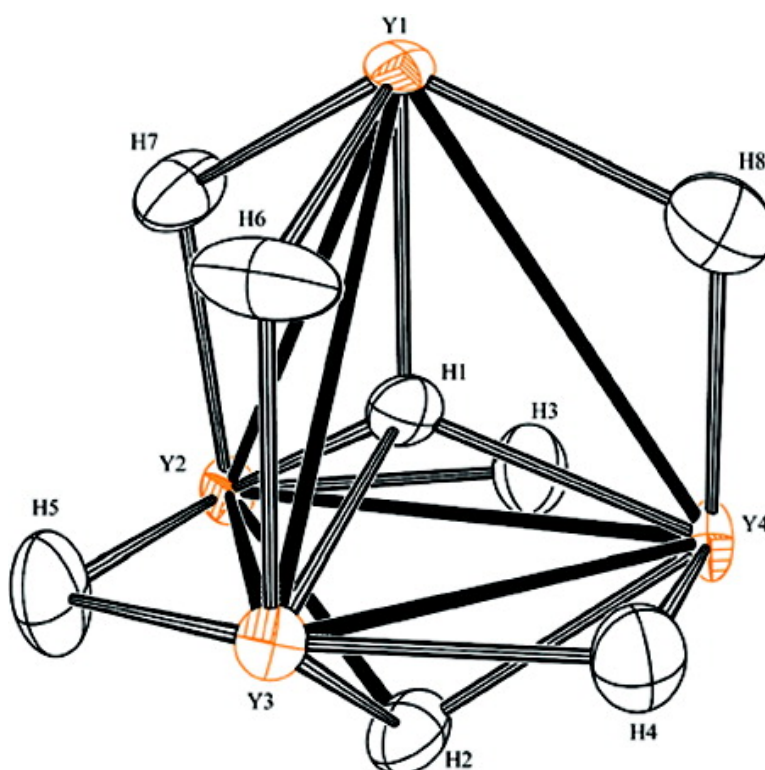


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## Neutron Diffraction Studies on a 4-Coordinate Hydrogen Atom in an Yttrium Cluster

Muhammed Yousufuddin,<sup>†</sup> Matthias J. Gutmann,<sup>‡</sup> Jens Baldamus,<sup>§</sup> Olivier Tardif,<sup>§</sup> Zhaomin Hou,<sup>\*,§</sup> Sax A. Mason,<sup>||</sup> Garry J. McIntyre,<sup>||</sup> and Robert Bau<sup>\*,†</sup>

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**Abstract:** A four-coordinate hydrogen atom has been unambiguously located, by single-crystal neutron diffraction for the first time, in the center of the tetrahedral metal complex  $Y_4H_8(Cp')_4(THF)$  [ $Cp' = C_5Me_4(SiMe_3)$ ]. The core of the molecule consists of a tetranuclear cluster with one interstitial, one face-bridging, and six edge-bridging hydride ligands. The compound was prepared via the reaction of  $YCp'(CH_2SiMe_3)_2(THF)$  with gaseous  $H_2$ . Neutron data were collected on a 4 mm<sup>3</sup> crystal at the Quasi-Laue diffractometer VIVALDI at ILL (Grenoble)<sup>1a</sup> and on an 8 mm<sup>3</sup> crystal at the SXD diffractometer at ISIS (Didcot). The final agreement factor is  $R = 8.9\%$  for 4171 reflections. The existence of 4-coordinate hydrogen now completes the series of high-connectivity hydride ligands located in the interstitial cavities of molecular cluster complexes. We had previously reported the existence of 6-coordinate hydrogen in the octahedral cavity of  $[HCo_6(CO)_{15}]^-$  in 1979, and 5-coordinate hydrogen in the square pyramidal cavities of  $[H_2Rh_{13}(CO)_{24}]^{3-}$  in 1997, also via single-crystal neutron analyses.

