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Formation of a Cationic Calcium Hydride Cluster with a "Naked" Triphenylsilyl Anion by Hydrogenolysis of Bis(triphenylsilyl)calcium

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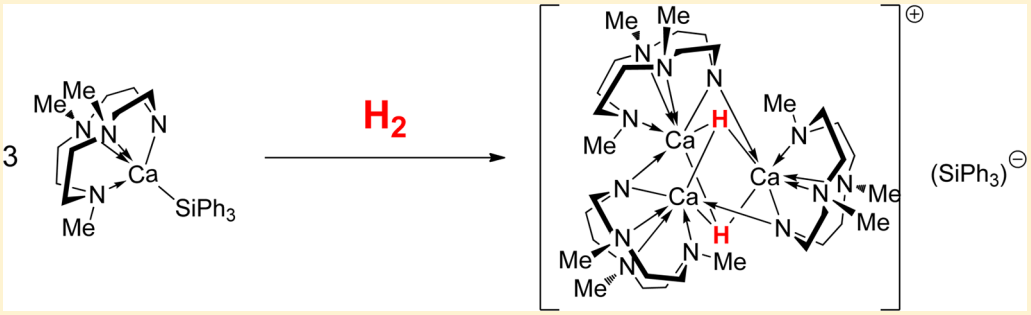
Supporting Information



ABSTRACT: Protonolysis of bis(triphenylsilyl)calcium $[Ca(SiPh_3)_2(THF)_4]$ (**1**; THF = tetrahydrofuran) with the NNNN-type macrocyclic amido triamine $(Me_3TACD)H$ (TACD = 1,4,7-triazacyclododecane) gave the heteroleptic calcium complex $[Ca(Me_3TACD)SiPh_3]$ (**2**) in quantitative yield. Hydrogenolysis of **2** gave the cationic tricalcium dihydride cluster $[Ca_3H_2(Me_3TACD)_3]^+(SiPh_3)^-\cdot 2THF$ (**4a**) in high yield with concomitant formation of $HSiPh_3$. In the crystal, **4a** consists of a cluster cation and a free triphenylsilyl anion. ^1H NMR spectroscopy and deuterium labeling experiments confirmed the selective cleavage of dihydrogen by the highly polar Ca−Si bond in **1**.

INTRODUCTION

Calcium hydride, CaH_2, is a thermodynamically stable compound with an ionic lattice of $PbCl_2$-type.[1] As molecular hydrides of electropositive metals such as magnesium attract interest as homogeneous catalysts and as models for hydrogen storage materials,[2] it is surprising that only two examples for molecular calcium hydrides are known so far. The first compound, a nacnac-supported dimer with a $Ca_2(\mu\text{-}H)_2$ core was prepared by Harder et al. by the reaction of [Ca(DIPP-nacnac){N(SiMe$_3$)$_2$}(THF)] (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$_3$); THF = tetrahydrofuran) with $PhSiH_3$ as hydride source to give [{CaH(DIPP-nacnac)(THF)}$_2$] in 61% yield.[3] Using the NNNN-type macrocyclic amido triamine ligand 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane[6a,b] $(Me_3TACD)H$, we isolated in low to moderate yields a trinuclear cluster $[Ca_3H_2(Me_3TACD)_3]^+(A)^-$ (A = $SiPh_3H_2$, $N(SiMe_3)(SiPh_3)$, $(Ph_2SiH)CHPh$) featuring two μ_3-H ligands (Scheme 1).[4] Since the presumed formation of this unusual hydride cluster by σ-bond metathesis suffered from irreproducibility and the originally anticipated heteroleptic hydride $[CaH(Me_3TACD)]$ remained elusive despite many efforts to isolate it, we now turn to bis(triphenylsilyl)calcium $[Ca(SiPh_3)_2(THF)_4]$ (**1**) as a starting material. Compound **1** was recently shown to smoothly undergo hydrogenolysis to give a soluble, probably colloidal form of CaH_2.[5] We report here a rational high yield synthesis of $[Ca_3H_2(Me_3TACD)_3]^+(SiPh_3)$ starting from **1** using dihydrogen.

RESULTS AND DISCUSSION

Reacting bis(triphenylsilyl)calcium $[Ca(SiPh_3)_2(THF)_4]$ (**1**)[5] with the macrocyclic tetradentate ligand $(Me_3TACD)H$ in benzene at room temperature afforded the triphenylsilyl complex $[Ca(Me_3TACD)SiPh_3]$ (**2**) as yellow powder in quantitative yield (Scheme 2). The calcium complex **2** was isolated only when the reaction was performed in benzene. Attempts to isolate **2** from THF solutions resulted in the isolation of the homoleptic calcium complexes $[Ca(SiPh_3)_2(THF)_4]$ (**1**) and $[Ca(Me_3TACD)_2]$ (**3**), due to apparently fast Schlenk equilibrium in THF.

