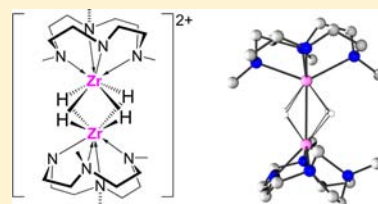


Cationic Zirconium Hydrides Supported by an NNNN-Type Macrocyclic Ligand: Synthesis, Structure, and Reactivity

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Supporting Information

ABSTRACT: An air- and light-sensitive, but thermally stable tris[(trimethylsilyl)methyl]zirconium complex containing an NNNN-type macrocyclic ligand [Zr(Me₃TACD)(CH₂SiMe₃)₃] (**1**; Me₃TACD = Me₃[12]aneN₄: 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane) was prepared by reacting [Zr(CH₂SiMe₃)₄] with (Me₃TACD)H. Reaction of the zirconium tris(alkyl) **1** with a Lewis or Brønsted acid gave a dialkyl cation with a weakly coordinating anion [Zr(Me₃TACD)(CH₂SiMe₃)₂][A] [A = Al{OC(CF₃)₃}₄ (**2a**), B{3,5-C₆H₃(CF₃)₂}₄ (**2b**), B(3,5-C₆H₃Cl₂)₄ (**2c**), and BPh₄) (**2d**)]. Hydrogenolysis of **2a–2c** resulted in the formation of the dinuclear tetrahydride dication [Zr(Me₃TACD)(μ-H)₂]₂[A]₂ (**3a–3c**). Compounds **1–3** were characterized by multinuclear NMR spectroscopy, and the solid-state structures of **1**, **2c**, and **3b** were established by single-crystal X-ray diffraction studies. The dinuclear hydride complex **3b** exhibits a quadruply bridged {Zr₂(μ-H)₄} core in solution and in the solid state with a relatively short Zr...Zr distance of 2.8752(11) Å. Density functional theory computations at the B3PW91 level reproduced this structure (Zr...Zr distance of 2.900 Å). The cationic hydride complex **3b** reacted with excess carbon monoxide in tetrahydrofuran at room temperature to give ethylene in 25% yield based on **3b**. Upon analysis of ¹³C NMR spectra of the reaction mixture using ¹³CO, oxymethylene and enolate complexes were detected as intermediates among other complexes.

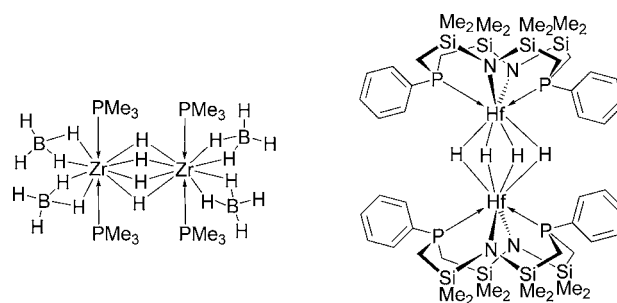


INTRODUCTION

The first molecular hydride complex of zirconium was reported in 1970 by Wailes and Weigold.¹ Since then, metallocene hydride complexes [Zr(η⁵-C₅H₄R)₂H(μ-H)]₂ with R = CH₃,² C(CH₃)₃,³ and Si(CH₃)₃⁴ have been intensely studied, including the “latent hydrides” tetrahydridoborate⁵ and hydridoaluminate⁶ complexes. In particular, decamethylzirconocene dihydride [Zr(η⁵-C₅Me₅)₂H₂] introduced by Bercaw et al. played a pioneering role in elucidating the reactivity patterns of molecular early-transition-metal hydrides.⁷ Although cationic group 4 complexes are thought to be the active species in homogeneous olefin polymerization and hydrogenation catalysis, only a few cationic hydride complexes, in particular those without cyclopentadienyl ligands, have been structurally authenticated so far.^{5a–c,8–10} Apart from complexes with terminal⁸ as well as with a single and a double hydride bridge,^{2–4,5a,c,d,8b,9} a number of triply bridged hydride complexes with a variety of noncyclopentadienyl ancillary ligands are known.^{5a,d,10} While only recently has a cationic triply bridged hydride complex been reported,^{10b} examples of dinuclear complexes with quadruply bridged hydrides [Zr{(μ-H)₂BH₂}₂(PMe₃)₂]₂(μ-H)₄^{5b} and [Zr{(P₂N₂)M}₂(μ-H)₄][P₂N₂ = PhP(CH₂SiMe₂NSiMe₂CH₂)₂PPh]; M = Zr, Hf] are limited so far to neutral species (Chart 1).¹¹

We report here on the first example of cationic zirconium complexes with quadruple hydride bridges that are supported by the monoanionic NNNN-type macrocyclic ligand, (Me₃TACD)[−] derived from 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane (Me₃TACD)H (Me₃[12]aneN₄).¹² This L₃₊₁X-type or 10-electron-donor ligand has previously been used to

Chart 1. Group 4 Metal Complexes with Quadruple Hydride Bridges



stabilize a series of Lewis base-free rare-earth metal alkyl and hydride compounds^{12a,c,d} as well as some alkaline-earth metal compounds.^{12b,e,f} We hypothesized that Me₃TACD would also be a suitable ligand to support cationic zirconium alkyl and hydride fragments. The cationic charge and the absence of bulky electron-rich cyclopentadienyl ancillary ligands were surmised to increase the electrophilicity and thus reactivity of the zirconium hydride.

RESULTS AND DISCUSSION

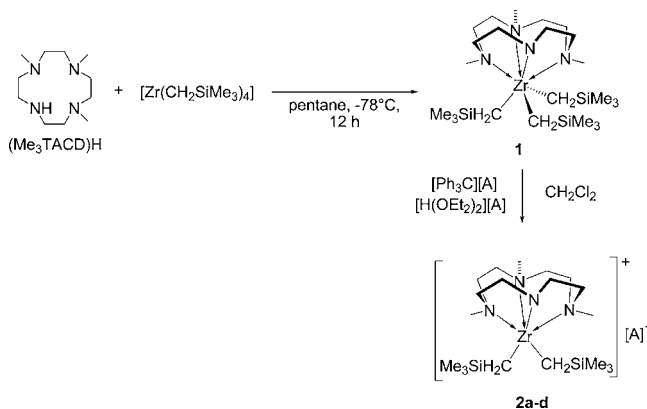
Synthesis and Characterization of [Zr(Me₃TACD)(CH₂SiMe₃)₃] (1**) and [Zr(Me₃TACD)(CH₂SiMe₃)₂][A] (**2a–2d**).** The solvent-free tris[(trimethylsilyl)methyl] complex **1**

Received: August 28, 2012

Published: October 31, 2012

was prepared by reacting thermally stable and air-, moisture-, and light-sensitive $[\text{Zr}(\text{CH}_2\text{SiMe}_3)_4]^{13}$ with $(\text{Me}_3\text{TACD})\text{H}$ (Scheme 1) and isolated as a thermally stable but still air-, moisture-, and light-sensitive compound. **1** was characterized by NMR spectroscopy and single-crystal X-ray diffraction.

Scheme 1. Synthesis of **1 and **2a–2d**^a from $[\text{Zr}(\text{CH}_2\text{SiMe}_3)_4]$ and $(\text{Me}_3\text{TACD})\text{H}$**



^a $[\text{Zr}(\text{Me}_3\text{TACD})(\text{CH}_2\text{SiMe}_3)_2][\text{A}]$, where $\text{A} = \text{Al}\{\text{OC}(\text{CF}_3)_3\}_4$ (**2a**), $\text{B}\{3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2\}_4$ (**2b**), $\text{B}\{3,5\text{-C}_6\text{H}_3\text{Cl}_2\}_4$ (**2c**), and BPh_4 (**2d**).

The ^1H NMR spectrum of **1** in a benzene- d_6 solution shows C_s symmetry. Broad resonances for the CH_2CH_2 groups at ambient temperature indicate fluxional behavior, which was studied by variable-temperature ^1H NMR spectroscopy in toluene- d_8 (Figure 1). Between -40 and -60 °C, four sharp as well as two broad resonances for the CH_2CH_2 groups of Me_3TACD are observed. The four sharp resonances can be

assigned to the axial and equatorial protons and can be explained by a slow exchange process between the two macrocyclic $\lambda\delta\delta\delta$ and $\delta\lambda\lambda\lambda$ ring conformations on the NMR time scale.^{12a,d} Lowering the temperature to -80 °C results in the broadening of all resonances.

Single crystals suitable for X-ray diffraction studies were obtained by the slow evaporation of a saturated cyclohexane solution at room temperature. The coordination geometry around the seven-coordinate zirconium atom can be described as capped trigonal prismatic (Figure 2). Three carbon atoms (C12, C16, and C20) and three nitrogen atoms (N1, N3, and N4) constitute two faces of the prism, and N2 caps one side. The Zr1–C distances are similar [Zr1–C12 = 2.3230(15) Å, Zr1–C16 = 2.2995(14) Å, and Zr1–C20 = 2.3680(15) Å] and in the expected range of Zr–C bonds [2.215(9)–2.640(5) Å].¹⁴ The Zr1–N1 distance [2.1224(13) Å] is significantly shorter than the zirconium–amino distances [Zr1–N2 = 2.6639(13) Å, Zr1–N3 = 2.5628(13) Å, and Zr1–N4 = 2.6335(14) Å]. Both are in the expected range of the corresponding Zr–N distances [2.063–2.192 Å for Zr–N(amido)]^{15b–d,16} and 2.414–2.977 Å for Zr–N(amine)¹⁵] for polydentate ligands with amine and amido donors. The Me_3TACD ligand is distorted due to the sp^2 -hybridized amido nitrogen atom (sum of the C–N1–C and C–N1–Zr1 angles: 359.7°), resulting in a coplanar orientation of the five atoms [C–C–N(sp^2)–C–C] around the amido nitrogen atom.^{12a,b} Calculating the available cavity radii [$r(\text{H})_{\text{cavity}}$]¹⁷ from the distances determined crystallographically gives the same size as that in the hydrochloride salt $[(\text{Me}_3\text{TACD})\text{H}]\text{Cl}$ [$r(\text{H})_{\text{cavity}} = 1.244$ Å].^{12c} The size of the macrocyclic ligand cavity forces the metal to sit below the macrocyclic ligand. The distance between Zr1 and the mean plane formed by the nitrogen atoms N1–N4 is 1.4926(7) Å.

