Main-Group Chemistry

International Edition: DOI: 10.1002/anie.201600552
German Edition: DOI: 10.1002/ange.201600552

Molecular Calcium Hydride: Dicalcium Trihydride Cation Stabilized by a Neutral NNNN-Type Macrocyclic Ligand

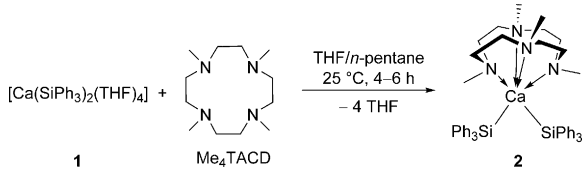
Valeri Leich, Thomas P. Spaniol, Laurent Maron, and Jun Okuda**

In memory of Yoshiharu Izumi

Abstract: *Hydrogenolysis of bis(triphenylsilyl)calcium containing the neutral NNNN-type macrocyclic amine ligand Me_4TACD $[Ca(Me_4TACD)(SiPh_3)_2]$ (**2**), gave the cationic dinuclear calcium hydride $[Ca_2H_3(Me_4TACD)_2](SiPh_3)$ (**3**), characterized by NMR spectroscopy, single-crystal X-ray analysis, and DFT calculations. Compound **3** reacted with deuterium to give the deuteride $[D_3]$-**3**.*

Molecular magnesium hydrides are of current interest in the context of hydrogen-storage materials.[1] Several families of molecular magnesium hydride complexes are known and their structure, reactivity, including hydrogen release and uptake behavior have been studied in some detail.[2] In contrast, only two molecular calcium hydrides have been reported, namely Harder's dimeric nacnac-supported calcium hydride $[\{CaH(DIPP\text{-}nacnac)(THF)\}_2]$[3] (DIPP-nacnac = (2,6-^{i}Pr$_2$C$_6$H$_3$)-NC(Me)C(H)-C(Me)N(2,6-^{i}Pr$_2$C$_6$H$_3$)) and the cationic tricalcium dihydride $[Ca_3H_2(Me_3TACD)_3](A)$[4] (A = $SiPh_3H_2$, $N(SiMe_3)(SiPh_3)$, $(Ph_3SiH)CHPh$, $SiPh_3$; Me_3TACD-H = 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane). These calcium hydride complexes are stabilized by mono-anionic LX- and L_3X-type ligands, which prevent the formation of insoluble calcium dihydride with a stable $PbCl_2$-type ionic lattice.[5] Following the observation that bis(triphenylsilyl)calcium $[Ca(SiPh_3)_2(THF)_4]$ (**1**) undergoes hydrogenolysis to give what appears to be a colloidal calcium dihydride,[6] the Me_4TACD ligated bis(triphenylsilyl)calcium is regarded a suitable precursor for the molecular calcium dihydride $[CaH_2(Me_4TACD)]$ (Me_4TACD = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane). Herein we report the synthesis and structural characterization of the cationic calcium hydride $[Ca_2H_3(Me_4TACD)_2](SiPh_3)$ (**3**), obtained by hydrogenolysis of $[Ca(Me_4TACD)(SiPh_3)_2]$ (**2**) that contains a neutral NNNN-type macrocyclic ligand.

First we treated **1** with Me_4TACD[7] to give the yellow THF-free bis(triphenylsilyl)calcium $[Ca(Me_4TACD)(SiPh_3)_2]$ (**2**; Scheme 1). This complex is soluble in THF and insoluble in aliphatic as well as in aromatic hydrocarbons. Complex **2** is less soluble in THF than **1** and could therefore be isolated in quantitative yield by crystallization from a THF/*n*-pentane mixture at 25 °C. Elemental analysis and NMR spectroscopic data of **2** agree with the proposed formula (see the Supporting Information).



Scheme 1. Synthesis of the Me_4TACD adduct of bis(triphenylsilyl)-calcium (**2**).

