Synthesis and Characterization of a Tetranuclear Hydride Cluster of Yttrium $[{(\eta^5-C_5Me_4SiMe_3)Y}_4(\mu-H)_4(\mu_3-H)_4(THF)_2]$

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Dedicated to Professor Heinrich Nöth on the Occasion of his 75th Birthday

Abstract: Hydrogenolysis of the dialkyl complexes $[Y(\eta^5-C_5Me_4SiMe_2R)(CH_2SiMe_3)_2(THF)]$ (**1a**, R = Me; **1b**, R = Ph) results in the formation of the tetranuclear dihydrido complexes $[\{(\eta^5-C_5Me_4SiMe_2R)Y\}_4(\mu-H)_4(\mu_3-H)_4(THF)_2]$ (**2a**, R = Me; **2b**, R = Ph), characterized by NMR spectroscopy. **2a** was studied by single crystal X-ray diffraction. In the solid state, an unsymmetrical tetrahedral configuration of four

 $[Y(\eta^5-C_5Me_4SiMe_3)]$ units is observed, two of which contain each one molecule of THF. Each yttrium atom is bonded to two μ_2 -as well as three μ_3 -bridging hydrido ligands.

Keywords: Dihydrides; Hydrogenolysis; Half-sandwich hydrido complexes

Synthese und Charakterisierung eines vierkernigen Hydrid-Clusters von Yttrium $[{\eta^5-(C_5Me_4SiMe_3)Y}_4(\mu-H)_4(\mu_3-H)_4(THF)_2]$

Inhaltsübersicht. Die Hydrogenolyse von Dialkyl-Komplexen $[Y(\eta^5-C_5Me_4SiMe_2R)(CH_2SiMe_3)_2(THF)]$ (1a, R = Me; 1b, R = Ph) führt zu vierkernigen Dihydrido-Komplexen $[\{(\eta^5-C_5Me_4SiMe_2R)Y\}_4(\mu-H)_4(\mu_3-H)_4(THF)_2]$ (2a, R = Me; 2b, R = Ph), die mit NMR Spektroskopie untersucht wurden. Der

Introduction

Since the discovery of metallocene hydrido complexes by *Evans* et al. as the first examples of molecular hydrides of the rare earth metals [1], this class of complexes has gained enormous importance in the context of homogeneous catalysis [2]. Although scattered examples of hydrido complexes of the non-metallocene class are known, half-sand-wich hydrido complexes remain relatively unexplored [3]. Moreover, despite the rich chemistry of transition metal polyhydrides [4], only a few reports on commonly poorly characterized dihydrido complexes have emerged [5]. We have recently systematically studied the synthesis, characterization, and reactivity of rare-earth metal mono(hydrido)

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Komplex **2a** wurde mit einer Einkristallstrukturanalyse untersucht. Im Festkörper wurde eine unsymmetrische tetraedrische Anordnung der vier [Y(η^5 -C₅Me₄SiMe₃)]-Einheiten gefunden, von denen zwei je ein Molekül THF koordinieren. Jedes Yttriumatom ist an zwei μ_{2^-} und an drei μ_3 -verbrückende Hydridoliganden gebunden.

complexes that contain a dianionic linked amido-cyclopentadienyl ligand [6]. We report here the structural characterization of hydrido yttrium complexes of the general composition $[Y(\eta^5-C_5R_5)H_2L_n]$ with tetranuclear structure [7].

Results and Discussion

When the dialkyl complexes $[Y(\eta^5-C_5Me_4SiMe_2R)-(CH_2SiMe_3)_2(THF)]$ (1a, R = Me; 1b, R = Ph), prepared by the C-H activation method using the trialkyl yttrium complex $[Y(CH_2SiMe_3)_3(THF)_2]$ and the corresponding cyclopentadiene $(C_5Me_4H)SiMe_2R$ as previously described [6a], are hydrogenated under 4 bar of dihydrogen at 25 °C in pentane, good yields of the colorless dihydrido complexes 2a and 2b are obtained (Scheme 1). The dihydrido complexes 2a and 2b can be also prepared without isolating the dialkyl complexes 1a and 1b. Recrystallization of 2a from pentane afforded single crystals suitable for X-ray diffraction study. Figure 1 shows an ORTEP diagram and Table 1 gives selected bond parameters.