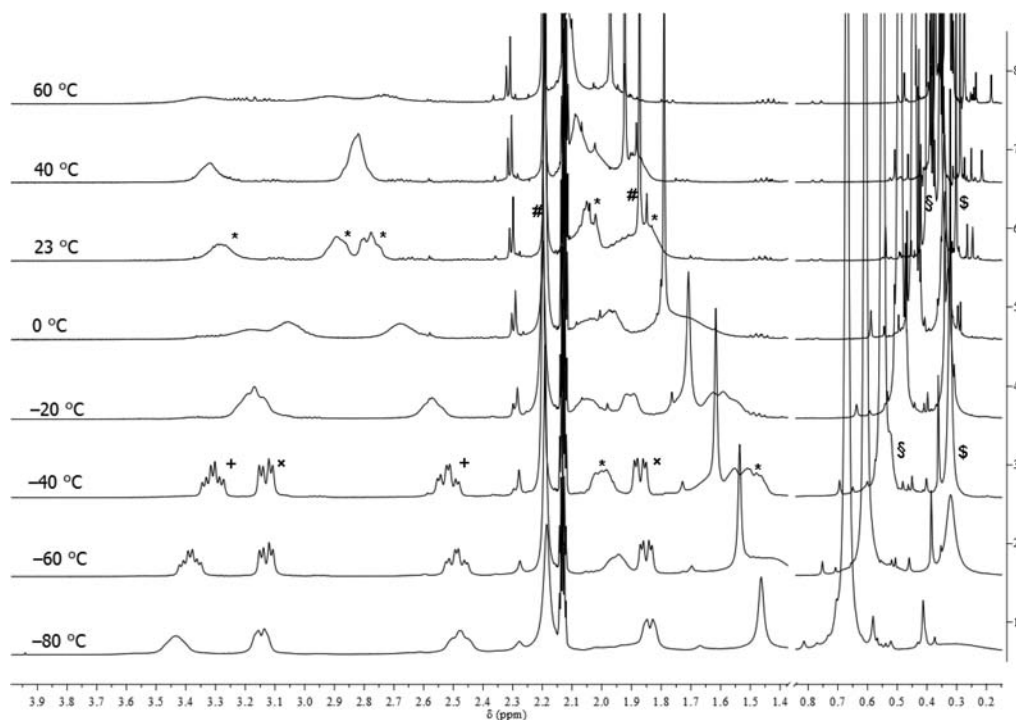


Figure 1. Variable-temperature ^1H NMR spectra of **1** in toluene- d_8 : resonances for CH_2CH_2 protons (*) split into resonances of the axial (x) and equatorial protons (+); resonances for the methyl groups (#) of Me_3TACD ; the methyl (\$) and CH_2 groups (\$) of the (trimethylsilyl)methyl groups.

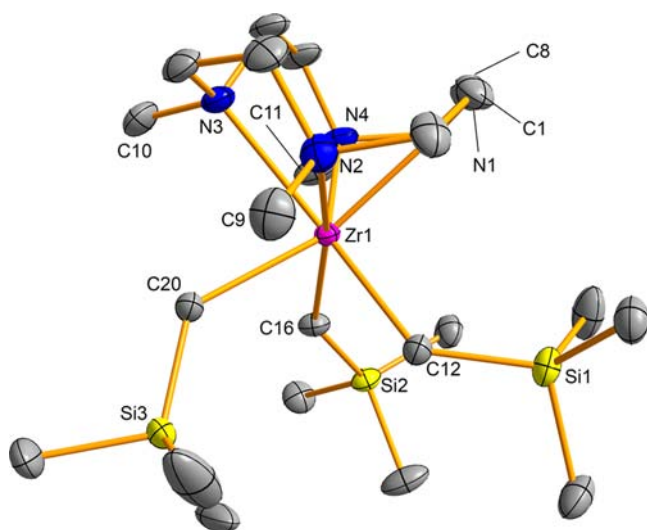


Figure 2. ORTEP drawing of the molecular structure of **1**. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Zr1–N1 2.1224(13), Zr1–N2 2.6639(13), Zr1–N3 2.5628(13), Zr1–N4 2.6335(14), N_{4-plane}...Zr1 1.4926(7), Zr1–C12 2.3230(15), Zr1–C16 2.2995(14), Zr1–C20 2.3680(15); N1–Zr1–N3 86.12(5), N2–Zr1–N4 120.49(4). $r(\text{H})_{\text{cavity}} = 1.244$ Å; $\Sigma(\text{C} - \text{N1} - \text{C}/\text{Zr1}) = 359.7^\circ$.

One of the (trimethylsilyl)methyl groups in **1** can be abstracted with either $[\text{Ph}_3\text{C}][\text{A}]$ or $[\text{H}(\text{OEt}_2)_2][\text{A}]$ ($\text{A} = \text{Al}\{\text{OC}(\text{CF}_3)_3\}_4$, $\text{B}\{3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2\}_4$, $\text{B}\{3,5\text{-C}_6\text{H}_3\text{Cl}_2\}_4$, and BPh_4) to give $[\text{Zr}(\text{Me}_3\text{TACD})(\text{CH}_2\text{SiMe}_3)_2][\text{A}]$ ($\text{A} = \text{Al}\{\text{OC}(\text{CF}_3)_3\}_4$ (**2a**), $\text{B}\{3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2\}_4$ (**2b**), $\text{B}\{3,5\text{-C}_6\text{H}_3\text{Cl}_2\}_4$

(**2c**), BPh_4 (**2d**); Scheme 1). With the exception of **2d**, these complexes are soluble in polar, aprotic solvents such as dichloromethane (DCM), 1,2-difluorobenzene, 1,2-dichlorobenzene, and tetrahydrofuran (THF) but not in hydrocarbons. **2d** is only slightly soluble in DCM and THF.

The ^1H NMR spectra of the cations show C_s symmetry in CD_2Cl_2 . The resonances of the CH_2CH_2 groups of the ligand at ambient temperature are sharp and allow for discrimination between the axial and equatorial protons. This indicates a rigid conformation in solution and a stronger interaction of the Me_3TACD ligand with the metal center than in the neutral complex **1**.

Single crystals of **2c** suitable for single-crystal X-ray diffraction experiments were obtained by diffusion of pentane into a 1,2-difluorobenzene solution. The crystal structure of **2c** contains disordered ligands within the complex cation. This disorder was modeled with split positions for each carbon and nitrogen atom. The occupancy factors for all atoms involved were close to 0.5. Attempted refinement with anisotropic displacement parameters led to physically meaningless values, but these atoms could be refined with isotropic displacement parameters. Because of disorder in the crystal associated with low values for R_{int} and R_σ as well as poor refinement parameters (Table 1), details on interatomic distances and angles in **2c** are not discussed. **2c** crystallizes as a separated ion pair without any close interaction or coordination of the counterion with the cationic zirconium center (see the Supporting Information, SI).¹⁸ The zirconium atom in **2c** is six-coordinate, bonded to two carbon atoms and four nitrogen atoms (Figure 3). The coordination geometry around the metal center can be described as a distorted trigonal prism. Two nitrogen atoms and one carbon atom (N1A, N2A, C12A and N3A, N4A,

Table 1. Crystallographic and Refinement Data^{a,b} for **1**, **2c**, **3b**, and **4b**

	1	2c	3b	4b
formula	$\text{C}_{23}\text{H}_{58}\text{N}_4\text{Si}_3$	$\text{C}_{19}\text{H}_{47}\text{N}_4\text{Si}_2\text{Zr}\cdot\text{C}_{24}\text{H}_{12}\text{BCl}_8$	$\text{C}_{22}\text{H}_{34}\text{N}_8\text{Zr}_2\cdot 2\text{C}_{32}\text{H}_{12}\text{BF}_{24}$	$\text{C}_{26}\text{H}_{62}\text{N}_8\text{SiZr}_2\cdot 2\text{C}_{32}\text{H}_{12}\text{BF}_{24}\cdot \text{C}_6\text{H}_{12}\cdot \text{C}_6\text{H}_4\text{F}_2$
fw, g/mol	566.22	1073.75	2339.62	2622.07
cryst size, mm	$0.25 \times 0.30 \times 0.36$	$0.06 \times 0.08 \times 0.33$	$0.01 \times 0.03 \times 0.35$	$0.15 \times 0.28 \times 0.32$
cryst syst	monoclinic	tetragonal	triclinic	monoclinic
space group	$\text{C}2/c$	$I 4_1cd$	$\bar{P}1$	$P 2_1/c$
T , K	130	100	100	100
a , Å	12.1670(9)	24.293(2)	13.658(3)	24.6582(17)
b , Å	17.0955(13)		17.059(4)	18.4059(13)
c , Å	30.775(13)	34.827(3)	20.564(3)	25.2129(18)
α , deg			94.157(4)	
β , deg	92.2364(11)		90.002(4)	106.717(2)
γ , deg			95.107(5)	
U , Å ³	6399.7(8)	20553(3)	4759.6(18)	10959.4(13)
Z	8	16	2	4
D_{calc} , mg/m ³	1.175	1.388	1.633	1.589
$F(000)$	2448	8864	2344	5296
θ range, deg	1.3–30.8	1.7–24.7	1.0–26.4	0.9–26.4
refns collected	46831	78510	56956	132363
indep refns (R_{int})	9432 (0.0550)	8772 (0.1540)	19473 (0.1174)	22449 (0.0997)
reflns obsd [$I > 2\sigma(I)$]	8262	5226	10385	13335
data/restraints/params	9432/0/292	8772/114/521	19473/0/1333	22449/41/1598
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0333, 0.0805	0.0740, 0.1670	0.0905, 0.2187	0.0730, 0.1972
$R1$, $wR2$ (all data)	0.0390, 0.0869	0.1179, 0.1875	0.1651, 0.2650	0.1221, 0.2297
GOF on F^2	1.075	0.921	1.038	0.995
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$, e/Å ³	0.722, –0.542	0.564, –0.329	2.188, –1.326	2.356, –1.072