### Introduction

The existence of hydrogen atoms in the interstitial cavities of solid-state metal hydrides is not uncommon:<sup>1b</sup> the presence of what may loosely be called 4-coordinate hydrogen is well established in the tetrahedral sites of materials such as  $UH_3$ ,<sup>2</sup>  $Th_4H_{15}$ ,<sup>3</sup> and many non-stoichiometric hydrides of lanthanides<sup>4</sup> and closely related metals such as yttrium.<sup>5</sup> Among *organo-metallic* cluster hydride complexes, (that is, soluble molecular compounds) however, 4-coordinate hydrogens are, until recently<sup>6</sup> unknown (also, ref 7).

This situation changed, however, in 2003, when the first indications of molecular species containing  $\mu_4$ -H atoms were

reported by some of us<sup>6a</sup> in the complexes  $[Cp''LuH_2]_4(THF)$  [ $Cp'' = C_5Me_4(SiMe_3)$ ],  $[Cp''YH_2]_4(THF)$ ,<sup>6b</sup>  $[Cp''YH_2]_4$ ,<sup>6c</sup>  $[Cp''_4Y_4H_7][B(C_6F_5)_4]$ ,<sup>6d</sup> and  $[Cp''_4Y_4H_7(THF)][B(C_6F_5)_4]$ .<sup>6d</sup> Low-temperature X-ray analyses and DFT studies suggested the presence of  $\mu_4$ -H atoms situated at the centers of those tetrahedral clusters. In this article, we describe a single-crystal neutron diffraction study of one of these cluster complexes, which demonstrates unambiguously that a hydrogen atom simultaneously bonded to four metal atoms can exist in a molecular species.

### Results and Discussion

$[Cp''YH_2]_4(THF)$  was prepared as described previously<sup>6b</sup> (the formation of this complex and other related rare earth metal hydrides have been discussed in a recent review<sup>6e</sup>), and large crystals were grown from a minimum amount of hexane at  $-30$  °C. Details of the experiment are described in the experimental section. Table 1 lists crystallographic data for  $[Cp''YH_2]_4(THF)$  for the two quite distinct neutron data collections.

Even though there is a difference in the final agreement factors because of the largely different data collection times, and even though the experimental techniques are extremely different (Quasi-Laue from a conventional nuclear reactor source

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<sup>‡</sup> Rutherford Appleton Laboratory.

<sup>§</sup> RIKEN (Institute of Physical and Chemical Research).

<sup>||</sup> Institut Laue-Langevin.

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- (7) The central hydrogen atom in the compound  $[HMo_4(O\text{-neopentyl})_{12}]^-$  synthesized in 1994 by Chisholm and co-workers (Budzichowski, T. A.; Chisholm, M. H.; Huffman, J. C.; Eisenstein, O. *Angew. Chem., Int. Ed.* **1994**, *33*, 191) comes close to being considered four-coordinate. However, in that case the hydrogen atom is surrounded by an open-butterfly arrangement of metal atoms and is not truly interstitial (in the sense that it is not encapsulated by a tetrahedron of metal atoms).

**Table 1.** Neutron Crystallographic Data for [(Cp<sup>''</sup>Me<sub>4</sub>SiMe<sub>3</sub>)YH<sub>2</sub>]<sub>4</sub>(THF)