The crystal structure analysis confirms the presence of a tetranuclear cluster consisting of four LYH_2 units of which two contain a THF ligand, as postulated previously [6a]. The structure can be thought of derived from a Y₄-tetrahedron with four triply bridging and four doubly

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Scheme 1





Fig. 1 ORTEP diagram of $[\{\eta^5-C_5Me_4SiMe_3)Y\}_4(\mu-H)_4(\mu_3-H)_4(THF)_2]$ (2a). Thermal ellipsoids are drawn at the 50 % probability level. All hydrogen atoms, except the hydrido ligands, are omitted for clarity.

bridging hydrido ligands, somewhat resembling to $[(\eta^5-C_5Me_4Et)_4Cr_4(\mu_2-H)_5(\mu_3-H)_2]$ [8]. The Y₄-tetrahedron is considerably distorted by the *trans*-influence of the coordinated THF molecules to Y1 and Y2 resulting in a significant elongation by 0.5 Å of the Y1...Y4 (3.9097(5) Å) and Y2...Y3 (3.9144(5) Å) distance compared to the range of

Fig. 2 Structure of the Y_4H_8 core in 2a. The THF ligands are only denoted by their oxygen atoms. Thermal ellipsoids are drawn at the 50 % probability level.

3.3299(5) to 3.4084(5) Å found for the remaining Y…Y distances. While the latter Y…Y distances are the shortest ones observed so far [9,10], the former represent among the longest ones, only surpassed by the distance of 4.10(1) Å found in the trimeric $[(\eta^5-C_5H_3Me_2)_2Y(\mu-H)]_3$ [9b]. The positions of all eight hydrido ligands could be determined and in-

Y1…Y2	3.4084(5)	Y4 - H1	2.12(3)
Y1…Y4	3.9097(5)	Y4 - H3	2.13(5)
Y1…Y3	3.3940(5)	Y4 - H4	2.28(4)
Y2…Y3	3.9144(5)	Y4 - H7	2.30(4)
Y2…Y4	3.3864(5)	Y4 – H8	2.08(4)
Y3…Y4	3.3299(5)	Y1 - Y2 - Y3	54.696(10)
Y1 - O1	2.411(3)	Y1 - Y3 - Y2	55.042(9)
Y2 – O2	2.411(3)	Y2 - Y1 - Y3	70.262(11)
Y1 - H1	2.46(3)	Y2 - Y1 - Y4	54.609(10)
Y1 - H2	2.27(4)	Y2 - Y4 - Y1	55.137(10)
Y1 - H3	2.39(3)	Y3 - Y1 - Y4	53.686(9)
Y1 - H5	2.19(3)	Y3 - Y4 - Y1	55.213(10)
Y1 - H6	2.14(4)	Y3 - Y4 - Y2	71.293(11)
Y2 - H1	2.22(3)	Y4 - Y2 - Y1	70.254(11)
Y2 - H2	2.19(4)	Y4 - Y2 - Y3	53.682(9)
Y2 - H4	2.26(4)	Y4 - Y3 - Y1	71.100(11)
Y2 - H5	2.10(3)	Y4 - Y3 - Y2	55.025(9)
Y2 – H7	2.14(4)	O1 - Y1 - Y2	99.67(7)
Y3 - H2	2.27(4)	O1 - Y1 - Y3	100.35(7)
Y3 - H3	2.08(5)	O1 - Y1 - Y4	146.53(7)
Y3 - H4	2.19(4)	O2 - Y2 - Y1	103.11(7)
Y3 - H6	1.97(4)	O2 - Y2 - Y3	148.65(7)
Y3 - H8	2.23(4)	O2 - Y2 - Y4	100.45(7)
		O1 - Y1 - Y2 - O2	106.95(10)