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = \{ \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \}^{1/2}.$$

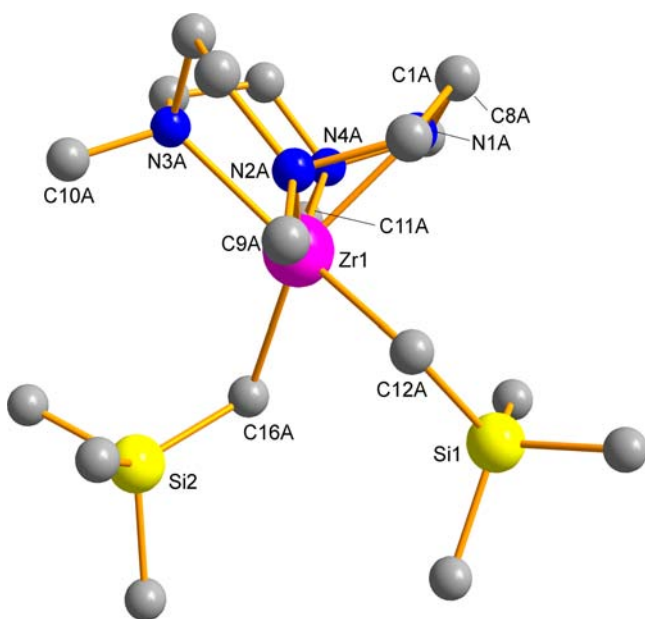
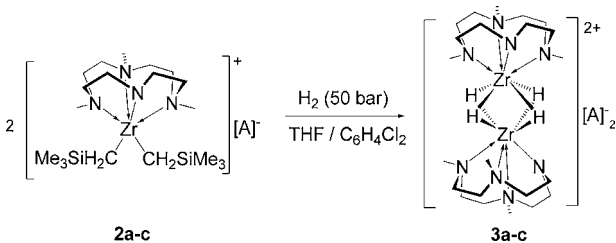


Figure 3. Ball-and-stick drawing of the molecular structure of the cationic part of **2c**. Only one of the split positions for the carbon and nitrogen atoms of the disordered ligands are shown. The counterion and hydrogen atoms are omitted for clarity.

C16A) constitute one face of the prism. The Me₃TACD ligand coordinates as in **1**. The structure can be compared to the isoelectronic, neutral rare-earth metal complexes of this macrocyclic ligand [M(Me₃TACD)(CH₂SiMe₃)₂] (M = Sc, Y, Lu).^{12a,d}

Synthesis and Characterization of [Zr(Me₃TACD)(μ-H)₂][A]₂ (3a–3c**).** When the bis[(trimethylsilyl)methyl] complexes **2a–2c** were treated with 50 bar of dihydrogen in THF or 1,2-dichlorobenzene at room temperature, the formation of the hydride complexes **3a–3c** were observed with concomitant formation of SiMe₄ (Scheme 2). When high

Scheme 2. Synthesis of **3a–3c** from **2a–2c**^a



^aA = Al{OC(CF₃)₃}₄⁺ (a), B{3,5-C₆H₃(CF₃)₂}₄⁺ (b), and B(3,5-C₆H₃Cl₂)₄⁺ (c).

pressure (50 bar) was applied to a solution of **2a–2c**, both (trimethylsilyl)methyl groups were cleaved at room temperature within 24 h and the dinuclear complexes **3a–3c** were obtained in good yield. ¹H NMR spectroscopy shows that **3a–3c** are stable in a THF solution for several months at room temperature.

When a lower hydrogen pressure (≈1 bar) was applied to a THF solution of **2a–2c**, complete conversion to give **3a–3c** took several days. Under these conditions, the dinuclear μ-alkylidene dihydride [(Me₃TACD)Zr(μ-CHSiMe₃)(μ-H)₂Zr(Me₃TACD)][B{3,5-C₆H₃(CF₃)₂}₄]₂ (**4b**) was formed from

2b and fully characterized (see the SI). Isolated **4b** was slowly converted to the tetrahydride **3b** over a period of 7 days. Formation of a similar dinuclear μ-benzylidene dihydride complex [{2,6-CH₂-4-MeC₆H₂OMe(2-^tBu-4-Me-C₆H₂O)}₂Zr₂(μ-H)₂(μ-CHPh)] with a bis(phenolate) ancillary ligand was reported to form upon hydrogenolysis of the dibenzyl complex [{2,6-CH₂-4-MeC₆H₂OMe(2-^tBu-4-Me-C₆H₂O)}Zr(CH₂Ph)₂].^{9e}

In the ¹H NMR spectra of **3a–3c**, the hydrides are observed as three triplets between δ 6.00 and 6.60 ppm with an integral ratio of 1:2:1. These three triplets, each with a different coupling constant (6.56 ppm, ¹J_{HH} = 16.6 Hz; 6.30 ppm, ¹J_{HH} = 14.7 Hz; 5.98 ppm, ¹J_{HH} = 13.0 Hz), are explained by two Me₃TACD ligands, which are orthogonal to each other in a dimeric structure (Figure 4). A NOESY experiment shows the close vicinity of the hydrides to each other and to the methyl groups of the macrocycle. The chemical shift difference of Δδ = 0.6 ppm between the hydride resonances is small compared to that of complexes bearing a {ZrH(μ-H)}₂ core such as [{Zr(η⁵-C₅H₄R)₂H(μ-H)}₂] [R = CH₃,² C(CH₃)₃,³ and Si(CH₃)₃,⁴ and related complexes.^{9h,i}], where a Δδ(H_{term},H_{brid}) value between 6.73 and 9.35 ppm is observed. With a decrease in the temperature to –40 °C, the hydride resonances are broadened (Figure 5). Above +40 °C, these resonances also become broad, but three different resonances can still be resolved. All four hydrides are exchanged against deuterium by treating **3c** with D₂ (1 bar) in a THF solution over a period of 48 h. A 1:1 mixture of **3b** and the tetradeuteride **3b**[D₄] does not give any scrambled products after 14 days at room temperature, suggesting the high stability of the dimeric structure in solution.

Single crystals of **3b** suitable for X-ray diffraction were obtained directly by treating a solution of **2b** in 1,2-dichlorobenzene with dihydrogen (50 bar). The molecular structure of **3b** was determined by single-crystal X-ray diffraction analysis (Figure 6). The data set is not good enough to draw closer conclusions about the hydride positions as reflected by the R_{int} value of 0.1174 as well as by the values for R1 and wR2 (Table 1). The Zr...Zr distance of 2.8752(11) Å is significantly shorter than that in other zirconium complexes with bridging hydrides (Figure 7). This compound represents a rare example for a compound with a {Zr(μ-H)₄Zr} core in the solid state.^{5b,9s} The two macrocyclic ligands are coplanar and twisted with respect to each other, as expressed by the N1–Zr1–Zr2–N5 torsion angle of 87.3(4)°, and the nitrogen atoms are nearly eclipsed. The distance of the four nitrogen atoms to the zirconium [N_{4-plane}...Zr = 1.181(3) and 1.200(3) Å] and the large angles of N1–Zr1–N3 and N5–Zr2–N7 [98.5(2)° and 97.0(2)°] are comparable to those in **2c**.

The bonding in **3b** was investigated using density functional theory (DFT) methods with focus on the nature of the hydrides and the Zr...Zr interaction. Geometry optimization of **3b** was carried out at the DFT(B3PW91) level. All geometrical parameters agree well with the structure that was found in the solid state. In particular, the experimental Zr...Zr distance of 2.8752(11) Å was reproduced with 2.899 Å within 0.024 Å, and the Zr–N1(amido) distances agree with a maximum deviation of 0.03 Å. This indicates that this method is suitable for describing cationic zirconium complexes. All attempts to locate structures with terminal hydrides failed, and only the structure with four bridging hydrides was obtained. Notably, the Wiberg indices (0.89) suggest a significant interaction between the two zirconium atoms. This interaction is also found at the natural bond order (NBO) level. The Lewis structure may be written

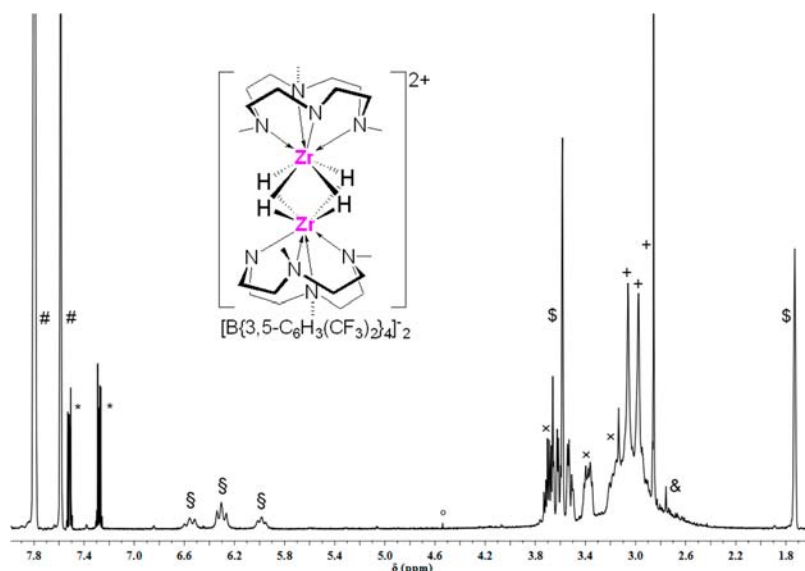


Figure 4. ^1H NMR spectrum of **3b** in $\text{THF-}d_8$ at 25 °C: ZrH ($\text{\$}$), dihydrogen (\textcirc), CH_2CH_2 (\times), methyl groups ($\text{\text{+}}$) of the Me_3TACD ligand, $\text{B}\{3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2\}_4$ (\#), $\text{THF-}d_8$ ($\text{\text{S}}$), traces of $1,2\text{-C}_6\text{H}_4\text{Cl}_2$ ($\text{\text{*}}$), and impurities (\&).