The heteroleptic complex $[Ca(Me_3TACD)SiPh_3]$ (**2**) is highly soluble in THF (due to the Schlenk equilibrium) but insoluble in aliphatic and aromatic hydrocarbons. Performing the reaction in benzene offers two advantages: first, **2** precipitates from the reaction mixture after a few minutes, and second, **2** can be separated from triphenylsilane $HSiPh_3$ efficiently. All attempts to isolate the heteroleptic compound from THF solutions failed (vide supra). ^1H NMR analysis indicated the presence of residual $HSiPh_3$, which could not be removed by washing with pentane. NMR spectroscopic and elemental analyses of **2** are in agreement with the proposed formula (see Experimental Section). The ^1H NMR spectrum of **2** shows two singlets at δ = 2.18 and 2.38 ppm for the methyl groups and four sharp multiplets in the range of δ = 2.14−3.15

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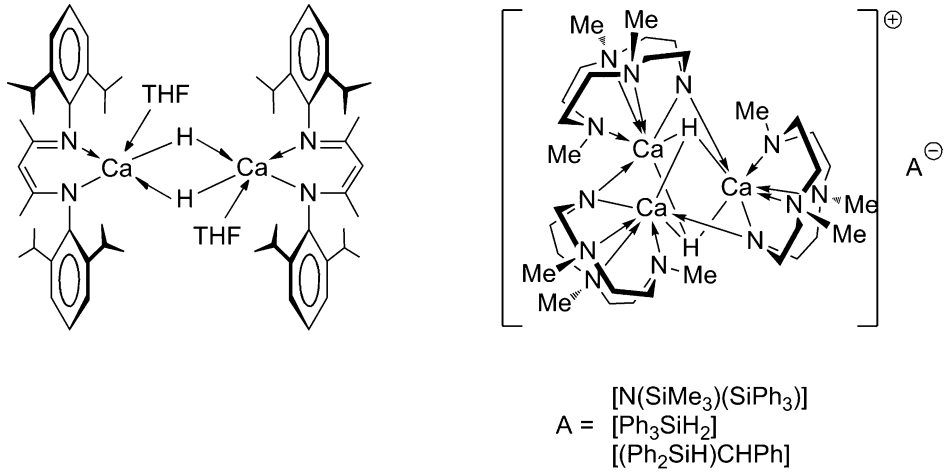
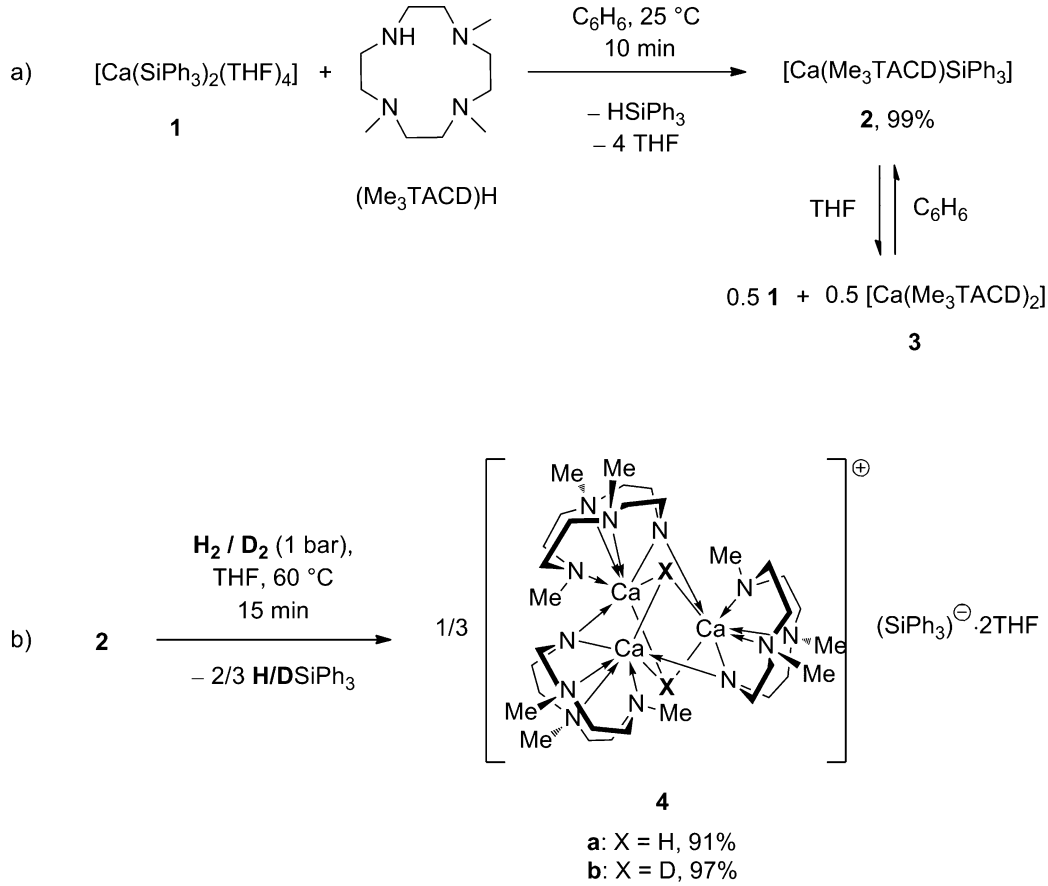
Scheme 1. Molecular Calcium Hydride Compounds