|                                   |  |                                 |
|-----------------------------------|--|---------------------------------|
| empirical formula                 | C <sub>52</sub> H <sub>100</sub> OSi <sub>4</sub> Y <sub>4</sub> |                                 |
| fw                                | 1209.36  |                                 |
| cryst syst                        | triclinic $P\bar{1}$   |                                 |
| Z                                 | 2  |                                 |
| unit cell parameters <sup>a</sup> | <i>VIVALDI (ILL)</i>   | <i>SXD (ISIS)</i>               |
|                                   | <i>a</i> = 13.009(2) Å   | <i>a</i> = 12.988(2) Å          |
|                                   | <i>b</i> = 13.146(2) Å   | <i>b</i> = 13.134(2) Å          |
|                                   | <i>c</i> = 19.688(4) Å   | <i>c</i> = 19.626(3) Å          |
|                                   | $\alpha$ = 80.526(3)°  | $\alpha$ = 80.443(11)°          |
|                                   | $\beta$ = 86.782(3)°   | $\beta$ = 86.673(10)°           |
|                                   | $\gamma$ = 74.290(2)°  | $\gamma$ = 74.379(10)°          |
| <i>V</i>                          | 3196.7(9) Å <sup>3</sup>   | 3179.2(9) Å <sup>3</sup>        |
| <i>T</i>                          | 150(2) K   | 100(2) K                        |
| cryst size                        | 2.0 × 2.0 × 1.0 mm <sup>3</sup>                                  | 2.0 × 2.0 × 2.0 mm <sup>3</sup> |
| wavelength range                  | 0.9–2.7 Å  | 0.37–8.8 Å                      |
| min <i>d</i> spacing              | 0.72 Å   | 0.38 Å                          |
| observed                          |  |                                 |
| no. of patterns                   | 13   | 10                              |
| data-collection time              | 13 h   | 125 h                           |
| no. of reflns collected           | 18 589   | 11 132                          |
| no. of unique reflns              | 4900   | 4171                            |
| no. of params refined             | 1434   | 1434                            |
| no. of reflns ( <i>I</i> > 2σ)    | 3566   | 4171                            |
| final                             | R1 = 0.1094  | R1 = 0.0885                     |
| R[ <i>I</i> > 2σ(1) data]         | wR2 = 0.2347   | wR2 = 0.2240                    |

<sup>a</sup> Unit cell dimensions for the ILL analysis were taken from an X-ray study at 150 K.<sup>6</sup>

at the Institut Laue-Langevin (ILL)<sup>8</sup> vs time-of-flight data from a pulsed spallation source at the ISIS neutron spallation source at Didcot, England<sup>9</sup>), it is gratifying to note that the final results from the two analyses, especially those results concerning the central Y<sub>4</sub>H<sub>8</sub> core, are remarkably consistent. Table 2 lists the distances and angles in the Y<sub>4</sub>H<sub>8</sub> cores from the two neutron structural determinations.

Our neutron data analysis has provided the first accurate neutron-diffraction measurement of a 4-coordinate hydrogen atom in a covalent molecular species. Figure 1 shows a view of the core of [Cp<sup>''</sup>YH<sub>2</sub>]<sub>4</sub>(THF), and Figure 2 shows an ORTEP representation of the title complex. The 4-coordinate hydrogen atom occupies the interstitial site of the tetrahedral cluster. In addition to the 4-coordinate hydrogen atom, the H<sub>8</sub>Y<sub>4</sub> core contains six edge-bridging hydrides and one face-bridging hydride, giving each yttrium atom a valency of three (together with the negatively charged Cp<sup>''</sup> ligands).

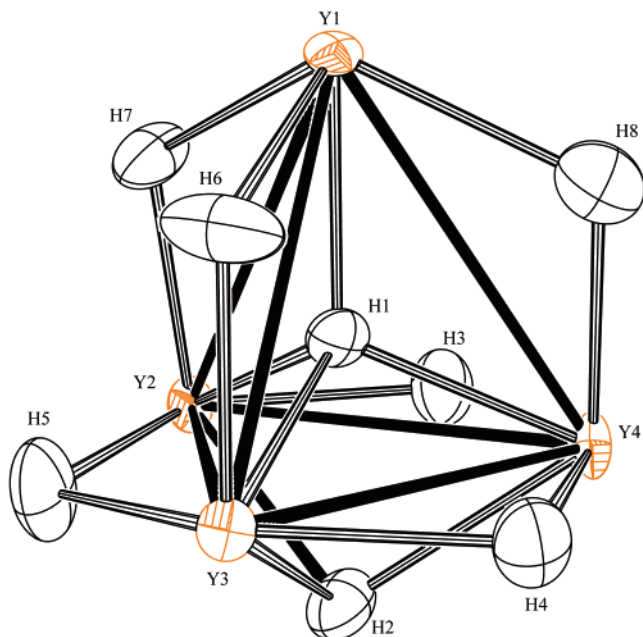
The interstitial hydrogen atom is bonded to the four yttrium atoms, giving an average Y–H distance of 2.195(7) Å (Table 2). The individual angles are, as expected, close to the ideal tetrahedral angle of 109°. The cluster is slightly distorted from ideal tetrahedral symmetry because there is one unique yttrium atom, Y(1), that contains an extra THF (tetrahydrofuran) ligand, which is absent from the other three metal atoms. The most obvious manifestation of the lowered symmetry is the presence