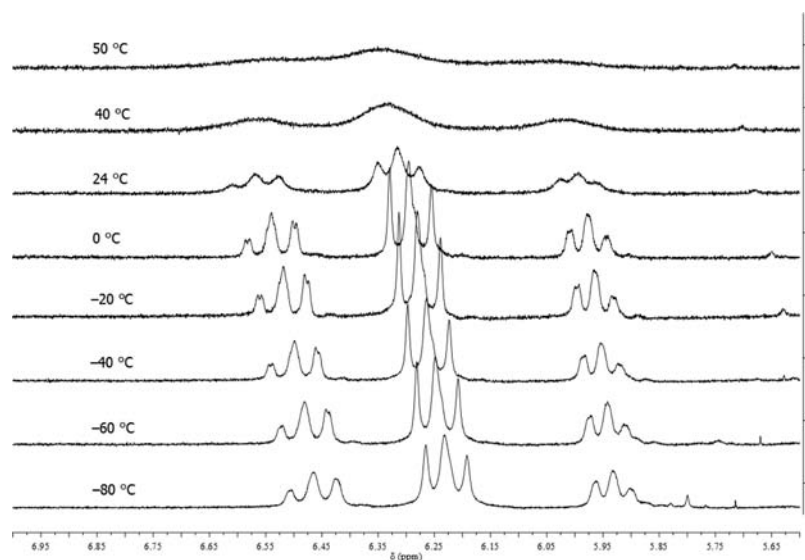


Figure 5. Variable-temperature ^1H NMR spectra of **3a** in $\text{THF-}d_8$. The hydride region between +50 and -80 °C is shown.

with four three-center Zr–H–Zr bonds involving bridging hydrogen atoms. Thereby, the d_z^2 orbital of each zirconium is partially filled (0.5 electron each), allowing some d–d interactions to be in agreement with the second-order NBO analysis. The stabilizing interaction of more than 40 kcal/mol seems to be crucial for the stability of this dinuclear complex. Similar interactions between two metals were reported in other transition-metal complexes, in particular $d^8\dots d^8$ interactions.²⁰ To the best of our knowledge, the compound presented here is the first example with this interaction between two d^0 metal centers.

Reactivity of 3a–3c toward Acetone and Carbon Monoxide (CO). According to ^1H NMR spectroscopic studies in $\text{THF-}d_8$, 2 equiv of acetone reacted with **3b** in THF at room temperature to form a dimeric isopropoxy hydride **5b**. This complex slowly reacted with more acetone to give **6b**. Although we do not know the nuclearity of both **5b** and **6b**, plausible structures are shown in Scheme 3. The ^1H NMR spectrum of

5b in $\text{THF-}d_8$ at ambient temperature shows a sharp singlet for the bridging hydrides at δ 5.28 ppm. As in **2b**, the resonances of the Me_3TACD ligand indicate C_s symmetry and a rigid geometry in solution. The isopropyl groups appear as a septet and a doublet at δ 4.44 and 1.26 ppm ($^3J_{\text{HH}} = 6.3$ Hz). **6b** was also obtained from **2b** and excess isopropyl alcohol. The ^1H NMR spectrum of **6b** shows broad resonances for the Me_3TACD ligand. The isopropyl groups appear as a septet and a doublet at δ 4.69 and 1.27 ppm ($^3J_{\text{HH}} = 6.3$ Hz). The methyl groups of the Me_3TACD ligand appear at δ 2.70 (s, 3H) and 2.60 (s, 6H) ppm. Analogous reactions of the deuteride **3b**[D_4] with acetone confirmed the formation of **5b**[D_4] and **6b**[D_2].

In the past, the reactivity of organometallic hydride complexes toward CO has been intensely studied in the context of model reactions for Fischer–Tropsch synthesis. Late-transition-metal hydrides react with CO to give formyl species $\text{MC}(\text{=O})\text{H}$,²¹ whereas early transition metals includ-

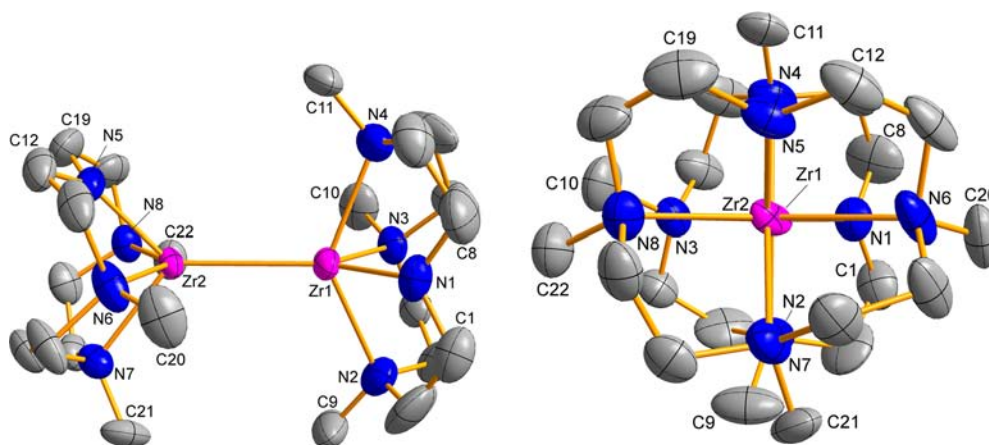


Figure 6. ORTEP drawings of the molecular structure of the cationic part of **3b**: (left) side view; (right) top view. Displacement ellipsoids are drawn at the 50% probability level; the counterions and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Zr1–Zr2 2.8752(11), Zr1–N1 2.109(7), Zr1–N2 2.373(7), Zr1–N3 2.287(6), Zr1–N4 2.382(7), Zr2–N5 2.063(6), Zr2–N6 2.394(6), Zr2–N7 2.350(6), Zr2–N8 2.369(6), $N_{4\text{-plane}2}$ –Zr2 1.200(3), $N_{4\text{-plane}1}$ –Zr1 1.181(3); N1–Zr1–N3 98.5(2), N5–Zr2–N7 97.0(2); N1–Zr1–Zr2–N5 87.3(4). $\Sigma(\text{C–N1–C}/\text{Zr1}) = 358.4^\circ$; $\Sigma(\text{C–N5–C}/\text{Zr2}) = 359.2^\circ$.

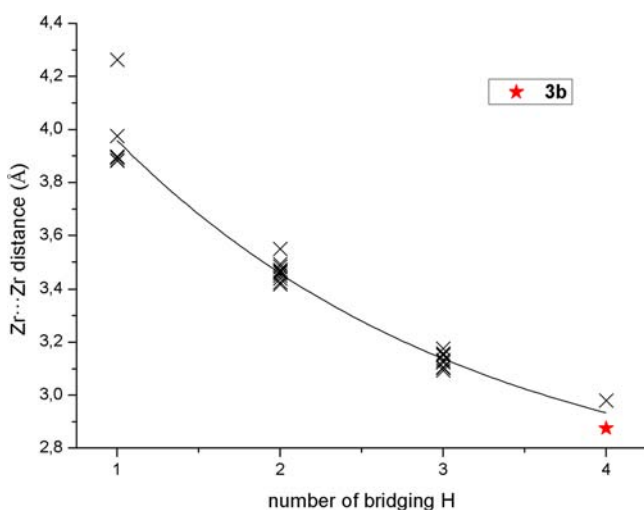
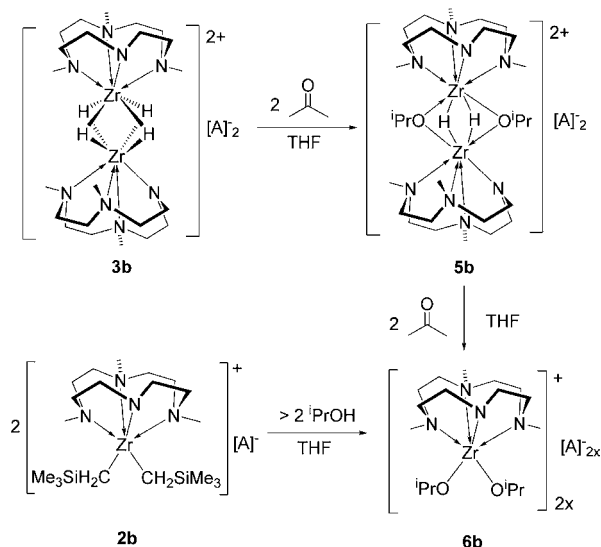


Figure 7. Plot of Zr...Zr distances against the number of bridging hydrides in dinuclear zirconium hydride complexes.¹⁹

Scheme 3. Reactions of **3b** with Acetone in THF-*d*₈



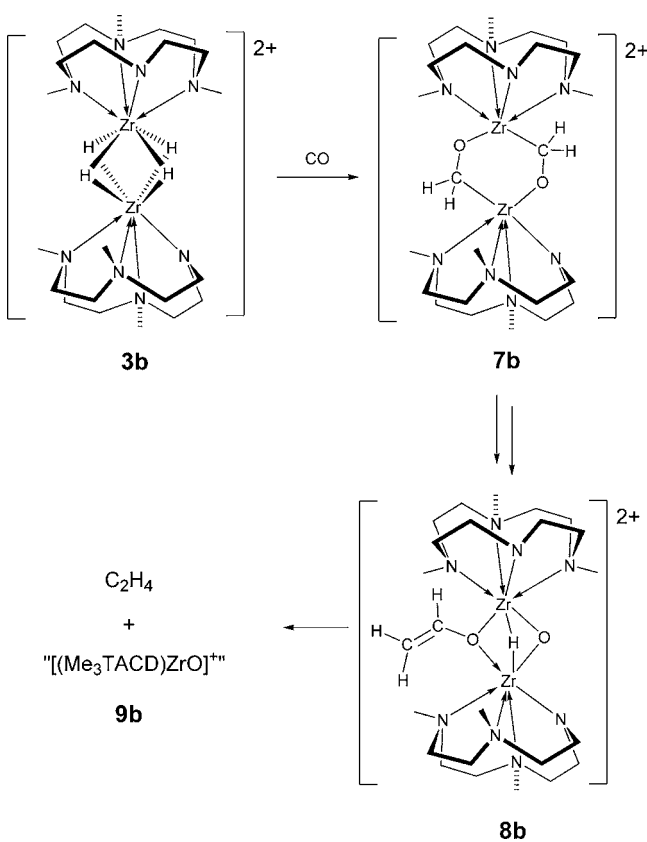
ing lanthanide and actinide hydrides form more reduced fragments such as oxymethylenes $\text{MOCH}_2\text{M}^{9e,22}$ and enediolates $\text{MOCH}=\text{CHOM}^{22a,23-26}$. A trimeric (η^2 -formaldehyde)-zirconocene complex formed when zirconocene dihydride $[\text{Cp}_2\text{ZrH}_2]_x$ was treated with CO.^{22b} More recently, tetranuclear yttrium dihydride $[\{\text{Cp}'\text{Y}(\mu\text{-H})_2\}_4(\text{THF})]$ ($\text{Cp}' = \text{C}_5\text{Me}_4\text{SiMe}_3$) was reported to react with CO to give ethylene via oxymethylene, enolate, and oxo hydride intermediates.²⁶