Single crystals of **2** were obtained from a concentrated THF solution; the compound crystallizes in the monoclinic space group *C*2/*c* (No. 15) with $Z = 4$ and crystallographic C_2 symmetry. The calcium atom resides in a distorted trigonal prism, is located on the C_2 axis and bonded to two silyl ligands as well as to one κ^4*N*-Me_4TACD ligand (Figure 1). The Ca–Si bond length (Ca1–Si1 3.1654(15) Å) is comparable to that in $[Ca(SiPh_3)_2(THF)_4]$[6] (**1**) and in $[Ca\{Si(SiMe_3)_3\}_2(THF)_3]$.[8] The small Si1-Ca1-Si1′ angle of 85.68(5)° is notable. The Ca–N bond lengths (Ca1–N1 2.559(3) Å; Ca1–N2 2.603(4) Å) are inconspicuous. The overall structure is reminiscent of the lutetium dialkyl complex $[Lu(Me_4TACD)(CH_2SiMe_3)_2][B\{3,5\text{-}C_6H_3(CF_3)_2\}_4]$.[9]

The ^{1}H NMR spectrum of **2** in [D$_8$]THF at 25 °C shows two sharp singlets at $\delta = 2.18$ and 2.50 ppm for the protons of

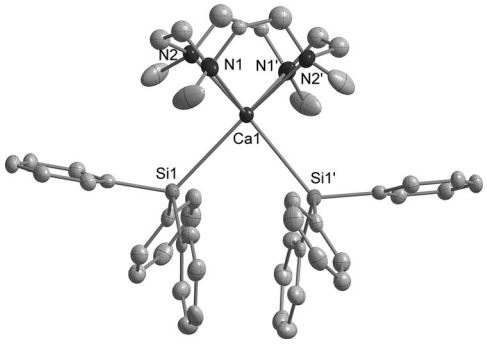


Figure 1. Molecular structure of **2**. Displacement ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ca1-Si1 3.1654(15), Ca1-N1 2.559(3), Ca1-N2 2.603(4); Si1-Ca1-Si1′ 85.68(5), N1-Ca1-N1′ 117.82(17), N2-Ca1-N2′ 99.37(16).

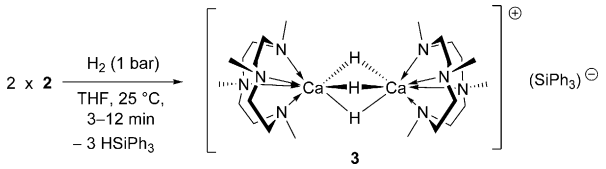
[*] V. Leich, Dr. T. P. Spaniol, Prof. Dr. J. Okuda
Institute of Inorganic Chemistry
RWTH Aachen University
Landoltweg 1, 52056 Aachen (Germany)
E-mail: jun.okuda@ac.rwth-aachen.de
Prof. Dr. L. Maron
CNRS, INSA, UPS, UMR 5215, LPCNO, Université de Toulouse
135 avenue de Rangueil, 31077 Toulouse (France)

Supporting information for this article (including experimental procedures, kinetic experiments, crystallographic and spectroscopic details, and computational analyses) can be found under http://dx.doi.org/10.1002/anie.201600552.

the methyl and CH_2CH_2 groups of Me_4TACD, the CH_2CH_2 protons being equivalent as a result of the dissociated Me_4TACD ligand. The silyl groups result in three multiplets for *para*/*meta*/*ortho*-CH protons in the expected ratio between $\delta = 6.87$ and 7.41 ppm. The $^{29}Si\{^1H\}$ NMR spectrum at −60 °C shows one singlet at $\delta = -15.20$ ppm; the absence of a signal at room temperature indicates fast dissociation in $[D_8]$THF on the NMR time scale. Variable temperature (VT) ^1H NMR measurements in $[D_8]$THF reveal coalescence of the CH_2CH_2 resonance signals at −40 °C, with a calculated value of $\Delta G^{\ddagger} = 48.8\ kJ\,mol^{-1}$ (see the Supporting Information). At −80 °C, two broad signals ($\delta = 2.20$–2.70 ppm) with relative intensities of 1:1 are observed for the diastereotopic CH_2CH_2 protons of the macrocycle Me_4TACD. This result indicates that this ligand exchanges with THF molecules, indicating a labile bonding of Me_4TACD to the calcium center in **2**.