**Table 2.** Key Distances and Angles in the Y<sub>4</sub>H<sub>8</sub> Cores (the ILL Data Represent Results from the VIVALDI Instrument, whereas the ISIS Data Represent Results from the SXD Instrument)

|                               | ILL results | ISIS results |
|-------------------------------|-------------|--------------|
| Y–Y Distances                 |             |              |
| Y(1)–Y(2)                     | 3.670(6)    | 3.685(4)     |
| Y(1)–Y(3)                     | 3.702(5)    | 3.699(4)     |
| Y(1)–Y(4)                     | 3.683(5)    | 3.695(3)     |
| avg                           | 3.685       | 3.693        |
| Y(2)–Y(3)                     | 3.430(4)    | 3.429(4)     |
| Y(2)–Y(4)                     | 3.492(4)    | 3.510(4)     |
| Y(3)–Y(4)                     | 3.432(4)    | 3.438(4)     |
| avg                           | 3.451       | 3.459        |
| Y–(central H) Distances       |             |              |
| Y(1)–H(1)                     | 2.163(10)   | 2.179(6)     |
| Y(2)–H(1)                     | 2.189(9)    | 2.187(7)     |
| Y(3)–H(1)                     | 2.229(8)    | 2.222(6)     |
| Y(4)–H(1)                     | 2.195(7)    | 2.198(6)     |
| avg                           | 2.193       | 2.197        |
| Y–(face-bridging H) Distances |             |              |
| Y(2)–H(2)                     | 2.342(8)    | 2.344(6)     |
| Y(3)–H(2)                     | 2.368(9)    | 2.348(7)     |
| Y(4)–H(2)                     | 2.329(9)    | 2.339(8)     |
| avg                           | 2.346       | 2.344        |
| Y–(edge-bridging H) Distances |             |              |
| Y(2)–H(3)                     | 2.216(8)    | 2.203(7)     |
| Y(4)–H(3)                     | 2.196(8)    | 2.202(7)     |
| Y(3)–H(4)                     | 2.133(8)    | 2.142(7)     |
| Y(4)–H(4)                     | 2.139(8)    | 2.123(7)     |
| Y(2)–H(5)                     | 2.127(8)    | 2.135(8)     |
| Y(3)–H(5)                     | 2.149(8)    | 2.127(8)     |
| Y(1)–H(6)                     | 2.203(8)    | 2.189(7)     |
| Y(3)–H(6)                     | 2.138(10)   | 2.132(7)     |
| Y(1)–H(7)                     | 2.182(9)    | 2.184(8)     |
| Y(2)–H(7)                     | 2.165(11)   | 2.184(7)     |
| Y(1)–H(8)                     | 2.197(8)    | 2.203(8)     |
| Y(4)–H(8)                     | 2.191(11)   | 2.171(9)     |
| avg                           | 2.170       | 2.166        |
| H(1)···H(2)                   | 2.175(14)   | 2.153(9)     |
| Selected Bond Angles          |             |              |
| Y(1)–H(1)–Y(2)                | 115.2(3)    | 115.1(2)     |
| Y(1)–H(1)–Y(3)                | 114.9(4)    | 114.4(3)     |
| Y(1)–H(1)–Y(4)                | 115.4(4)    | 115.1(3)     |
| avg                           | 115.2       | 114.9        |
| Y(2)–H(1)–Y(3)                | 102.0(4)    | 102.1(3)     |
| Y(2)–H(1)–Y(4)                | 105.8(4)    | 106.3(3)     |
| Y(3)–H(1)–Y(4)                | 101.7(3)    | 102.1(2)     |
| avg                           | 103.2       | 103.5        |
| Y(2)–H(2)–Y(3)                | 93.5(3)     | 93.9(2)      |
| Y(2)–H(2)–Y(4)                | 96.8(3)     | 97.1(3)      |
| Y(3)–H(2)–Y(4)                | 93.9(4)     | 94.4(3)      |
| avg                           | 94.7        | 95.1         |
| Y(2)–H(3)–Y(4)                | 104.6(3)    | 105.7(3)     |
| Y(3)–H(4)–Y(4)                | 106.9(3)    | 107.4(3)     |
| Y(2)–H(5)–Y(3)                | 106.7(3)    | 107.1(3)     |
| avg                           | 106.1       | 106.7        |
| Y(1)–H(6)–Y(3)                | 117.0(4)    | 117.7(3)     |
| Y(1)–H(7)–Y(2)                | 115.2(4)    | 115.0(3)     |
| Y(1)–H(8)–Y(4)                | 114.1(4)    | 115.3(4)     |
| avg                           | 115.4       | 116.0        |