Upon treatment of **3b** with excess CO at room temperature, ethylene (^1H NMR, δ 5.36; $^{13}\text{C}\{^1\text{H}\}$ NMR, δ 123.4) was detected as the sole volatile product (0.25 equiv of ethylene per **3b**). Monitoring this reaction by ^1H and ^{13}C NMR spectroscopy using either CO or ^{13}CO in THF-*d*₈ at room temperature suggests the formation of ethylene via an oxymethylene^{22b} and an enolate²⁴⁻²⁶ intermediate (Scheme 4). Although the reaction mixture contained several other species (see the SI), resonances in the ^1H and ^{13}C NMR spectra were observed that could be assigned to the oxymethylene **7b** and an enolate hydride complex **8b**. The oxymethylene intermediate **7b** shows a diagnostic triplet in the ^{13}C NMR spectrum at δ 79.3 (t, $^1J_{\text{CH}} = 138.7$ Hz), and its concentration is at a maximum after 30 min. The NMR resonances of the enolate hydride **8b** [^1H NMR, δ 6.75 (dd, $^3J_{\text{HH}} = 13.9$ Hz, $^3J_{\text{HH}} = 5.8$ Hz), 4.31 (d, $^3J_{\text{HH}} = 13.9$ Hz), and 4.14 (d, $^3J_{\text{HH}} = 5.8$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR, δ 153.5 (d, $^1J_{\text{CC}} = 78.3$ Hz), 95.4 (d, $^1J_{\text{CC}} = 78.3$ Hz)] are comparable with those reported for other enolate complexes such as $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}(\text{OCH}=\text{CH}_2)]$,²⁴ $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Y}(\text{OCH}=\text{CH}_2)]$,²⁵ and $[(\text{Cp}'\text{Y})_4(\text{OCH}=\text{CH}_2)(\mu\text{-O})(\mu\text{-H})_3(\text{THF})]$ ($\text{Cp}' = \eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3$).²⁶ Apparently, **8b** formed from **7b** to give ethylene eventually in a reaction sequence similar to that established for $[(\text{Cp}'\text{Y})_4(\mu\text{-H})_8(\text{THF})]$.^{26b} All attempts at isolating any of these intermediates or the final oxo complex **9b** in pure form remained unsuccessful.

CONCLUSION

Hydrogenolysis of a cationic zirconium dialkyl complex supported by the macrocyclic ancillary ligand Me_3TACD led to the dicationic dinuclear tetrahydride complex with a $\{\text{Zr}_2(\mu\text{-H})_4\}$ core featuring a short Zr...Zr distance. The dicationic tetrahydride reacted with CO to give ethylene, albeit in low yield. The absence of bulky electron-rich cyclopentadienyl

Scheme 4. Suggested Formation of Ethylene from CO and 3b



ligands combined with the cationic charge significantly enhances the reactivity toward CO, comparable with that recently reported for rare-earth metal hydride complexes.^{25,26} Although the insertion reaction of CO into neutral zirconium hydride complexes has been studied intensely in the past,^{22–24} the reduction of CO to give ethylene has not been reported before, to the best of our knowledge. The reduction of CO to give ethylene is limited to the reaction of CO with [$\text{Cp}^*\text{Y}(\mu\text{-H})_2$] $(\text{THF})_2$,²⁶ alane (AlH_3) reduction of coordinated CO in [$\text{M}(\text{CO})_n$] ($\text{M} = \text{Cr}, \text{Mo}, \text{W}, \text{Ru}$),²⁷ and CO hydrogenation on the surface of $\text{ZrO}_2/\text{Al}_2\text{O}_3$.²⁸

EXPERIMENTAL SECTION

General Procedures. All manipulations were performed under an inert atmosphere of argon using a standard Schlenk-line or glovebox technique but in the dark by covering all glass vessels with aluminum foil. Hydrogenolysis reactions were performed in a Parr steel reactor (series 4700) with 50 bar pressure or in J. Young NMR tubes equipped with a Teflon valve with a maximum pressure of 1 bar. *n*-Pentane, tetrahydrofuran (THF), diethyl ether, and dichloromethane (DCM) were dried using a MBraun SPS-800 solvent purification system. Benzene- d_6 and THF- d_8 were distilled from sodium/benzophenone ketyl. CD_2Cl_2 and $1,2\text{-C}_6\text{D}_4\text{Cl}_2$ as well as the nondeuterated solvents 1,2-difluorobenzene and 1,2-dichlorobenzene were distilled from CaH_2 . Acetone was distilled several times from molecular sieves (4 Å). $(\text{Me}_3\text{TACD})\text{H}$,^{12c} [$\text{Zr}(\text{CH}_2\text{SiMe}_3)_4$],¹³ [Ph_3C][OTf],²⁹ [Ph_3C]-[B{3,5- $\text{C}_6\text{H}_3(\text{CF}_3)_2$ }]₄,³⁰ [Ph_3C][Al{OC(CF₃)₃}]₄,³¹ [Ph_3C]-[BPh₄],³² [H(OEt₂)₂][B{3,5- $\text{C}_6\text{H}_3(\text{CF}_3)_2$ }]₄,³³ and Na[B{3,5- $\text{C}_6\text{H}_3(\text{CF}_3)_2$ }]₄³⁴ were synthesized according to literature procedures. [Ph_3C][B{3,5- $\text{C}_6\text{H}_3(\text{CF}_3)_2$ }]₄ and [H(OEt₂)₂][B{3,5- $\text{C}_6\text{H}_3(\text{CF}_3)_2$ }]₄ were prepared analogously to related compounds.^{30,33}

NMR spectra were recorded on a Bruker Avance II spectrometer at 25 °C (¹H, 400.1 MHz; ¹³C{¹H}, 100.1 MHz; ¹¹B{¹H}, 128.4 MHz;

²⁷Al, 104.3 MHz). ¹⁹F NMR spectra were recorded on a Varian Mercury NMR spectrometer (¹⁹F, 188.1 MHz) or on a Bruker Avance II spectrometer (¹⁹F, 376.5 MHz). Chemical shifts for ¹H and ¹³C{¹H} NMR spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. ¹¹B, ¹⁹F, and ²⁷Al NMR spectra are referenced externally to a 1 M solution of NaBH₄ in D₂O, neat CFCl₃, and aqueous Al(NO₃)₃ solutions, respectively. Elemental analyses were performed by the microanalytical laboratory of this department. The analytical data for most complexes were consistently too low in carbon. This is likely due to metal carbide formation during combustion, and this phenomenon has been observed by other workers for related zirconium complexes.^{15a,16a,35,36}

The best values are reported.

[Zr(Me₃TACD)(CH₂SiMe₃)₃] (1). A solution of (Me₃TACD)H (700 mg, 3.27 mmol) in 30 mL of pentane was added at -78 °C to a solution of tetrakis(trimethylsilyl)methylzirconium (1.440 mg, 3.27 mmol) in 30 mL of pentane. The mixture was allowed to warm up and stirred for 12 h at room temperature. The product was filtered at -78 °C and washed three times with 10 mL of pentane. The crude product was recrystallized from pentane at -30 °C to afford colorless, light-sensitive microcrystals; yield 1.027 g (1.81 mmol, 55%). Single crystals suitable for X-ray diffraction studies were obtained by recrystallization from a cyclohexane solution.

¹H NMR (benzene- d_6): δ 3.26 (br s, 2H, NCH₂), 2.87 (br s, 2H, NCH₂), 2.75 (br s, 2H, NCH₂), 2.14 (s, 6H, NCH₃), 1.98 (br s, 5H, NCH₂), 1.80 (br s, 5H, NCH₂), 1.80 (s, 3H, NCH₃), 0.44 (s, 27H, SiCH₃), 0.38 (s, 6H, ZrCH₂). ¹³C{¹H} NMR (benzene- d_6): δ 58.16 (br s, NCH₂), 57.95 (s, NCH₃), 53.31 (br s, NCH₂), 52.63 (s, ZrCH₂), 49.24 (br s, NCH₂), 45.75 (s, NCH₃), 4.46 (s, SiCH₃). Anal. Calcd for C₂₃H₅₈N₄Si₃Zr: C, 48.79; H, 10.32; N, 9.89. Found: C, 46.89; H, 9.85; N, 9.88.

[Zr(Me₃TACD)(CH₂SiMe₃)₂][Al{OC(CF₃)₃}]₄ (2a). A solution of [Ph₃C][Al{OC(CF₃)₃}]₄ (500 mg, 413.0 μmol) in 10 mL of DCM was added to 1 (240.0 mg, 423.9 μmol) in 20 mL of DCM and the reaction mixture stirred for 1 h at room temperature. After removal of all volatiles under vacuum, the residue was suspended in pentane, filtered through a pad of glass fiber, and washed with pentane (3 \times 25 mL). After drying, an off-white solid was obtained; yield 440.0 mg (304.3 μmol , 74%).