DFT calculations at the B3PW91 level were performed to understand the bonding in **2**. The optimized structure compares well with the crystal structure and NBO analysis showed three slightly bonding orbitals between Me_4TACD and calcium. Two strong interactions between calcium and the silyl ligands were identified with the HOMO and HOMO−1 orbitals (see the Supporting Information). Since the calculations did not explain the lability of the Me_4TACD ligand, we computed the enthalpy required to replace Me_4TACD by THF: $[Ca(SiPh_3)_2(THF)_4] + Me_4TACD \rightarrow [Ca(Me_4TACD)(SiPh_3)_2] + 4\,THF$. The value of $\Delta H = 36.4\ kJ\,mol^{-1}$ agrees well with the observed exchange reaction.

Bis(triphenylsilyl) **2** reacted with H_2 (1 bar) in THF at room temperature to give the red calcium hydride $[Ca_2H_3(Me_4TACD)_2](SiPh_3)$ (**3**) in 95% yield. The hydrogenolysis proceeded fast at room temperature, whereas the deuterolysis to give the trideuteride $[Ca_2D_3(Me_4TACD)_2](SiPh_3)$ ([D_3]-**3**) in 95% yield was noticeably slower (12 vs. 3 min for a 0.1 M solution). Compound **3** is soluble in THF ($t_{1/2} \approx 12$ h), but insoluble in aromatic and aliphatic hydrocarbons and was characterized by elemental analysis and NMR spectroscopy (Scheme 2).[10] Reaction of **3** with Ph_3SiH did not regenerate the starting silyl complex **2** under release of H_2.



Scheme 2. Synthesis of cationic calcium trihydride **3**.

A single crystal of the cationic calcium hydride **3** was obtained from THF/*n*-hexane solution at −30 °C. Compound **3** crystallized in the triclinic space group $P\bar{1}$ (No. 2). X-ray crystallography revealed a separated ion pair with a cationic dicalcium trihydride core $[Ca_2H_3(Me_4TACD)_2]^+$ and a non-coordinating triphenylsilyl anion $(SiPh_3)^-$ (Figure 2 and Supporting Information for the silyl anion). The hydrogen atoms H1, H2, and H3 within the Ca_2H_3 core of **3** were located and refined in their positions. Each calcium atom is coordinated by four nitrogen atoms of the Me_4TACD ligand and

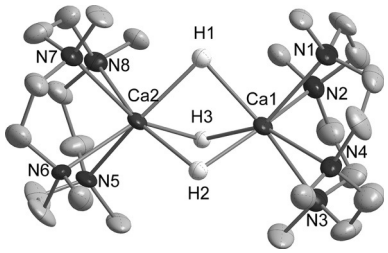


Figure 2. Molecular structure of **3**. Displacement ellipsoids are set at 50% probability; the triphenylsilyl anion and the hydrogen atoms except for those of the Ca_2H_3 core are omitted for clarity. Selected interatomic distances [Å]: Ca1···Ca2 3.233(2), Ca1-N1 2.614(6), Ca1-N2 2.576(8), Ca1-N3 2.590(6), Ca1-N4 2.674(7), Ca2-N5 2.589(6), Ca2-N6 2.670(7), Ca2-N7 2.612(6), Ca2-N8 2.587(6).

three bridging hydrides leading to a coordination number of seven and a tetragonally monocapped trigonal-prismatic coordination geometry around the calcium atom. The hydrides bridge the metal centers in a μ_2 manner. The intermetallic distance in **3** (Ca1···Ca2 3.233(2) Å) is shorter than that in trinuclear calcium hydride complexes $[Ca_3H_2(Me_3TACD)_3](A)$[4] (Ca···Ca 3.3551(10) Å) and comparable to those in bimetallic lanthanide trihydrides $[Ln_2H_3]$ (Ln = Y and Lu; Ln···Ln = 2.93–3.75 Å),[9,11] although the ionic radius of Ca^{2+} ions (1.06 Å with coordination number (CN) = 7) is larger than those of Y^{3+} ions (0.96 Å with CN = 7) and Lu^{3+} ions (0.86 Å with CN = 6).[12]

The stability of the cationic calcium hydride **3** was investigated by an NBO analysis using DFT calculations at the same level as for **2**. The optimized structure compares well with the crystal structure. Expectedly, no bonding molecular orbitals connect the calcium atoms. Strong two-electron three-center bonds between the calcium and hydrogen atoms stabilize the calcium hydride complex (see the Supporting Information).