of the unique face-bridging hydrogen atom, H(2), which lies above the Y(2)–Y(3)–Y(4) face of the tetrahedron but is absent from the other faces of the cluster. Other (subtler) manifestations of this slightly lowered symmetry are the fact that the Y–Y distances involving Y(1) are slightly longer than the other three (Table 2) and the concomitant larger interstitial Y–H–Y angles involving Y(1) as compared to those involving the other three yttriums.

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**Figure 1.** ORTEP plot of the core of  $[(C_5Me_4SiMe_3)YH_2]_4(THF)$  (figure derived from ISIS results with thermal ellipsoids drawn at 50% probability).

It has been suggested that face-bridging hydrides can serve as a model for chemisorption of hydrogen atoms on metal surfaces.<sup>10</sup> The arrangement of ligands surrounding the core suggests a possible role for the face and edge-bridging hydrides. The bridging hydrides appear to clamp onto the edges and surfaces of the tetrahedron in a manner that allows the central hydride to occupy the interstitial site without causing the cluster to disintegrate. This particular bonding arrangement would probably not exist without the stabilizing presence of the other seven bridging hydrides.<sup>6c</sup>

The fluxionality of hydrides in metal clusters is well-known, and one can hypothesize exchange of the hydrides occurring in solution. In fact, the eight hydrides showed a quintet at  $\delta$  4.32 ( $J_{Y-H} = 15.26$  Hz) in the  $^1H$  NMR spectrum in  $C_6D_6$  at room temperature, suggesting that all of these hydrides are equivalent on the NMR time scale.

We had previously noted<sup>10</sup> that there appears to be a relationship between the number of metal atoms surrounding a hydrogen atom and its corresponding M–H distances. In a series of cobalt compounds containing the following bonds, Co–H (terminal),  $Co_2(\mu_2-H)$ ,  $Co_3(\mu_3-H)$ , and  $Co_6(\mu_6-H)$ , one observes a gradual increase in the Co–H distance (1.56, 1.64, 1.73, and 1.82 Å, respectively) along the above series. This may reflect a decrease in Co–H bond order as the coordination number of hydrogen increases. A similar trend appears among Rh–H distances, in which Rh–H (terminal),  $Rh_2(\mu_2-H)$ , and  $Rh_5(\mu_5-H)$  also show a gradual increase in Rh–H distance (1.56, 1.76, and 1.95 Å, respectively).<sup>10</sup>

Curiously, the analogous trend for the Y–H distances is not observed in the title complex. The title molecule allows us (uniquely) to compare the three different types of linkages in the same compound: ( $\mu_2-H$ ), ( $\mu_3-H$ ), as well as ( $\mu_4-H$ ) metal-hydrogen bonds. The result is rather interesting: although there is the usual (expected) increase as one goes from  $Y_2(\mu_2-H)$

[2.168(9) Å] to  $Y_3(\mu_3-H)$  [2.345(8) Å], the Y–H distance actually decreases in the next step, from  $Y_3(\mu_3-H)$  [2.345(8) Å] to  $Y_4(\mu_4-H)$  [2.195(7) Å]. The relative shortness of the  $Y_4(\mu_4-H)$  distance probably reflects the tightness of a tetrahedral cavity.