Scheme 2[a]



[a](a) Synthesis of the heteroleptic calcium silyl $[Ca(Me_3TACD)SiPh_3]$ (**2**) and the Schlenk equilibrium. (b) Formation of the trinuclear calcium cluster $[Ca_3H_2/D_2(Me_3TACD)_3]^+(SiPh_3)^-\cdot 2THF$ **4a** and **4b** from the heteroleptic calcium complex **2**.

ppm for the CH_2 protons of the macrocyclic ligand in the right ratio (6:3:4:4:4:4) in THF-d_8 at room temperature. Together with the $^{13}C\{^1H\}$ NMR data this suggests a monomeric or dimeric structure in solution.[6] The triphenylsilyl anion shows three multiplets in the range of δ = 6.88−7.43 ppm for the *para*/*meta*/*ortho*-CH protons (ratio 3:6:6). A 1:1 mixture of the homoleptic complexes $[Ca(SiPh_3)_2(THF)_2]$ (**1**) and $[Ca(Me_3TACD)_2]$ (**3**) shows only one set of signals in the ^1H NMR spectrum in THF-d_8 at room temperature. The ^1H NMR shifts of the mixture are similar to those of the heteroleptic complex $[Ca(Me_3TACD)SiPh_3]$ (**2**) (see Supporting Information). These findings indicate a fast Schlenk equilibrium between the homoleptic complexes **1** and **3** and the heteroleptic complex **2**.

The calcium complex **2** was fully converted into the trinuclear calcium complex $[Ca_3H_2(Me_3TACD)_3]^+(SiPh_3)^-\cdot 2THF$ (**4a**) upon reaction with dihydrogen (1 bar) in THF at 60 °C. Owing to the low solubility in THF, the hydride **4a** was

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isolated by crystallization from the reaction mixture in high yield (91%). The corresponding deuteride complex $[Ca_3D_2(Me_3TACD)_3]^+(SiPh_3)^-\cdot 2THF$ (**4b**) was isolated in 97% yield starting from **2** and deuterium (1 bar). Longer reaction times (>30 min) led to drastically lower yields.

Compound **4** is soluble in THF and sparingly soluble in aliphatic and aromatic hydrocarbons. ^{1}H NMR spectra of the products after prolonged reaction time suggested the formation of an unknown anion, presumably $(SiPh_{3-x}H_x)^-$ ($x \leq 3$), but with the intact $[Ca_3H_2(Me_3TACD)_3]^+$ cation. Such scrambling processes for silyl anions are well-documented in the literature.[7] The ^{1}H NMR spectrum of **4a** in THF-d_8 is in agreement with the D_3-symmetrical solid-state structure and shows two singlets at δ = 2.24 and 2.56 ppm for the methyl groups and three broad signals in the range of δ = 2.16−3.20 ppm for the CH_2 protons of the Me_3TACD ligand in the expected ratio. The hydride ligands appear as a sharp singlet at δ = 4.00 ppm. The triphenylsilyl anion give rise to three multiplets in the range of δ = 6.62−7.39 ppm for the *para*/*meta*/*ortho*-CH protons in the correct ratio (see Supporting Information). The ^{1}H NMR shift of the two hydride ligands in **4a** at δ = 4.00 ppm is in agreement with the reported one for the other cationic calcium hydride clusters.[8] This value is shifted by 0.45 ppm upfield when compared with that reported for $[\{CaH(DIPP\text{-}nacnac)(THF)\}_2]$.[3] ^{1}H NMR chemical shifts of bridging magnesium hydrides are in the range of δ = 0.55−3.83 ppm,[2c,9] whereas terminal magnesium hydride shifts are in the range of δ = 4.65−5.68 ppm.[10] NMR spectroscopic data of the deuterated complex $[Ca_3D_2(Me_3TACD)_3]^+(SiPh_3)^-\cdot 2THF$ (**4b**) are similar to the data of **4a**. The ^{2}H NMR spectrum in THF-d_8 of **4b** shows a singlet at δ = 4.09 ppm (see Supporting Information).