The ^1H NMR spectrum of **3** in $[D_8]$THF at 25 °C shows one singlet at $\delta = 2.54$ ppm for the methyl groups of Me_4TACD and two broad signals in the range of $\delta = 1.95$–3.23 ppm for the CH_2CH_2 protons, indicating highly fluxional CH_2CH_2 bridges. The hydride signal at $\delta = 4.72$ ppm appears as a sharp singlet and is shifted downfield compared to the corresponding resonance in $[\{CaH(DIPP\text{-}nacnac)(THF)\}_2]$[3] ($\delta = 4.45$ ppm) and $[Ca_3H_2(Me_3TACD)_3](A)$[4] ($\delta = 4.00$ ppm). The *para*/*meta*/*ortho*-CH protons of the triphenylsilyl anion appear as multiplets in the range of $\delta = 6.70$–7.39 ppm. The $^{29}Si\{^1H\}$ NMR spectrum shows one singlet at $\delta = -9.96$ ppm at −40 °C. NMR spectroscopic data of the cationic calcium deuteride [D_3]-**3** are similar to those of **3** and the ^2H NMR spectrum of [D_3]-**3** shows one singlet at $\delta = 4.81$ ppm (see Supporting Information).

VT ^1H NMR measurements of **3** in $[D_8]$THF show two doublets and two pseudo triplets with a ratio of 1:1:1:1 for an AA′XX′ spin system above the coalescence temperature of 0 °C (see the Supporting Information).[13] Line-shape analysis revealed fluxional CH_2CH_2 bridges with values of $\Delta H^{\ddagger} = 61.6 \pm 0.3\ kJ\,mol^{-1}$ and $\Delta S^{\ddagger} = 34.7 \pm 2\ J\,mol^{-1}\,K^{-1}$ values that compare well with those of similar CH_2CH_2-containing macrocyclic ligands ($\Delta H^{\ddagger} = 60.4 \pm 3.1\ kJ\,mol^{-1}$ for $[Fe(L)(MeCN)_2](PF_6)_2$; L = NNNN-type macrocyclic ligand).[14]

When a solution of the cationic calcium hydride **3** in [D$_8$]THF was treated with D$_2$ (1 bar), the hydride signal in the ^{1}H NMR spectrum decreased with concomitant formation of HD ($\delta = 4.51$ ppm, $^1J_{HD} = 42.66$ Hz). Deuteration of **3** to give [D$_3$]-**3** was indicated by the gradual appearance of the hydride resonances of the isotopomers (see the Supporting Information). As expected,[15] the hydride resonances of the monodeuteride [D$_1$]-**3** and dideuteride [D$_2$]-**3** are shifted by $\delta = 0.01$ and 0.02 ppm upfield compared to **3**. The H/D exchange between **3** and [D$_3$]-**3** is similar to the previously reported deuteration of the lanthanide hydride [Lu$_2$H$_4$(Me$_4$TACD)$_2$]-[B{3,5-C$_6$H$_3$(CF$_3$)$_2$}$_4$]$_2$.[9] The conversion of **3** into [D$_3$]-**3** followed pseudo-first-order kinetics with $k_H(H_2) = 2.82(3) \times 10^{-5}\ s^{-1}$ and $k_D(D_2) = 1.80(8) \times 10^{-5}\ s^{-1}$. A kinetic isotope effect (KIE) of $k_H/k_D = 1.6$ indicates that the H–H (D–D) bond cleavage is the rate-determining step during the dihydrogen activation by the cationic calcium hydride **3** ([D$_3$]-**3**). A KIE of $k_H/k_D = 1.40$ was found for a β-phase palladium hydride[16] for the H/D exchange reaction and similar reactivities were observed for iron hydride complexes,[17] a magnesium,[18] and a calcium borohydride.[19]

When the cationic calcium hydride **3** was deuterated in [D$_8$]THF at 25 °C in the presence of one equivalent of HSiPh$_3$, the Si–H resonance had disappeared after 12 h and DSiPh$_3$ was formed. This indicates that the silyl anion (SiPh$_3$)$^-$ is involved in the activation of dihydrogen. We also observed that **3** undergoes dissociation in THF. An initial 1:1 mixture of **3** and [D$_3$]-**3** in [D$_8$]THF at 25 °C equilibrated over 5 min, leading to a ^{1}H NMR spectrum with signals indicating the presence of **3**, [D$_1$]-**3**, [D$_2$]-**3**, and [D$_3$]-**3** (Figure 3).