¹H NMR (CD₂Cl₂): δ 3.69 (td, ³J_{HH} = 12.2 Hz, ³J_{HH} = 6.3 Hz, 2H, NCH₂), 3.40 (dd, ³J_{HH} = 13.9 Hz, ³J_{HH} = 6.2 Hz, 2H, NCH₂), 3.30 (m, 2H, NCH₂), 3.20 (m, 4H, NCH₂), 3.08 (dd, ³J_{HH} = 12.8 Hz, ³J_{HH} = 5.2 Hz, 2H), 2.88 (s, 6H, NCH₃), 2.79 (m, 6H, NCH₂), 2.66 (s, 3H, NCH₃), 0.74 (s, 4H, ZrCH₂), 0.08 (s, 18H, SiMe₃). ¹³C{¹H} NMR (CD₂Cl₂): δ 121.7 (q, ¹J_{CF} = 292.3 Hz, CF₃), 63.5 (s, ZrCH₂), 61.5 (s, NCH₂), 56.0 (s, NCH₂), 54.3 (s, NCH₂), 52.5 (s, NCH₂), 51.1 (s, NCH₃), 46.2 (s, NCH₃), 3.0 (s, SiMe₃). ¹³C NMR (101 MHz, CD₂Cl₂): δ 63.5 (t, ¹J_{CH} = 104.0 Hz, ZrCH₂). ²⁷Al NMR (CD₂Cl₂): δ -34.7. ¹⁹F NMR (188.1 MHz, CD₂Cl₂): δ -73.8. Anal. Calcd for C₃₅H₄₇AlF₃₆N₄O₄Si₂Zr: C, 29.07; H, 3.28; N, 3.87. Found: C, 28.74; H, 2.91; N, 4.19.}}}}}}}}

[Zr(Me₃TACD)(CH₂SiMe₃)₂][B{3,5- $\text{C}_6\text{H}_3(\text{CF}_3)_2$ }]₄ (2b). A solution of trityl tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1.940 g 1.75 mmol) in 25 mL of DCM was slowly added to a solution of 1 (1.000 g 1.77 mmol) in 25 mL of DCM. The reaction mixture was stirred for 3 h at room temperature. After removal of all volatiles under vacuum, the solid residue was suspended in 80 mL of pentane, filtered through a pad of glass fiber, washed with pentane, and dried under reduced pressure for 24 h to give an off-white powder; yield 2.075 g (1.55 mmol, 87.5%). Alternatively, [H(OEt₂)₂][B{3,5- $\text{C}_6\text{H}_3(\text{CF}_3)_2$ }]₄ in CD₂Cl₂ was used to generate 2b.

¹H NMR (CD₂Cl₂): δ 7.73 (br t, ⁴J_{HF} = 2.4 Hz, 8H, BPh-2), 7.58 (s, 4H, BPh-4), 3.67 (td, ³J_{HH} = 12.2 Hz, ³J_{HH} = 6.4 Hz, 2H, NCH₂), 3.38 (dd, ³J_{HH} = 14.0 Hz, ³J_{HH} = 6.3 Hz, 2H, NCH₂), 3.21 (m, 4H, NCH₂), 3.05 (dd, ³J_{HH} = 12.7 Hz, ³J_{HH} = 5.2 Hz, 2H, NCH₂), 2.86 (s, 6H, NCH₃), 2.75 (m, 6H, NCH₂), 2.63 (s, 3H, NCH₃), 0.73 (s, 4H, ZrCH₂), 0.08 (s, 18H, SiCH₃). ¹³C{¹H} NMR (CD₂Cl₂): δ 162.2 (q, ¹J_{BC} = 50.0 Hz, BPh-1), 135.3 (s, BPh-2), 129.3 (m, BPh-3), 125.1 (q, ¹J_{CF} = 273.8 Hz, CF₃), 117.9 (m, BPh-4), 63.6 (s, ZrCH₂), 61.5 (s,}}}}}}}}}

NCH₂), 56.0 (s, NCH₂), 54.3 (s, NCH₂), 52.5 (s, NCH₂), 51.1 (s, NCH₂), 46.2 (s, NCH₃), 3.0 (s, SiMe₃). ¹¹B NMR (CD₂Cl₂): δ -6.60 (s). ¹⁹F NMR (188 MHz, CD₂Cl₂): δ -60.91 (s). Anal. Calcd for C₅₁H₅₉BF₂₄N₄Si₂Zr: C, 45.64; H, 4.43; N, 4.17. Found: C, 43.25; H, 3.64; N, 4.35.

[Zr(Me₃TACD)(CH₂SiMe₃)₂][B(3,5-C₆H₃Cl₂)₄] (**2c**). A solution of trityl tetrakis(3,5-dichlorophenyl)borate (1.470 g 1.75 mmol) in 25 mL of DCM was slowly added to a solution of **1** (1.000 g 1.77 mmol) in 25 mL of DCM. The reaction mixture was stirred at room temperature for 3 h. All volatiles were removed under reduced pressure, and the resulting solid residue was suspended in pentane, filtered, and washed with pentane (3 × 40 mL). The crude product was dried under reduced pressure for 72 h to remove traces of pentane. An off-white powder was obtained; yield 1.660 g (1.55 mmol, 87.6%). Single crystals suitable for X-ray analysis were obtained by diffusion of pentane into a 1,2-difluorobenzene solution of the compound.

¹H NMR (CD₂Cl₂): δ 7.04 (m, 8H, BPh-2), 7.02 (m, 4H, BPh-4), 3.60 (td, ³J_{HH} = 12.3 Hz, ³J_{HH} = 6.3 Hz, 2H, NCH₂), 3.32 (dd, ³J_{HH} = 14.0 Hz, ³J_{HH} = 6.3 Hz, 2H, NCH₂), 3.19 (m, 2H, NCH₂), 3.03 (m, 3H, NCH₃), 2.98 (dd, ³J_{HH} = 12.7 Hz, ³J_{HH} = 5.2 Hz, 2H, NCH₂), 2.79 (s, 6H, NCH₃), 2.62 (m, 5H, NCH₂), 2.54 (s, 3H, NCH₃), 0.68 (s, 4H, ZrCH₂), 0.07 (s, 18H, SiCH₃). ¹³C{¹H} NMR (CD₂Cl₂): δ 165.1 (q, ¹J_{BC} = 48.9 Hz, BPh-1), 133.5 (d, ²J_{BC} = 1.8 Hz, BPh-2), 133.4 (q, ³J_{BC} = 4.0 Hz, BPh-3), 123.6 (s, Ph-4), 63.1 (s, ZrCH₂), 61.4 (s, NCH₂), 55.9 (s, NCH₂), 54.2 (s, NCH₂), 52.4 (s, NCH₂), 51.0 (s, NCH₃), 46.1 (s, NCH₃), 3.1 (s, SiCH₃). ¹¹B NMR (CD₂Cl₂): δ -6.95 (s). Anal. Calcd for C₄₃H₅₉BCl₈N₄Si₂Zr: C, 48.10; H, 5.54; N, 5.22. Found: C, 45.93; H, 4.75; N, 5.21.

[Zr(Me₃TACD)(CH₂SiMe₃)₂][BPh₄] (**2d**). A solution of trityl tetraphenylborate (250.0 mg 0.444 mmol) in 20 mL of DCM was slowly added to a solution of **1** (252.0 mg, 0.445 mmol) in 20 mL of DCM. The mixture was stirred at room temperature for 3 h. All volatiles were removed under vacuum, and the resulting solid residue was suspended in pentane, filtered through a glass fiber, and washed with pentane (3 × 40 mL). After drying, a colorless solid was obtained; yield 281.0 mg (0.352 mmol, 79%).

¹H NMR (CD₂Cl₂): δ 7.32 (br d, ³J_{HH} = 1.5 Hz, 8 H, BPh-2), 7.04 (t, ³J_{HH} = 7.4 Hz, 8H, BPh-3), 6.90 (t, ³J_{HH} = 7.2 Hz, 4H, BPh-4), 3.50 (td, ³J_{HH} = 12.3 Hz, ³J_{HH} = 6.4 Hz, 2H, NCH₂), 3.26 (dd, ³J_{HH} = 14.0 Hz, ³J_{HH} = 6.4 Hz, 2H, NCH₂), 3.14 (m, 2H, NCH₂), 2.89 (dd, ³J_{HH} = 12.6 Hz, ³J_{HH} = 5.3 Hz, 4H, NCH₂), 2.76 (m, 4H, NCH₂), 2.70 (s, 6H, NCH₃), 2.40 (m, 2H, NCH₂), 2.36 (s, 3H, NCH₃), 0.58 (s, 4H, ZrCH₂), 0.04 (s, 18H, SiCH₃). ¹³C{¹H} NMR (MHz, CD₂Cl₂): δ 164.4 (q, ¹J_{BC} = 49.1 Hz, BPh-1), 136.4 (d, ²J_{BC} = 1.5 Hz, BPh-2), 126.1 (q, ³J_{BC} = 2.8 Hz, BPh-3), 122.3 (s, Ph-4), 62.1 (s, ZrCH₂), 61.2 (s, NCH₂), 55.6 (s, NCH₂), 52.4 (s, NCH₂), 50.9 (s, NCH₃), 45.9 (s, NCH₃), 3.1 (s, SiCH₃). ¹¹B NMR (CD₂Cl₂): δ -6.65 (s). Anal. Calcd for C₄₃H₆₇BN₄Si₂Zr: C, 64.70; H, 8.46; N, 7.02. Found: C, 60.18; H, 7.46; N, 7.55.

[Zr(Me₃TACD)(μ-H)₂][Al(OC(CF₃)₃)₄] (**3a**). A solution of **2a** (500 mg, 0.346 μmol) in 3 mL of THF was treated with 50 bar of hydrogen in a microreactor for 72 h. The yellow solution was filtered, all volatiles were removed under reduced pressure, and the residue was washed with pentane (2 × 5 mL) and dried for 10 min. The crude product was suspended in 20 mL of benzene for 20 min, filtered, washed with pentane (4 × 10 mL), and gently dried for 10 min. Yellow microcrystals were obtained; yield 240 mg (0.0942 μmol, 54.5%).