Single crystals of **4a** were obtained from a THF solution at −30 °C. The calcium hydride complex **4a** crystallizes in the trigonal space group *P*31*c* with Z = 2. The X-ray crystal structure determination shows a solvent-separated ion pair, consisting of a D_3-symmetric cationic tricalcium hydride unit $[Ca_3H_2(Me_3TACD)_3]^+$ and a "naked" silyl anion $(SiPh_3)^-$ (Figure 1). The lattice contains noncoordinated THF disordered around a C_3 axis. This could not be removed by drying the solid in vacuo. The disorder of all carbon and nitrogen atoms could be well-modeled with split positions. The positions for the two hydrides could clearly be located from a Fourier difference map, but were not refined. The central $[Ca_3H_2(Me_3TACD)]^+$ fragment can be compared to that in $[Ca_3H_2(Me_3TACD)_3]^+(A)^-$ (A = $N(SiMe_3)(SiPh_3)$, Ph_3SiH_2, and $(Ph_2SiH)CHPh$.[4,8a]

The structure reveals a noncoordinating triphenylsilyl anion $(SiPh_3)^-$. The end-for-end disorder of this molecular fragment could be modeled well (see Supporting Information, Figure S15). To the best of our knowledge, such a bonding situation has never been reported in the literature. The triphenylsilyl anion $(SiPh_3)^-$ is isoelectronic with triphenylphosphine PPh_3.[11,12] Structural parameters can be compared to known triphenylsilyl metal complexes (C−Si−C_{av} = 100−106°: $[Li(THF)_3SiPh_3]$,[13] $[K(18\text{-crown-}6)SiPh_3]$,[14] $[Li(12\text{-crown-}4)SiPh_3]\cdot(THF)_{0.5}$/$[Na(15\text{-crown-}5)SiPh_3]\cdot(THF)_{0.5}$/$[K(18\text{-crown-}6)SiPh_3(THF)]$,[15] $[Ca(SiPh_3)_2(THF)_4]$,[5] $[ZrCp_2ClSiPh_3]$,[16] $[Co(CO)_5SiPh_3]$,[17] $[Os_3H_3(CO)_9SiPh_3]$,[18] $[Rh_2H_3(P\text{-}i\text{-}Pr_3)_2ClSiPh_3]$,[19] *cis*-$[Pt(SiPh_3)_2(PMe_2Ph)_2]$[20]).

The course of the formation of cationic calcium hydride **4a** was investigated by ^{1}H NMR spectroscopy. A degassed solution of the heteroleptic calcium complex **2** was charged with H_2 (1 bar) and heated for 15 min at 60 °C. The ^{1}H NMR spectrum of the reaction solution shows the formation of the hydride $[Ca_3H_2(Me_3TACD)_3]^+(SiPh_3)^-$ (**4**), identified by the Ca*H* and *meta*/*para*-Ph resonances and $HSiPh_3$[21] in the ratio of 1:2 (Figure 2b). $HSiPh_3$ was consumed completely within 24 h, whereas the cation $[Ca_3H_2(Me_3TACD)]^+$ remained intact (Figure 2d). During the reaction time of 24 h, the triphenylsilyl anion $(SiPh_3)^-$ underwent degradation, and the ^{1}H NMR spectra show the presence of the dihydridotriphenylsilicate $(SiH_2Ph_3)^-$ (δ = 5.96 ppm for the hydrido resonances). The chemical shift of the hydrido resonance is in agreement with literature values.[8,22] At the end of the reaction time several resonances were found in the range of δ = 6.5−7.1 ppm, and a new resonance at δ = 4.49 ppm ($^1J_{Si-H}$ = 96.1 Hz) was found, which can be assigned to hydridodiphenylsilyl anion $(SiHPh_2)^-$. Such a silyl anion in $[KSiHPh_2]$ was mentioned before without spectroscopic data[23] and is well-known for late transition metals (Ni, Pd, and Pt).[24]