On the basis of these observations, we propose the deuteration of the cationic calcium hydride **3** to the deuterated complex [D$_3$]-**3** via an intermediate dideuterium complex **A**.[9] A dissociated complex **B**[20] may also be formed (Scheme 3). Deuterium is activated either by the Lewis acidic calcium center in **A** or by σ-bond metathesis in complex **B** to give the neutral dicalcium monodeuteride trihydride **C** under release of DSiPh$_3$. The silane DSiPh$_3$ reacts with **C** to the monodeuterated calcium hydride [D$_1$]-**3**. The presence of a suitable NNNN-type macrocyclic ligand and a protic silane in the reaction solution prevents the formation of insoluble calcium hydride and protonates the neutral calcium dihydride complex **C**. DFT calculations indicate that the protonation of

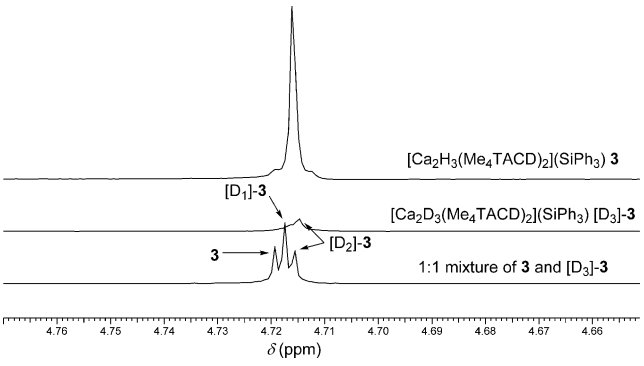
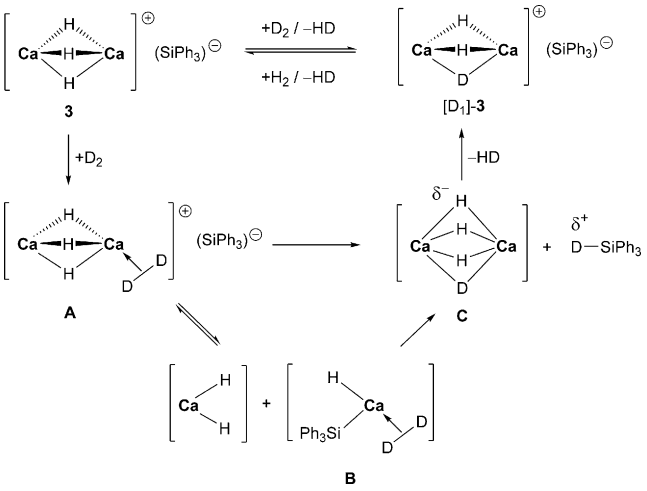


Figure 3. ^{1}H NMR spectra of **3**, [D$_3$]-**3** and a 1:1 mixture in [D$_8$]THF at 25 °C. For the full ^{1}H NMR spectra see Supporting Information.

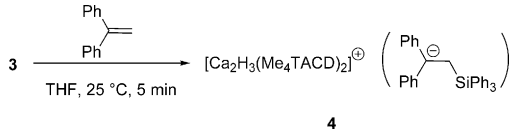


Scheme 3. Proposed mechanism for the reaction of the cationic calcium hydride **3** with D$_2$ to give [D$_1$]-**3**. The neutral macrocyclic NNNN-type ligand Me$_4$TACD is omitted for clarity.

calcium dihydride complex **C** is favorable by $\Delta H = -9.2\ kJ\,mol^{-1}$, whereas the dissociation of dimeric **3** into the monomers [CaH$_2$(Me$_4$TACD)] and [Ca(Me$_4$TACD)H-(SiPh$_3$)] (**B**) is unfavorable by $\Delta H = 107.6\ kJ\,mol^{-1}$.