Table 1 Selected Bond lengths/Å and angles/° of $[Y(\eta^5-C_5Me_4SiMe_3)(\mu-H)_2]_4(THF)_2$ (2a).

cluded in the refinement. Thus each yttrium atom is bonded to five hydrido ligands, two in a μ_2 - and three in a μ_3 -bridging mode. As a result of the elongated Y1...Y4 and Y2...Y3 distances the μ_2 -hydrido bridges span over the shorter edges of the distorted Y₄-tetrahedron. The Y-H bond lengths of the μ_2 -hydrido ligands range from 1.97(4) Å (Y3-H6) to 2.30(4) Å (Y4–H7), which is the typical range found in dimeric yttrium hydrido complexes [9]. The Y-H bond distances for triply bridging hydrido ligands are longer and range from 2.08(5) (Y3-H3) to 2.46(3) Å (Y1-H1). The THF ligands are coordinated in a transoidal fashion related to Y1-Y2 edge of the tetrahedron (torsion angle O1-Y1-Y2-O2 107(1)°). The Y-O(THF) bond lengths are equal (2.411(3) Å) and fall within the usual range (2.35-2.45 Å) found in other THF-containing yttrium complexes [11]. Similarly, the Y-C(Cp) bond lengths (2.614(3)-2.720(3) Å) are similar to those found in yttrocene complexes [12].

Not unexpectedly, the complexes 2a and 2b exhibit high fluxionality. In the ¹H NMR spectrum of 2a in C₆D₆ at room temperature (Figure 3) a quintet at 4.29 ppm (4.45 ppm for **2b**) with ${}^{1}J_{YH} = 15.3$ Hz is recorded for all eight hydrido ligands, suggesting that all eight hydrido ligands are equivalent on the NMR timescale. The two THF ligands appear to be dissociatively labile. The YH coupling constant is similar to the typical range of 17 - 18 Hz for μ_3 -hydrido ligands found in $[{(\eta^5-C_5H_5)_2Y(\mu_2-H)_x} (OMe)_{1-x}_{3}(\mu_{3}-H)$] (x = 0, 1/3, 2/3, 1) [1b,10] as well as 16.25 Hz found in the supposedly trimeric $[Tp^{Me}YH_2(THF)_x]$ [5c] $(Tp^{Me} = tris(3,5-dimethyl-1-pyrazo$ lyl)borohydride). These coupling constants are significantly smaller than the values of 27 - 35 Hz , usually found for m₂-hydrido ligands [6c]. The ⁸⁹Y NMR spectrum shows a quintet at 338.9 ppm with ${}^{1}J_{YH} = 15$ Hz, the same coupling constant as found in the ¹H NMR spectrum. The fluxional

behavior of **2a** contrasts the non-fluxionality observed in the ate-complex [Li(THF)₄][{(η^5 -C₅H₅)₂Y(μ_2 -H)}₃(μ_3 -H)] [1b], which displays distinctive signals for the μ_2 - and the μ_3 -hydrido ligands at room temperature.



Fig. 3 1 H NMR spectrum of 2a in C₆D₆ at 25 °C. The insert shows the Y-H region.



Fig. 4 ¹H NMR spectrum (Y-H region) of 2a in THF- d_8 a) at 25 °C and b) at -80 °C.

Variable-temperature studies in THF- d_8 suggest a rather complicated decoalescence pattern for the hydride quintet. At -80 °C, four signals in the intensity ratio of 4:1:2:1