On the basis of these observations, we propose that the heteroleptic calcium complex $[Ca(Me_3TACD)SiPh_3]$ (**2**) is able to cleave dihydrogen under formation of the trinuclear calcium hydride cluster $[Ca_3H_2(Me_3TACD)_3]^+(SiPh_3)^-$ and $HSiPh_3$. The thermodynamically favored formation of the hydride cluster[4,8] proceeds fast, and the product **4** is formed in quantitative yield. ^{1}H NMR spectra so far showed only the formation of one calcium hydride cluster. Nevertheless, we

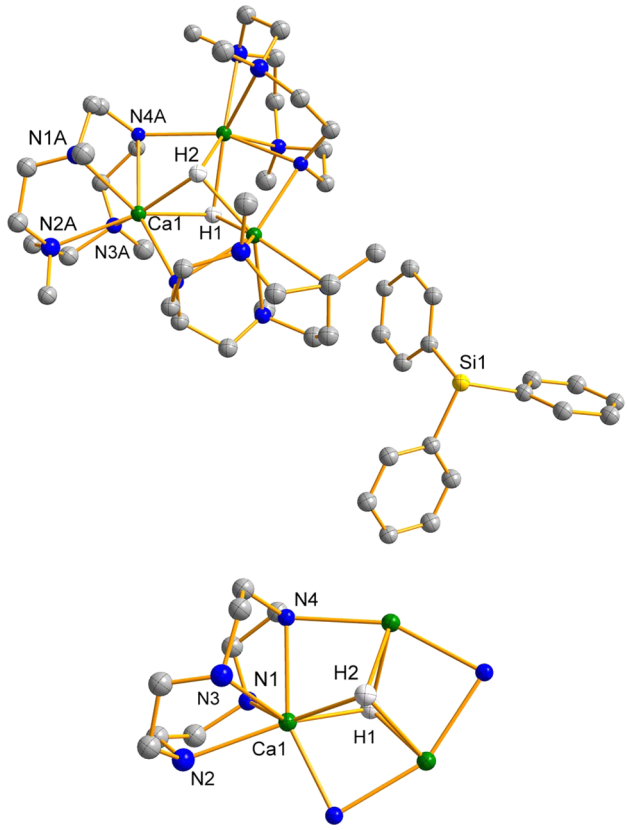

Figure 1. Molecular structure of the calcium hydride **4a** (upper) and cutout of the cationic part (lower). Ellipsoids are shown at the 50% probability level. Hydrogen atoms except for those of the Ca_3H_2 core and the THF molecules within the lattice are omitted for clarity. The disordered atoms are only shown with one split position. In the cation part, methyl groups of the amine nitrogen atoms are omitted. Selected bond lengths [Å] and angles [deg]: Ca···Ca 3.351(2); Ca1−N1A 2.65(2); Ca1−N2A 2.60(1); Ca1−N3A 2.65(2); Ca1−N4A 2.47(2); Si1−C12A 1.964(5); C12A−Si1−C12A′ 100.3(3).