To study the reactivity of the cationic calcium hydride core [Ca$_2$H$_3$(Me$_4$TACD)$_2$]$^+$ in **3**, we sought to replace the reactive silyl anion (SiPh$_3$)$^-$ by a non-coordinating anion. The reaction of **3** with 1,1′-diphenylethylene (DPE) gave the new cationic calcium hydride [Ca$_2$H$_3$(Me$_4$TACD)$_2$](Ph$_2$CCH$_2$SiPh$_3$) (**4**) as red microcrystals, isolated in 95% yield and characterized by elemental analysis and NMR spectroscopy (Scheme 4).

The ^{1}H NMR spectrum of **4** in [D$_8$]THF at 25 °C agrees with the proposed formula, showing a singlet at $\delta = 2.68$ ppm for the Ph$_2$CC*H*$_2$SiPh$_3$ protons, a triplet of triplets at $\delta = 5.45$ ppm as well as two doublets of doublets at $\delta = 6.31$ and 6.81 ppm for the *para*/*meta*/*ortho*-CH atoms in the 1,1′-diphenylethyl moiety. For the SiPh$_3$-moiety two multiplets in the range of $\delta = 7.07$–7.57 ppm are found for the *para*/*meta*/*ortho*-CH atoms in the expected ratio. The ^{1}H NMR resonances of the cationic calcium hydride core [Ca$_2$H$_3$-(Me$_4$TACD)$_2$]$^+$ of **4** are comparable to those of **3**. The ^{29}Si{^{1}H} NMR spectrum of **4** in [D$_8$]THF at 25 °C shows one singlet at $\delta = -19.25$ ppm (see the Supporting Information). Compound **4** catalyzed the hydrogenation of 1,1′-DPE at 60 °C within 24 h.[3,5] B(C$_6$F$_5$)$_3$ catalyzed hydrogenation (4 atm of H$_2$) of 1,1′-DPE showed full conversion at 50 °C after 48 h,[21] whereas B(C$_6$F$_5$)$_3$-catalyzed transfer hydrogenation of 1,1′-DPE was complete at 25 °C after 8 h.[22] The transfer hydrogenation of 1,1′-DPE catalyzed by a cationic NHC gallium chloride at 20 °C showed 67% conversion after 1 h.[23]



4

Scheme 4. Synthesis of the cationic calcium hydride **4**.

In conclusion, the hydrogenolysis of the bis(triphenylsilyl) $[Ca(Me_4TACD)(SiPh_3)_2]$ (**2**) proceeded under mild conditions (1 bar of H_2) to give the cationic dicalcium trihydride core in $[Ca_2H_3(Me_4TACD)_2](SiPh_3)$ (**3**) instead of the neutral calcium dihydride $[CaH_2(Me_4TACD)]$. These reaction conditions contrast with the slow and complicated hydrogenolysis of the calcium allyl $[Ca(C_3H_5)(Me_3TACD)]$ to give $[Ca_3H_2(Me_3TACD)_3]^+(SiPh_3H_2)^-$.[4] As can be seen from the deuteration experiments of **3**, the inaccessibility of the neutral dihydride $[CaH_2(Me_4TACD)]$ may be related to the expected high polarity of Ca–H bonds that are capable of deprotonating even Si–H bonds. Nonetheless, hydrogenolysis of a M–Si bond (M = Ca,[4b] K[24]) may be applied to the synthesis of other molecular alkali- and alkaline-earth metal hydrides.

Acknowledgments

We thank the Cluster of Excellence "Tailor-Made Fuels from Biomass" for financial support, Dr. K. Beckerle for the lineshape analysis, and Dr. C. Räuber for ^{2}H NMR spectroscopic measurements.

Keywords: alkaline-earth metals · calcium · hydrides · hydrogen · Si ligands

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 4794–4797
Angew. Chem. **2016**, *128*, 4872–4876

[1] a) L. Schlapbach, A. Zuttel, *Nature* **2001**, *414*, 353–358; b) R. W. P. Wagemans, J. H. van Lenthe, P. E. de Jongh, A. J. van Dillen, K. P. de Jong, *J. Am. Chem. Soc.* **2005**, *127*, 16675–16680; c) S. Harder, J. Spielmann, J. Intemann, H. Bandmann, *Angew. Chem. Int. Ed.* **2011**, *50*, 4156–4160; *Angew. Chem.* **2011**, *123*, 4242–4246; d) E. Hevia, R. E. Mulvey, *Angew. Chem. Int. Ed.* **2011**, *50*, 9242–9243; *Angew. Chem.* **2011**, *123*, 9410–9411; e) S. Harder, *Chem. Commun.* **2012**, *48*, 11165–11177; f) C. J. Webb, *J. Phys. Chem. Solids* **2015**, *84*, 96–106.