¹H NMR (THF-*d*₈): δ 6.55 (t, ¹J_{HH} = 16.3 Hz, 1H, ZrH), 6.32 (t, ¹J_{HH} = 14.4 Hz, 2H, ZrH), 5.99 (t, ¹J_{HH} = 14.0 Hz, 1H, ZrH), 3.71 (m, 5H, NCH₂), 3.60 (m, 5H, NCH₂), 3.40 (m, 7H, NCH₂), 3.19 (m, 10H, NCH₂), 3.07 (s, 6H, NCH₃), 3.04 (m, 5H, NCH₂), 2.99 (s, 6H, NCH₃), 2.86 (s, 6H, NCH₃). ¹³C{¹H} NMR (THF-*d*₈): δ 122.3 (q, ¹J_{CF} = 290.8 Hz, CF₃), 63.8 (s, NCH₂), 63.5 (s, NCH₂), 57.7 (s, NCH₂), 55.7 (s, NCH₂), 54.9 (s, NCH₃), 54.2 (s, NCH₂), 53.9 (s, NCH₂), 53.7 (s, NCH₃), 47.5 (s, NCH₃). ²⁷Al NMR (THF): δ 32.71 (s). ¹⁹F NMR (188 MHz, THF-*d*₈): δ -72.27 (s). Anal. Calcd for C₆₂H₇₀AlF₇₂N₈O₁₀Zr₂: C, 27.67; H, 2.62; N, 4.16. Found: C, 26.15; H, 2.39; N, 4.42.

[Zr(Me₃TACD)(μ-H)₂][B(3,5-C₆H₃(CF₃)₂)₄] (**3b**). A solution of **2b** (1.000 g, 745 μmol) in 3 mL of THF was treated with 50 bar of hydrogen in a microreactor for 24 h. The solution was filtered, carefully dried (*p* ~ 1 × 10⁻¹ mbar), and washed with pentane to give a yellow oil. The addition of 2 mL of benzene led to precipitation of a yellow solid, which was washed with pentane and dried briefly to give yellow microcrystals; yield 650 mg (262 μmol, 70%). Alternative method: A solution of **2b** (600 mg, 447 μmol) in 3 mL of 1,2-dichlorobenzene was treated with 50 bar of hydrogen in a microreactor for 24 h. A total of 5 mL of pentane was added to the reaction mixture. The solvent was decanted, and the yellow residue was dried under an argon atmosphere in the glovebox to afford a yellow powder; yield 499.7 mg (213.6 μmol, 96%).

¹H NMR (THF-*d*₈): δ 7.80 (br t, ⁴J_{HF} = 2.5 Hz, 16H, BPh-2), 7.59 (br s, 8H, BPh-4), 6.56 (t, ¹J_{HH} = 16.6 Hz, 1H, ZrH), 6.31 (t, ¹J_{HH} = 14.5 Hz, 2H, ZrH), 5.99 (t, ¹J_{HH} = 13.1 Hz, 1H, ZrH), 3.66 (m, 8H, NCH₂), 3.38 (m, 6H, NCH₂), 3.15 (m, 12H, NCH₂), 3.06 (s, 6H, NCH₃), 2.98 (s, 6H, NCH₃), 2.88 (s, 6H, NCH₃), 2.76 (m, 6H, NCH₂). ¹³C{¹H} NMR (THF-*d*₈): δ 162.9 (q, ¹J_{BC} = 49.9 Hz, BPh-1), 135.7 (s, BPh-2), 130.1 (qq, ²J_{CF} = 31.4 Hz, ³J_{BC} = 2.6 Hz, BPh-3), 125.6 (q, ¹J_{CF} = 273.6 Hz, CF₃), 118.3 (dt, ³J_{CF} = 7.7 Hz, ⁴J_{BC} = 3.8 Hz, BPh-4), 71.4 (s, NCH₂), 63.7 (s, NCH₂), 63.4 (s, NCH₂), 57.7 (s, NCH₂), 56.0 (s, NCH₂), 55.7 (s, NCH₂), 54.9 (s, NCH₃), 54.2 (s, NCH₂), 53.9 (s, NCH₃), 53.6 (s, NCH₂), 49.1 (s, NCH₂), 47.9 (s, NCH₂), 47.7 (s, NCH₂), 47.5 (s, NCH₃). ¹¹B NMR (THF-*d*₈): δ -8.36 (s). ¹⁹F NMR (188 MHz, THF-*d*₈): δ -59.76 (s). Anal. Calcd for C₈₆H₇₈B₂F₄₈N₈Zr₂: C, 44.15; H, 3.36; N, 4.79. Found: C, 43.23; H, 3.16; N, 4.54.

[Zr(Me₃TACD)(μ-H)₂][B(3,5-C₆H₃Cl₂)₄] (**3c**). A solution of **2c** (250 mg, 233 μmol) in 3 mL of THF was treated with 50 bar of hydrogen in a microreactor for 24 h. The reaction mixture was filtered. Diethyl ether was allowed to diffuse into the THF solution to give yellow crystals; yield 146 mg (75.0 μmol, 64.4%). Solvent-free crystals were obtained by diffusion of diethyl ether into a THF/diglyme solution.

¹H NMR (THF-*d*₈): δ 7.04 (m, 16H, BPh-2), 7.01 (t, ⁴J_{HH} = 2.0 Hz, 8H, BPh-4), 6.47 (t, ¹J_{HH} = 16.4 Hz, 1H, ZrH), 6.23 (t, ¹J_{HH} = 14.7 Hz, 2H, ZrH), 5.92 (t, ¹J_{HH} = 12.6 Hz, 1H, ZrH), 3.52 (m, 10H, NCH₂), 3.31 (m, 6H, NCH₂), 3.04 (m, 8H, NCH₂), 3.97 (s, 6H, NCH₃), 2.91 (s, 6H, CH₃), 2.75 (s, 6H, CH₃), 2.65 (m, 8H, NCH₂). ¹³C{¹H} NMR (THF-*d*₈): δ 165.7 (q, ¹J_{BC} = 49.5 Hz, BPh-1), 134.1 (d, ²J_{BC} = 1.3 Hz, BPh-2), 133.9 (m, BPh-4), 124.0 (s, BPh-3), 63.8 (br s, NCH₂), 63.4 (br s, NCH₂), 60.9 (s, NCH₂), 57.7 (s, NCH₂), 57.1 (s, NCH₂), 55.7 (s, NCH₂), 55.0 (s, NCH₃), 54.2 (s, NCH₂), 54.0 (s, NCH₂), 53.9 (s, NCH₃), 53.7 (s, NCH₂), 53.6 (s, NCH₂), 47.7 (s, NCH₃). ¹¹B NMR (THF-*d*₈): δ -6.91 (s). Anal. Calcd for C₇₈H₉₄B₂Cl₁₆N₈O₂Zr₂: C, 48.12; H, 4.87; N, 5.76. Found: C, 48.15; H, 4.47; N, 5.64.

[Zr(Me₃TACD)(OCH(CH₃)(μ-H))₂][B(3,5-C₆H₃(CF₃)₂)₄] (**5b**). A solution of **3b** (30 mg, 12.8 μmol) in 0.6 mL of THF-*d*₈ was treated with a solution of acetone in THF-*d*₈ (62 μL, *c* = 0.413 mol/L, 2.0 equiv). A ¹H NMR spectrum was recorded 1 h after the addition.

¹H NMR (THF): δ 7.80 (t, ⁴J_{HF} = 2.4 Hz, 16H, BPh-2), 7.58 (s, 8H, BPh-4), 5.28 (s, 2H, Zr(μ-H)), 4.44 (sept, ³J_{HH} = 6.3 Hz, 2H, OCH(CH₃)₂), 3.72 (td, ³J_{HH} = 11.6 Hz, ³J_{HH} = 5.9 Hz, 4H, NCH₂), 3.43 (m, 8H, NCH₂), 3.29 (dd, ³J_{HH} = 13.7 Hz, ³J_{HH} = 5.8 Hz, 4H, NCH₂), 3.07 (m, 8H, NCH₂), 3.00 (m, 8H, NCH₂), 2.92 (s, 12H, NCH₃), 2.82 (s, 6H, NCH₃), 1.26 (d, ³J_{HH} = 6.3 Hz, 12H, OCH(CH₃)₂). ¹³C{¹H} NMR (THF-*d*₈): δ 162.9 (q, ¹J_{BC} = 50.9 Hz, BPh-1), 135.7 (s, BPh-2), 130.1 (qq, ²J_{CF} = 31.2 Hz, ³J_{BC} = 2.7 Hz, BPh-3), 125.6 (q, ¹J_{CF} = 271.0 Hz, CF₃), 118.3 (t, ³J_{CF} = 3.8 Hz, BPh-4), 72.5 (s, OCH(CH₃)₂), 94.0 (s, NCH₂), 56.8 (s, NCH₂), 55.8 (s, NCH₂), 53.5 (s, NCH₂), 49.9 (s, NCH₃), 49.1 (s, NCH₃), 26.9 (OCH(CH₃)₂).

[Zr(Me₃TACD)(OCD(CH₃)(μ-D))₂][B(3,5-C₆H₃(CF₃)₂)₄] (**5b**[D₄]). A solution of [Zr(Me₃TACD)(μ-D)₂][B(3,5-C₆H₃(CF₃)₂)₄] (**3b**[D₄]) (30 mg, 12.8 μmol) in 0.6 mL of THF-*d*₈ was treated with a solution of acetone in THF-*d*₈ (62 μL, *c* = 0.413 mol/L, 2.0 equiv). A ¹H NMR spectrum was recorded 1 h after the addition.