are observed at 2.99 (br m), 4.07 (t, ${}^{1}J_{YH} = 30$ Hz), 4.36 (t, ${}^{1}J_{\rm YH} = 30$ Hz), and 4.53 (t, ${}^{1}J_{\rm YH} = 32$ Hz) ppm (Figure 4). The broad signal of intensity 4 is assigned to the four triply bridging hydrides which remain fluxional at temperatures at which the doubly bridging ones are frozen out. The three different triplets in the ratio of 1:2:1 can be assigned to three sets of inequivalent hydrides bridging the edge Y1-Y2, Y1-Y3/Y2-Y4, and Y3-Y4, respectively. The inequivalence of the four ring ligands is also indicated at lower temperatures. For the SiMe₃ groups one singlet is found at room temperature, but at -40 °C, decoalescence occurs and at -80 °C two separated singlets are recorded at 0.30 and 0.25 ppm. For the ring methyl groups two singlets at 2.01 and 2.12 ppm are detected at room temperature in THF- d_8 . Upon lowering the temperature the signal at the lower field decoalesces at -30 °C and at -80 °C three slightly broadened signals for the C5Me4 groups are detected.

Experimental Part

All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. All solvents were purified by distillation from sodium/triglyme benzophenone ketyl under argon. (C5Me4H)SiMe3 [13a], (C5Me4H)SiMe2Ph [13b], and [Y(CH₂SiMe₃)₃(THF)₂] [6c,14] were prepared according to published procedures. NMR spectra were recorded on a Bruker DRX 400 spectrometer (¹H, 400 MHz; ¹³C, 101 MHz; ²⁹Si, 79.5 MHz, ⁸⁹Y, 19.6 MHz) at 25 °C, unless otherwise stated. Chemical shifts for ¹H and ¹³C spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. 89Y spectra were referenced externally to a 1 M solution of YCl_3 in D_2O . Elemental analyses were performed by the Microanalytical Laboratory of this department. In many cases the results were not satisfactory and the best values from repeated runs were given. Moreover the results were inconsistent from run to run and therefore not reproducible. We ascribe this difficulty observed also by other workers [9e] to the extreme sensitivity of the material. Metal analysis was performed by complexometric titration [15]. The sample (10 to 20 mg) was dissolved in acetonitrile (1 mL) and titrated with a 0.005 M solution of EDTA using xylenol orange as indicator and 1 M ammonium acetate as buffer solution (20 mL).

$[Y(\eta^5-C_5Me_4SiMe_3)(CH_2SiMe_3)_2(THF)] (1a)$

[Y(CH₂SiMe₃)₃(THF)₂] (1.03 g, 2.1 mmol) was dissolved in pentane (30 mL) and cooled to -78 °C. The cyclopentadiene (C₅Me₄H)SiMe₃ (0.40 g, 2.1 mmol) was added and the mixture was stirred for 3 h in which the mixture was warmed up to 0 °C. The solvent was reduced *in vacuo* and after cooling 12 h at -30 °C the product was obtained as colorless crystals in 43 % (480 mg) yield. C₂₄H₅₁OSi₃Y (528.83): C 52.72 (calc. 54.51), H 10.20 (9.72), Y 16.59 (16.81) %.

¹H NMR (C₆D₆): δ = -0.60 (d, ²J_{YH} = 2.6 Hz, 4 H, YCH₂), 0.30 (s, 18 H, CH₂SiMe₃), 0.42 (s, 9 H, ring SiMe₃), 1.13 (m, 4 H, β-THF), 1.96, 2.24 (s, 2 × 6 H, C₅Me₄), 3.50 (br s, 4 H, α-THF). ¹³C{¹H} NMR (C₆D₆): δ = 2.6 (ring SiMe₃), 4.6 (CH₂SiMe₃), 11.5, 14.7 (C₅Me₄), 24.8 (β-THF), 34.7 (d, ¹J_{YC} = 43.2 Hz, YCH₂), 70.4 (α-THF), 115.0 (ring C attached to Si), 123.3, 126.4 (ring C).

$[Y(\eta^5-C_5Me_4SiMe_2Ph)(CH_2SiMe_3)_2(THF)]$ (1b)

This compound was prepared analogously to the synthesis of 1a and isolated as an colorless oil in 97 % yield.