[2] a) D. V. Graham, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, *Acta Crystallogr. Sect. C* **2006**, *62*, m366–m368; b) M. Arrowsmith, M. S. Hill, D. J. MacDougall, M. F. Mahon, *Angew. Chem. Int. Ed.* **2009**, *48*, 4013–4016; *Angew. Chem.* **2009**, *121*, 4073–4076; c) S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards, G. J. McIntyre, *Chem. Eur. J.* **2010**, *16*, 938–955; d) J. Intemann, J. Spielmann, P. Sirsch, S. Harder, *Chem. Eur. J.* **2013**, *19*, 8478–8489; e) S. Harder, J. Spielmann, J. Intemann, *Dalton Trans.* **2014**, *43*, 14284–14290; f) D. J. Liptrot, M. S. Hill, M. F. Mahon, *Chem. Eur. J.* **2014**, *20*, 9871–9874; g) R. Lalrempuia, A. Stasch, C. Jones, *Chem. Asian J.* **2015**, *10*, 447–454; h) D. Martin, K. Beckerle, S. Schnitzler, T. P. Spaniol, L. Maron, J. Okuda, *Angew. Chem. Int. Ed.* **2015**, *54*, 4115–4118; *Angew. Chem.* **2015**, *127*, 4188–4191; i) S. Schnitzler, T. P. Spaniol, L. Maron, J. Okuda, *Chem. Eur. J.* **2015**, *21*, 11330–11334.

[3] S. Harder, J. Brettar, *Angew. Chem. Int. Ed.* **2006**, *45*, 3474–3478; *Angew. Chem.* **2006**, *118*, 3554–3558.

[4] a) P. Jochmann, J. P. Davin, T. P. Spaniol, L. Maron, J. Okuda, *Angew. Chem. Int. Ed.* **2012**, *51*, 4452–4455; *Angew. Chem.* **2012**, *124*, 4528–4531; b) V. Leich, T. P. Spaniol, J. Okuda, *Inorg. Chem.* **2015**, *54*, 4927–4933.

[5] S. Harder, *Chem. Rev.* **2010**, *110*, 3852–3876.

[6] V. Leich, T. P. Spaniol, L. Maron, J. Okuda, *Chem. Commun.* **2014**, *50*, 2311–2314.

[7] J. H. Coates, D. A. Hadi, S. F. Lincoln, *Aust. J. Chem.* **1982**, *35*, 903–909.

[8] W. Teng, K. Ruhlandt-Senge, *Organometallics* **2004**, *23*, 2694–2700.

[9] W. Fegler, A. Venugopal, T. P. Spaniol, L. Maron, J. Okuda, *Angew. Chem. Int. Ed.* **2013**, *52*, 7976–7980; *Angew. Chem.* **2013**, *125*, 8134–8138.

[10] Adding the ligand Me_4TACD to a hydrogenated solution of $[Ca(SiPh_3)_2(THF)_4]$ in THF, did not give the calcium hydride $[Ca_2H_3(Me_4TACD)_2](SiPh_3)$. The formation of insoluble calcium hydride clusters appears to be suppressed by the presence of the macrocyclic NNNN-type ligand.