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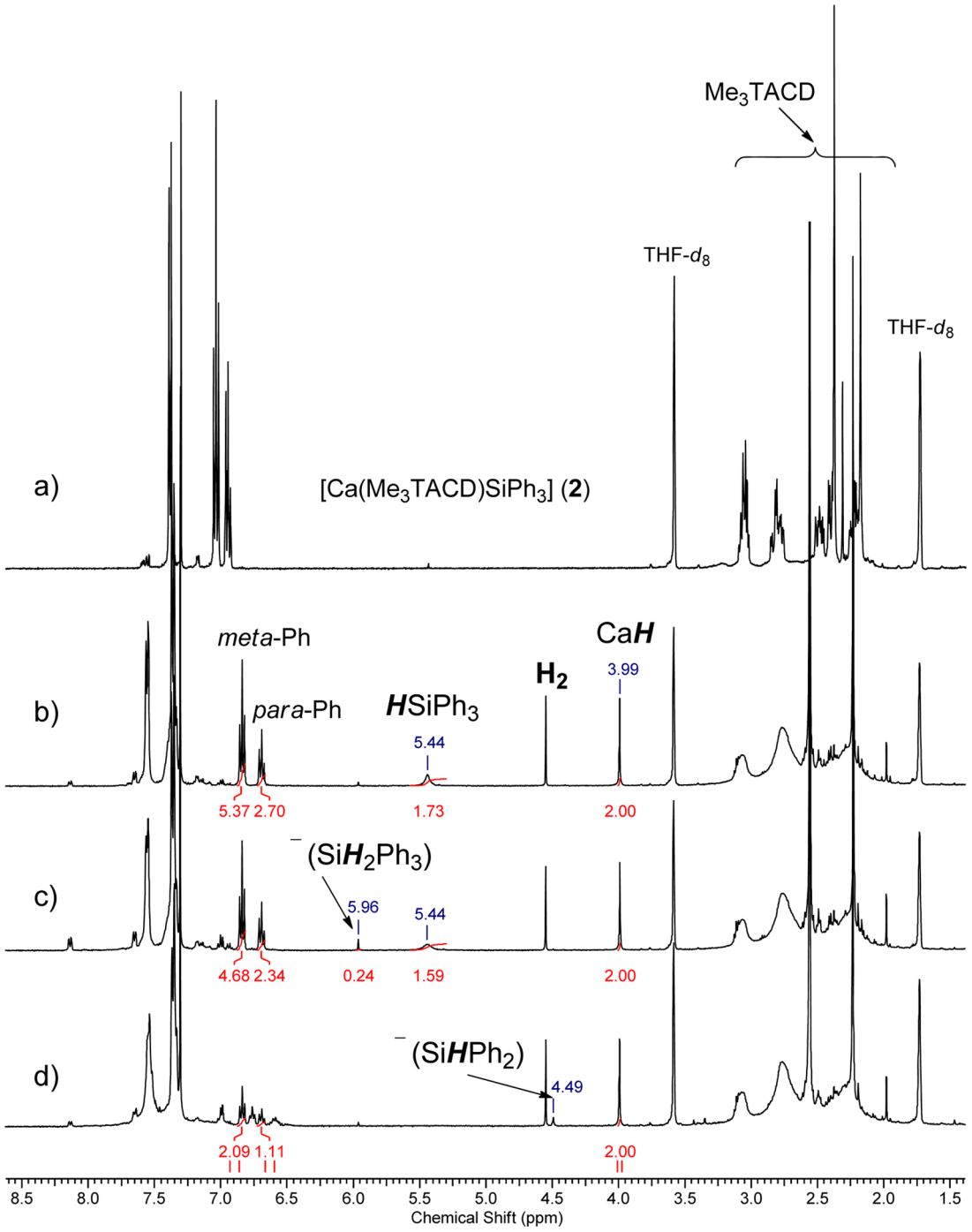

Figure 2. ^{1}H NMR spectra of the reaction mixture of **2** with dihydrogen in THF-d_8 at 60 °C. (a) ^{1}H NMR spectrum of pure **2**. (b–d) ^{1}H NMR spectra of the reaction solution after 15 min, 16 h, and 24 h.

propose the existence of monomeric or dimeric calcium hydride $[CaH(Me_3TACD)]_n$ (n = 1, 2), which reacts with $[Ca(Me_3TACD)SiPh_3]$ under formation of the calcium hydride cluster $[Ca_3H_2(Me_3TACD)_3]^+(SiPh_3)^-$ (Scheme 3).

CONCLUSION

Bis(triphenylsilyl)calcium, $[Ca(SiPh_3)_2(THF)_4]$ (**1**),[5] was converted into the heteroleptic calcium complex $[Ca(Me_3TACD)SiPh_3]$ (**2**) by Brønsted acid–base reaction with the macrocyclic amine $(Me_3TACD)H$. Compound **2** is suitable for selective hydrogenolysis under relatively mild conditions (1 bar of H_2 at 60 °C within 15 min) to give $[Ca_3H_2(Me_3TACD)_3]^+(SiPh_3)^-\cdot 2THF$ (**4a**) in high yield. Deuterium labeling experiments confirmed the activation of dihydrogen. $[Ca_3D_2(Me_3TACD)_3]^+(SiPh_3)^-\cdot 2THF$ (**4b**) was obtained from **2** and deuterium. The selective hydrogenolysis of the Ca–Si bond in **2** is a unique feature. Early main group metal hydrides are usually prepared by the so-called silane route or by β-hydride elimination.[25] These synthetic procedures involve an M–C or M–N/Si–H or M–C or M–N/C–H σ-bond metathesis to give the metal hydrides. Syntheses of metal hydrides by hydrogenolysis of hydrocarbyls and amides are well-established for rare-earth metals;[26] however, they are less