¹H NMR (C₆D₆): δ = -0.58 (d, ²J_{YH} = 3.1 Hz, 4 H, YCH₂), 0.30 (s, 18 H, CH₂SiMe₃), 0.69 (s, 6 H, SiMe₂Ph), 1.20 (m, 4 H, β-THF), 1.97, 2.15 (s, 2 × 6 H, ring CH₃), 3.47 (m, 4 H, α-THF), 7.17 (m, 3 H, C₆H₅), 7.53 (m, 2 H, C₆H₅). ¹³C{¹H} NMR (C₆D₆): δ = 1.8 (SiCH₃Ph), 4.6 (CH₂SiMe₃), 11.6, 14.8 (ring CH₃), 24.9 (β-THF), 34.9 (d, ¹J_{YC} = 43.7 Hz, YCH₂), 700 (α-THF), 112.6 (ring C attached to Si), 123.6, 127.1 (ring C), 128.0, 128.8, 134.3 (C₆H₅), 141.6 (ipso-C₆H₅). ²⁹Si{¹H} NMR (C₆D₆): δ = -13.8 (SiMe₂Ph), -3.2 (d, ²J_{YSi} = 2 Hz, CH₂SiMe₃).

$[{(\eta^5-C_5Me_4SiMe_3)Y}_4(\mu-H)_4(\mu_3-H)_4(THF)_2]$ (2a)

In a thick-walled glass reactor $[Y(CH_2SiMe_3)_3(THF)_2]$ (1.15 g, 2.3 mmol) was dissolved in pentane (30 mL) and $(C_5Me_4H)SiMe_3$ (0.45 g, 2.3 mmol) was added at room temperature. Hydrogen gas (5 bar) was charged and the mixture was stirred vigorously 12 h. After filtration the solution was reduced *in vacuo* and cooled to -30 °C. The product was isolated as colorless crystals in 43 % (290 mg) yield.

 $C_{56}H_{108}O_2Si_4Y_4$ (1281.4): C 51.93 (calc. 52.49), H 8.59 (8.49), Y 26.42 (27.75) %.

¹**H NMR** (C₆D₆): δ = 0.53 (s, 9 H, SiMe₃), 1.41 (m, 2 H, β-THF), 2.25, 2.36 (s, 2 × 6 H, C₅Me₄), 3.59 (br s, 2 H, α-THF), 4.29 (quint, ¹J_{YH} = 15.3 Hz, 2 H, YH). ¹³C[¹H] **NMR** (C₆D₆): δ = 3.0 (ring SiMe₃), 12.5, 15.3 (C₅Me₄), 25.5 (β-THF), 69.2 (α-THF), 114.6 (ring C attached to Si), 124.4, 127.0 (ring C). ¹H **NMR** ([D₈]-THF): δ = 0.24 (s, 9 H, SiMe₃), 1.69 (m, 2 H, β-THF), 2.01, 2.12 (s, 2 × 6 H, C₅Me₄), 3.53 (br s, 2 H, α-THF), 3.71 (quint, ¹J_{YH} = 15.3 Hz, 2 H, YH). ¹H **NMR** ([D₈]-THF, -80 °C): δ = 0.25, 0.30 (s, 18 H, SiMe₃), 1.74 (m, 8 H, β-THF), 1.93 (s, 3 H, C₅Me₄), 2.01 (s, 15 H, C₅Me₄), 2.34 (br s, 6 H, C₅Me₄), 2.99 (m, 4 H, YH), 3.59 (br s, 2 H, α-THF), 4.07 (t, ¹J_{YH} = 29.4 Hz, 1 H, YH), 4.36 (t, ¹J_{YH} = 30.6 Hz, 2 H, YH), 4.53 (t, ¹J_{YH} = 33.4 Hz, 1 H, YH). ⁸⁹Y **NMR** ([D₈]-toluene): δ = 338.9 (quin, ¹J_{YH} = 15 Hz).