In contrast, for an octahedral interstitial site it is well-known that there is sufficient space to allow the hydrogen atom to rattle around inside the cavity. In  $[HCo_6(CO)_{15}]^-$ <sup>11,12</sup> and  $[HRu_6(CO)_{18}]^-$ ,<sup>13</sup> the hydrogen atom is in the center of the octahedron, whereas in  $[HNi_{12}(CO)_{21}]^{3-}$  and  $[H_2Ni_{12}(CO)_{21}]^{2-}$ <sup>14</sup> they are significantly off-centered (by 0.48 Å in the case of  $[HNi_{12}(CO)_{21}]^{3-}$ ). Additionally, inelastic neutron scattering results on  $[HCo_6(CO)_{15}]^-$ <sup>15–17</sup> paint a far more complicated picture as far as the occupancy of the central hydrogen atom in this cluster is concerned, with results from  $Cs^+[HCo_6(CO)_{15}]^-$ <sup>15</sup> and  $K^+[HCo_6(CO)_{15}]^-$ <sup>16</sup> suggesting that, in the octahedral case, there could be enough room for the hydrogen atom to rattle around inside the octahedral cage. Additionally, low-temperature vibrational studies<sup>17</sup> on  $K^+[HCo_6(CO)_{15}]^-$  also suggest that the  $K^+$  salt of  $[HCo_6(CO)_{15}]^-$  appears to have a structure of lower symmetry than that of the  $Cs^+$  or  $[(Ph_3P)_2N]^+$  salts. It would be interesting to see if hydrogen atoms in solid-state binary metal hydrides<sup>1b</sup> are also more loosely held in octahedral cavities and more tightly held in tetrahedral cavities.

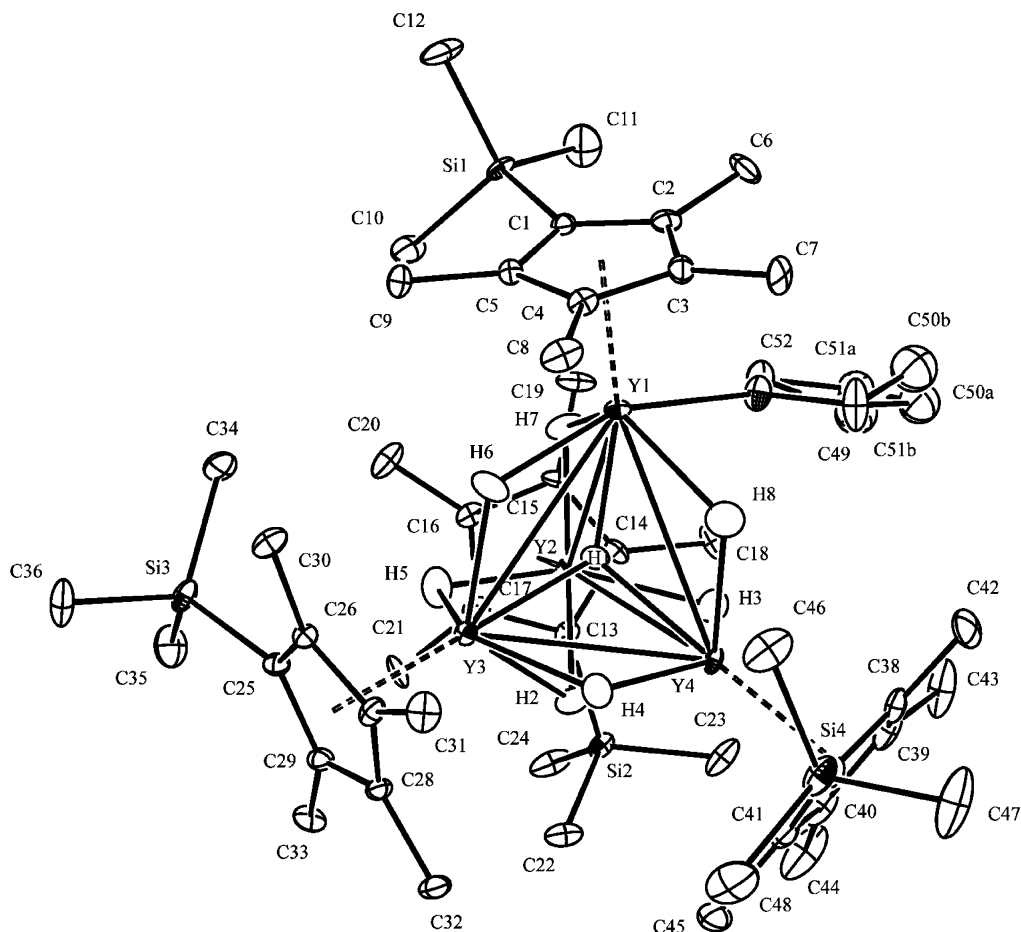
In summary, our results (a) unambiguously demonstrate, for the first time, the existence of a 4-coordinate hydrogen atom in a discrete molecular species, and (b) suggest that, in contrast to 6-coordinate hydrogen atoms (for which there is more than enough room to rattle around the six-atom cavity<sup>14</sup>), a 4-coordinate cavity is much less spacious, and, consequently, a hydrogen atom in a tetrahedral site is much more likely to be bound more tightly, as it were, as compared to its 6-coordinate analogue.