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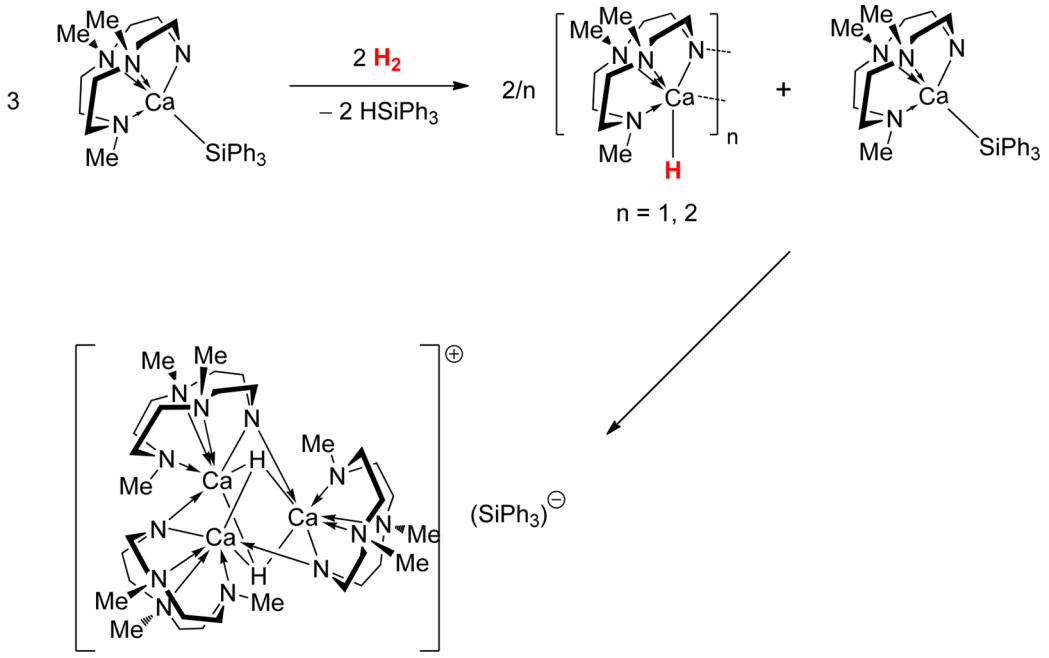
Scheme 3. Proposed Mechanism for the Calcium Hydride Cluster Formation



common for the more electropositive early main group metals.[27]

EXPERIMENTAL SECTION

General Considerations. All operations were performed under an inert atmosphere of dry argon using standard Schlenk line or glovebox techniques. THF-d_8, benzene, and hexane were distilled under argon from sodium/benzophenone ketyl prior to use. THF and pentane were purified using an MB SPS-800 solvent purification system. Triphenylsilane was purchased from Sigma-Aldrich and purified by vacuum sublimation. Hydrogen (99.999) and deuterium (99.8) were purchased from Praxair-Westfalen AG. Elemental analyses were performed on an elementar vario EL machine. Metal content was determined by metal titration following the subsequent procedure: 20−30 mg of the product was dissolved in 1 mL of THF and hydrolyzed. To this solution 1 mL of an aqueous ammonia solution (25%) and a buffer tablet (Eriochrome black T) were added, and the mixture was titrated with a 0.01 M solution of ethylenediaminetetraacetic acid disodium salt until the transition from red to green was observed. ^{1}H, ^{13}C{^{1}H}, and ^{29}Si{^{1}H} NMR spectra were recorded on a Bruker Avance II 400 or a Bruker Avance III HD 400 spectrometer at 25 °C in J. Young type NMR tubes. ^{2}H NMR spectrum was recorded on an Agilent VNMRS 400 spectrometer. Chemical shifts for ^{1}H, ^{13}C{^{1}H}, and ^{29}Si{^{1}H} NMR spectra were referenced internally using the residual solvent resonance and are reported relative to tetramethylsilane. The resonances in ^{1}H and ^{13}C NMR spectra were assigned on the basis of two-dimensional NMR experiments (COSY, HSQC, HMBC). $(Me_3TACD)H$,[5] $[Ca(SiPh_3)(THF)_4]$,[4] and $[Ca(C_3H_5)_2]$[8] were prepared according to published procedures.

*$[Ca(Me_3TACD)SiPh_3]$ (**2**).* A solution of $(Me_3TACD)H$ (43 mg, 0.2 mmol) in benzene (1 mL) was added to a solution of $[Ca(SiPh_3)_2(THF)_4]$ (**1**) (169 mg, 0.2 mmol) in benzene (3 mL) and stirred for 5 min at room temperature. During that time a yellow powder precipitated from the solution. The supernatant solvent was decanted off, the product was washed with pentane (3 × 5 mL), and the solvent was removed under reduced pressure. After drying in vacuo, $[Ca(Me_3TACD)SiPh_3]$ (**2**) (102 mg, 0.2 mmol, >99%) was isolated as pale yellow powder.