$[{(\eta^5-C_5Me_4SiMe_2Ph)Y}_4(\mu-H)_4(\mu_3-H)_4(THF)_2]$ (2b)

A solution of 1.10 g (1.87 mmol) [Y(η^5 -C₅Me₄SiMe₂Ph)-(CH₂SiMe₃)₂(THF)] (**1b**) in pentane (20 mL) was loaded in a thickwalled glass vessel. At room temperature, H₂ (4 bar) was charged and the solution was stirred vigorously. After 24 h, the solution was transferred to a Schlenk tube in the glovebox. The solvent was removed *in vacuo* and the colorless residue was recrystallized from pentane at -30 °C. The product was obtained in 91 % yield (650 mg) as colorless powder.

C₇₆H₁₁₆O₂Si₄Y₄ (1529.7): C 56.80 (calc. 59.67); H 6.90 (7.46).

¹**H-NMR** (C₆D₆): δ = 0.83 (s, 6 H, SiMe₂Ph), 1.36 (br s, 2 H, β-THF), 2.26, 2.28 (s, 2 × 6 H, C₅Me₄), 3.61 (br s, 2 H, α-THF), 4.45 (quint, 1 H, $^{1}J_{Y,H} = 15.3$ Hz, YH), 7.21 (m, 3 H, C₆H₅), 7.62 (d, $^{3}J_{H,H} = 7.8$ Hz, 2 H, 2-C₆H₅). ¹³C{¹H}**NMR** (C₆D₆): δ = 12.5 (SiCH₃Ph), 12.6, 15.4 (C₅Me₄), 25.1 (β-THF), 70.4 (α-THF), 112.4 (ring C at SiMe₂Ph), 124.9 (ring C), 128.1, 128.8, 134.3 (C₆H₅), 141.8 (ipso-C₆H₅). ²⁹Si NMR (C₆D₆): δ = -13.6. ⁸⁹Y NMR (C₆D₆): δ = 344 (m).

Crystal structure determination of 2a. Colorless crystals of $[\{(\eta^5-C_5Me_4SiMe_3)Y\}_4(\mu-H)_4(\mu_3-H)_4(THF)_2]$ (**2a**), $C_{56}H_{108}O_2Si_4Y_4$, 1281.45 g·mol⁻¹, were obtained from pentane solution at -30 °C. For a prism of dimensions $0.68 \times 0.46 \times 0.33$ mm, triclinic, PĪ, a = 12.4061(4) Å, b = 13.4975(4) Å, c = 22.1238(7) Å, $\alpha = 99.014(2)$, $\beta = 92.874(2)^\circ$, $\gamma = 114.320(2)$, V = 3307.1(2) Å³, Z = 2, $\rho_{calcd} = 1.287$ g cm⁻³, $\mu = 3.581$ mm⁻¹, F(000) = 1344, the data set was obtained with a Bruker AXS diffractometer at -70 °C in the ω -scan mode up to $2\theta_{max} = 56.6^\circ$ (*Mo-K* α radiation). 30744 reflections were collected, 16258 were unique [R(int) = 0.0551] of which 10271 were observed [$I > 2\sigma(I)$]. The data correction was carried out using the program system SAINT [16]. The structure was solved by Patterson and Fourier methods using the program

SHELXS-86 [17], the refinement was carried out using the program SHELXL-97 based on F^2 [18]. Anisotropic thermal parameters were refined for the non-hydrogen atoms. Hydrogen atoms of the methyl groups were included into calculated positions; the torsional angle was allowed to refine. All hydrogen atoms that are attached to the Y₄-fragment were located in a Fourier difference map and were refined in their positions with isotropic thermal parameters. $R_1 = 0.0456$, $wR_2 = 0.1040$ (obsd. data), goodness-of-fit on $F^2 = 0.959$; residual electron density (max/min) 1.211/-0.786 e Å⁻³. For the graphical representation, ORTEP-III for Windows was used as implemented in the program system WINGX [19].

Crystallographic data for the structure have been deposited with the Cambridge Data Centre. Copies of the data can be obtained free of charge on application The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; email: teched@chemcrys.cam.ac.uk).

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