## Experimental Section

Single-crystal neutron diffraction data from this compound were actually collected twice. In the first neutron diffraction analysis,<sup>1a</sup> data on a crystal of dimensions of  $2 \times 2 \times 1$  mm<sup>3</sup> were collected at 150 K on the VIVALDI instrument<sup>8</sup> at the Institut Laue-Langevin (ILL) in Grenoble, France, but in view of a rather high agreement factor ( $R \sim 11\%$ ) it was subsequently decided to repeat the neutron data analysis on a larger sample of dimensions of  $2 \times 2 \times 2$  mm<sup>3</sup>. The second data collection was carried out on the SXD instrument at the ISIS Spallation Neutron Source in Didcot, U.K.<sup>9</sup> In the latter case, the crystal was mounted at the end of an aluminum pin using adhesive aluminum tape. Data were collected at 100 K at 10 different settings with exposure times ranging from 12–15 h per crystal orientation. Data were processed using SXD2001 and intensities extracted using a least-squares procedure with a 3D Gauss-ellipsoid with time-of-flight asymmetry as the profile function.<sup>18</sup> In both cases, the structure was refined using SHELX.<sup>19</sup> Other details are listed in Table 1.

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**Figure 2.** Numbering scheme for  $[(C_5Me_4SiMe_3)YH_2]_4(THF)$ . Hydrogens attached to carbons have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

The structural analysis was complicated by extensive disorder of 10 of the 28 methyl groups in the molecule as well as by two of the methylene groups of the THF ligand. Thus, it was necessary to use the *SHELX* “DFIX” restraints to impose idealized geometries for those disordered groups. In all, 264 restraints were used in the least-squares refinement.

**Preparation of  $[(C_5Me_4SiMe_3)Y(\mu-H)_2]_4(THF)$ .** A toluene solution of  $(C_5Me_4SiMe_3)Y(CH_2SiMe_3)_2(THF)$  (0.793 g, 1.5 mmol) in a 300 mL Schlenk flask equipped with a J. Young valve was frozen in liquid nitrogen, pumped, and backfilled with  $H_2$ . The mixture was allowed to warm to room temperature and was stirred for 2 h. For complete conversion, a second charge of  $H_2$  was carried out in an identical way, and the solution mixture was then further stirred for 2 h. After removal of the solvent under vacuum, the resulting pale-yellow residue was extracted with hexane and filtered in a glove box. Slow evaporation of the solvent under reduced pressure precipitated  $[(C_5Me_4SiMe_3)Y(\mu-H)_2]_4(THF)$  as a pale-yellow crystalline powder (1.379 g, 1.14 mmol,

76% yield). Large single crystals were grown from a minimum amount of hexane in a refrigerator ( $-30\text{ }^\circ\text{C}$ ) equipped with a glove box.

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**Supporting Information Available:** Neutron crystallographic data for both neutron structural analyses are available in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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