^1H NMR (THF- d_8): δ 7.80 (t, $^4J_{\text{HF}} = 2.4$ Hz, 16H, BPh-2), 7.58 (s, 8H, BPh-4), 3.72 (td, $^3J_{\text{HH}} = 11.6$ Hz, $^3J_{\text{HH}} = 5.9$ Hz, 4H, NCH₂), 3.43 (m, 8H, NCH₂), 3.29 (dd, $^3J_{\text{HH}} = 13.7$ Hz, $^3J_{\text{HH}} = 5.8$ Hz, 4H, NCH₂), 3.07 (m, 8H, NCH₂), 3.00 (m, 8H, NCH₂), 2.92 (s, 12H, NCH₃), 2.82 (s, 6H, NCH₃), 1.26 (s, 12H, OCD(CH₃)₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8): δ 162.9 (q, $^1J_{\text{BC}} = 50.9$ Hz, BPh-1), 135.7 (s, BPh-2), 130.1 (qq, $^2J_{\text{CF}} = 31.2$ Hz, $^3J_{\text{BC}} = 2.7$ Hz, BPh-3), 125.6 (q, $^1J_{\text{CF}} = 271.0$ Hz, CF₃), 118.3 (t, $^3J_{\text{CF}} = 3.8$ Hz, BPh-4), 94.0 (s, NCH₂), 56.8 (s, NCH₂), 55.8 (s, NCH₂), 53.5 (s, NCH₂), 49.9 (s, NCH₃), 49.1 (s, NCH₃), 26.9 (OCD(CH₃)₂). The resonance for OCD(CH₃)₂ is not detected.

[Zr(Me₃TACD)(OCH(CH₃)₂)[B{3,5-C₆H₃(CF₃)₂]}₂] (6b). A solution of 3b (30 mg, 12.8 μmol) in 0.6 mL of THF- d_8 was treated with a solution of acetone in THF- d_8 (124 μL , $c = 0.413$ mol/L, 4.0 equiv). A ^1H NMR spectrum was recorded 30 min after the addition. Full conversion was achieved after 24 h. Alternative method: 2b (30.0 mg, 22.4 μmol) in 0.6 mL of THF- d_8 was treated with a solution of isopropyl alcohol in THF- d_8 (83 μL , $c = 0.540$ mmol/L, 44.9 μmol , 2.0 equiv). A ^1H NMR spectrum was recorded after 1 h.

^1H NMR (THF- d_8): δ 7.80 (m, 8H, BPh-2), 7.58 (s, 4H, BPh-4), 4.70 (sept, $^3J_{\text{HH}} = 6.1$ Hz, 2H, OCH(CH₃)₂), 3.39 (m, 1H, NCH₂), 3.07 (m, 3H, NCH₂), 2.80 (m, 10H, NCH₂), 2.70 (s, 3H, NCH₃), 2.65 (m, 2H, NCH₂), 2.60 (s, 6H, NCH₃), 1.28 (d, $^3J_{\text{HH}} = 6.1$ Hz, 12H, OCH(CH₃)₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8): δ 162.9 (q, $^1J_{\text{BC}} = 49.5$ Hz, BPh-1), 135.7 (s, BPh-2), 130.1 (qq, $^2J_{\text{CF}} = 31.1$ Hz, $^3J_{\text{BC}} = 2.6$ Hz, BPh-3), 125.6 (q, $^1J_{\text{CF}} = 272.7$ Hz, CF₃), 118.3 (t, $^3J_{\text{CF}} = 3.8$ Hz, Ph-4), 72.9 (s, OCH(CH₃)₂), 61.2 (s, NCH₂), 57.4 (s, NCH₂), 55.4 (s, NCH₂), 54.1 (s, NCH₂), 54.0 (s, NCH₂), 50.5 (s, NCH₃), 49.4 (s, NCH₃), 48.4 (s, NCH₃), 45.9 (s, NCH₃), 27.5 (s, OCH(CH₃)₂).

[Zr(Me₃TACD)(OCD(CH₃)₂)[B{3,5-C₆H₃(CF₃)₂]}₂] (6b[D₄]). A solution of 5b[D₄] (12.8 μmol) in 0.6 mL of THF- d_8 was treated with a solution of acetone in THF- d_8 (62 μL , $c = 0.413$ mol/L, 2.0 equiv).

^1H NMR (THF- d_8): δ 7.80 (m, 8H, BPh-2), 7.58 (s, 4H, BPh-4), 3.39 (m, 1H, NCH₂), 3.07 (m, 3H, NCH₂), 2.80 (m, 10H, NCH₂), 2.70 (s, 3H, NCH₃), 2.65 (m, 2H, NCH₂), 2.60 (s, 6H, NCH₃), 1.27 (s, 12H, OCD(CH₃)₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8): δ 162.9 (q, $^1J_{\text{BC}} = 49.5$ Hz, BPh-1), 135.7 (s, BPh-2), 130.1 (qq, $^2J_{\text{CF}} = 31.1$ Hz, $^3J_{\text{BC}} = 2.6$ Hz, BPh-3), 125.6 (q, $^1J_{\text{CF}} = 272.7$ Hz, CF₃), 118.3 (t, $^3J_{\text{CF}} = 3.8$ Hz, BPh-4), 61.2 (s, NCH₂), 57.4 (s, NCH₂), 55.4 (s, NCH₂), 54.1 (s, NCH₂), 54.0 (s, NCH₂), 50.5 (s, NCH₃), 49.4 (s, NCH₃), 48.4 (s, NCH₃), 45.9 (s, NCH₃), 27.4 (s, OCD(CH₃)₂). The resonance for OCD(CH₃)₂ is not detected.

Hydrogenolysis of CO. A solution of 3b (40 mg, 0.017 μmol) in 0.7 mL of THF- d_8 was treated with 1.0 bar of CO (either ^{12}CO or ^{13}CO). The yellow solution became nearly colorless within 5 min. ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ spectra were recorded at regular intervals.

Ethylene. ^1H NMR (THF- d_8): δ 5.36 (s, CH₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8): δ 123.4 (s, CH₂).

Oxymethylene Complex 7b. ^1H NMR (THF- d_8): δ 3.31 (s, ZrH₂CO). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8): δ 79.3 (s, ZrH₂CO). ^{13}C NMR (THF- d_8): δ 79.3 (t, $^1J_{\text{CH}} = 138.7$ Hz, ZrH₂CO).

Enolate Complex 8b. ^1H NMR (THF- d_8): δ 6.75 (dd, $^3J_{\text{HH}} = 13.9$ Hz, $^3J_{\text{HH}} = 5.8$ Hz, 1H, OCHCH₂), 4.31 (d, $^3J_{\text{HH}} = 13.9$ Hz, 1H, OCHCH₂), 4.14 (d, $^3J_{\text{HH}} = 5.8$ Hz, 1H, OCHCH₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8): δ 153.5 (d, $^1J_{\text{CC}} = 78.3$ Hz, OCHCH₂), 95.4 (d, $^1J_{\text{CC}} = 78.3$ Hz, OCHCH₂). ^{13}C NMR (THF- d_8): δ 153.5 (ddt, $^1J_{\text{CH}} = 177.5$ Hz, $^1J_{\text{CC}} = 78.3$ Hz, $^2J_{\text{CH}} = 5.8$ Hz, OCHCH₂), 95.4 (dddd, $^1J_{\text{CH}} = 160.6$ Hz, $^1J_{\text{CH}} = 154.9$ Hz, $^1J_{\text{CC}} = 78.3$ Hz, $^2J_{\text{CH}} = 12.4$ Hz, OCHCH₂).

Single-Crystal X-ray Structure Analysis of 1, 2c, 3b, and 4b. X-ray diffraction data were collected on a Bruker CCD area-detector diffractometer at 130 K (1) and 100 K (2c, 3b, and 4b) with Mo $K\alpha$ radiation (monolayer optics, $\lambda = 0.71073$ Å) using ω scans. The SMART program package was used for data collection and unit cell determination; processing of the raw frame data was performed using SAINT,^{36a} absorption corrections were applied with MULABS^{36b} (1 and 2c) or SADABS^{36c} (3b and 4b). The structures were solved by direct methods.^{36d} Compound 4b crystallizes as a solvate. Refinement was performed against F^2 using all reflections with the program SHELXL-97, as implemented in the program system WinGX.^{36e} The carbon and nitrogen atoms of the Me₃TACD ligand in 2c are

disordered, but the disorder could be modeled with split positions for these atoms. The occupancy factors for all atoms that are involved were close to 0.5. Because attempted refinement with anisotropic displacement parameters led to physically meaningless values, these atoms were refined with isotropic displacement parameters. The non-hydrogen atoms except those of the disordered Me₃TACD ligand in 2c were refined anisotropically; all hydrogen atoms were placed in calculated positions except for the hydrides in 3b and 4b. For both structures, the positions of these hydrides were localized in a difference Fourier map with peaks of 0.59, 0.63, 0.74, and 0.78 e/Å³ (3b) as well as 0.68 and 0.88 e/Å³ (4b). We are aware that these positions must not be overinterpreted, especially because both structures contain higher peaks of residual electron density in a distance of ca. 1 Å from zirconium. However, these positions are consistent with the results from NMR spectroscopy and match the metal–metal distance together with the DFT calculations. Distance restraints on C–C, C–N, and C–Si bonds were used in the refinement of 2c and also on C–C and C–N distances within the disordered part of the Me₃TACD ligand in 4b. Experimental details are given in Table 1.

■ ASSOCIATED CONTENT

Supporting Information

CIF file giving crystallographic data for compounds 1, 2c, 3b, and 4b, ORTEP drawing of 2c, ^1H – ^1H NOESY spectrum of 3a, ^1H – ^1H COSY spectrum of 3b, synthesis and characterization of 4b, reaction of 3b with CO, and computational details and optimized structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Fonds der Chemischen Industrie and the Cluster of Excellence “Tailor-Made Fuels from Biomass” for financial support. L.M. is a member of the Institut Universitaire de France. Calmip and CINES are acknowledged for a generous grant of computing time.

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- (19) This graphic is based on following examples for complexes with a $(\mu\text{-H})_1$ bridge: refs 5c, 5d, 9b, and 9c. Examples for complexes with a $(\mu\text{-H})_2$ -bridge: refs 2, 3, 4, 9e, 9f, 9g, 9h, 9i, 9j, and 9s. Examples for complexes with a $(\mu\text{-H})_3$ -bridge: refs 5a, 5d, 9c, 9d, 9e, 10a, and 10b. Example of a complex with a $(\mu\text{-H})_4$ -bridge: ref 5b.
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