[11] a) A. A. Trifonov, E. A. Fedorova, G. K. Fukin, M. N. Bochkarev, *Eur. J. Inorg. Chem.* **2004**, 4396–4401; b) A. A. Trifonov, G. G. Skvortsov, D. M. Lyubov, N. A. Skorodumova, G. K. Fukin, E. V. Baranov, V. N. Glushakova, *Chem. Eur. J.* **2006**, *12*, 5320–5327; c) M. Konkol, T. P. Spaniol, M. Kondracka, J. Okuda, *Dalton Trans.* **2007**, 4095–4102; d) D. M. Lyubov, A. M. Bubnov, G. K. Fukin, F. M. Dolgushin, M. Y. Antipin, O. Pelcé, M. Schappacher, S. M. Guillaume, A. A. Trifonov, *Eur. J. Inorg. Chem.* **2008**, 2090–2098; e) J. Cheng, T. Shima, Z. Hou, *Angew. Chem. Int. Ed.* **2011**, *50*, 1857–1860; *Angew. Chem.* **2011**, *123*, 1897–1900; f) E. Lu, Y. Chen, X. Leng, *Organometallics* **2011**, *30*, 5433–5441; g) A. Venugopal, W. Fegler, T. P. Spaniol, L. Maron, J. Okuda, *J. Am. Chem. Soc.* **2011**, *133*, 17574–17577; h) J. Cheng, H. Wang, M. Nishiura, Z. Hou, *Chem. Sci.* **2012**, *3*, 2230–2233; i) H. Kulinna, T. P. Spaniol, J. Okuda, *J. Organomet. Chem.* **2013**, *744*, 49–52.

[12] R. Shannon, *Acta Crystallogr. Sect. A* **1976**, *32*, 751–767.

[13] a) J. K. Beattie, *Acc. Chem. Res.* **1971**, *4*, 253–259; b) S. Aime, M. Botta, G. Ermondi, E. Terreno, P. L. Anelli, F. Fedeli, F. Uggeri, *Inorg. Chem.* **1996**, *35*, 2726–2736; c) S. Aime, M. Botta, M. Fasano, M. P. M. Marques, C. F. G. C. Geraldes, D. Pubanz, A. E. Merbach, *Inorg. Chem.* **1997**, *36*, 2059–2068; d) M. Ohashi, M. Konkol, I. Del Rosal, R. Poteau, L. Maron, J. Okuda, *J. Am. Chem. Soc.* **2008**, *130*, 6920–6921.

[14] a) A. Raba, M. Cokoja, S. Ewald, K. Riener, E. Herdtweck, A. Pöthig, W. A. Herrmann, F. E. Kühn, *Organometallics* **2012**, *31*, 2793–2800; b) I. Klawitter, M. R. Anneser, S. Dechert, S. Meyer, S. Demeshko, S. Haslinger, A. Pöthig, F. E. Kühn, F. Meyer, *Organometallics* **2015**, *34*, 2819–2825.

[15] D. Nanz, W. V. Philipsborn, U. E. Bucher, L. M. Venanzi, *Magn. Reson. Chem.* **1991**, *29*, S38–S44.

[16] W. Luo, D. F. Cowgill, *J. Phys. Chem. C* **2015**, *119*, 18099–18109.

[17] T. R. Dugan, E. Bill, K. C. MacLeod, W. W. Brennessel, P. L. Holland, *Inorg. Chem.* **2014**, *53*, 2370–2380.

[18] H. Hagemann, V. D'Anna, J.-P. Rapin, K. Yvon, *J. Phys. Chem. C* **2010**, *114*, 10045–10047.

[19] M. Sharma, D. Sethio, V. D'Anna, J. C. Fallas, P. Schouwink, R. Černý, H. Hagemann, *J. Phys. Chem. C* **2015**, *119*, 29–32.

[20] In the ^{1}H NMR spectrum of $[Ca_2H_3(Me_4TACD)_2](SiPh_3)$ (**3**) we always observe a resonance at $\delta = 4.84$ ppm, which we assign to the proposed monometallic calcium hydride silyl complex $[Ca(Me_4TACD)H(SiPh_3)]$ (**B**).

[21] L. J. Hounjet, C. Bannwarth, C. N. Garon, C. B. Caputo, S. Grimme, D. W. Stephan, *Angew. Chem. Int. Ed.* **2013**, *52*, 7492–7495; *Angew. Chem.* **2013**, *125*, 7640–7643.

[22] I. Chatterjee, Z.-W. Qu, S. Grimme, M. Oestreich, *Angew. Chem. Int. Ed.* **2015**, *54*, 12158–12162; *Angew. Chem.* **2015**, *127*, 12326–12330.

[23] B. Michelet, C. Bour, V. Gandon, *Chem. Eur. J.* **2014**, *20*, 14488–14492.

[24] V. Leich, T. P. Spaniol, J. Okuda, *Chem. Commun.* **2015**, *51*, 14772–14774.

Received: January 18, 2016
Published online: March 8, 2016