^{1}H NMR (THF-d_8, 400.1 MHz): δ 2.18 (s, 3H, CH_3), 2.14−2.29 (m, 4H, CH_2), 2.38 (s, 6H, CH_3), 2.33−2.53 (m, 4H, CH_2), 2.73−2.91 (m, 4H, CH_2), 2.99−3.15 (m, 4H, CH_2), 6.88−7.00 (m, 3H, *para*-Ph), 7.00−7.12 (m, 3H, *meta*-Ph), 7.34−7.43 (m, 3H, *ortho*-Ph) ppm. ^{13}C{^{1}H} NMR (THF-d_8, 100.6 MHz): δ 44.21 (CH$_3$), 47.43 (CH$_3$), 52.06 (CH$_2$), 55.76 (CH$_2$), 56.16 (CH$_2$), 64.01 (CH$_2$), 125.34 (*para*-Ph), 127.03 (*meta*-Ph), 137.12 (*ortho*-Ph), 154.31 (*ipso*-Ph) ppm. ^{29}Si{^{1}H} NMR (THF-d_8, 79.5 MHz): δ −10.25 (Ca*Si*) ppm. Anal. Calcd for $C_{29}H_{40}N_4CaSi$: C, 67.92; H, 7.86; N, 10.93; Ca, 7.82. Found: C, 64.79; H, 7.98; N, 10.47; Ca, 7.79%.

*$[Ca(Me_3TACD)_2]$ (**3**).* A solution of $(Me_3TACD)H$ (129 mg, 0.6 mmol) in pentane (2 mL) was added to a suspension of calcium bis(allyl)$[Ca(C_3H_5)_2]$ (37 mg, 0.3 mmol) in pentane (3 mL) and stirred for 6 h at room temperature. The solution was filtered and concentrated under reduced pressure. After 12 h at −30 °C a microcrystalline powder precipitated from the solution. After the supernatant was removed, the crystals were dried in vacuo, and $[Ca(Me_3TACD)_2]$ (**3**) (47 mg, 0.1 mmol, 33%) was isolated as colorless microcrystals.

^{1}H NMR (THF-d_8, 400.1 MHz): δ 1.91−2.24 (br, 12H, CH_2), 2.31 (s, 18H, CH_3), 2.47−2.61 (br, 4H, CH_2), 2.61−2.80 (br, 8H, CH_2), 2.98−3.10 (br, 4H, CH_2), 3.15−3.30 (br, 4H, CH_2) ppm. ^{13}C{^{1}H} NMR (THF-d_8, 100.6 MHz): δ 45.82 (CH$_3$), 49.17 (CH$_3$), 53.04 (CH$_2$), 58.29 (CH$_2$), 58.63 (CH$_2$), 63.60 (CH$_2$) ppm. Anal. Calcd for $C_{22}H_{50}N_8Ca$: C, 56.61; H, 10.80; N, 24.01; Ca, 8.59. Found: C, 56.16; H, 10.80; N, 23.77; Ca, 8.73%.

*$[Ca_3H_2(Me_3TACD)_3](SiPh_3)\cdot 2THF$ (**4a**).* A degassed solution of $[Ca(Me_3TACD)SiPh_3]$ (**2**) (51 mg, 0.1 mmol) in THF (2 mL) was charged with H_2 (1 bar) in a glass autoclave and stirred for 15 min at 60 °C. The reaction mixture was layered with hexane (1 mL) and cooled to −30 °C. Single crystals grew within 12 h. After the supernatant was removed, the crystals were washed with pentane, and the solvent was removed under reduced pressure. After drying in vacuo, $[Ca_3H_2(Me_3TACD)_3](SiPh_3)\cdot 2THF$ (**4a**) (35 mg, 0.03 mmol, 91%) was isolated as red crystals. Single crystals of **4a** suitable for X-ray diffraction were grown from THF at −30 °C over a period of 24 h.

^{1}H NMR (THF-d_8, 400.1 MHz): δ 1.78 (m, 8H, THF), 2.16−2.38 (br, 16H, CH_2), 2.24 (s, 9H, CH_3), 2.56 (s, 18H, CH_3), 2.60−2.90 (br, 24H, CH_2), 2.92−3.20 (br, 8H, CH_2), 3.62 (m, 8H, THF), 4.00 (s, 2H, Ca*H*), 6.62−6.72 (m, 3H, *para*-Ph), 6.78−6.88 (m, 6H, *meta*-Ph), 7.30−7.39 (m, 6H, *ortho*-Ph) ppm. ^{13}C{^{1}H} NMR (THF-d_8, 100.6 MHz): δ 26.44 (THF), 44.23 (CH$_3$), 46.06 (CH$_3$), 51.16 (CH$_2$), 54.06 (CH$_2$), 55.14 (CH$_2$), 58.98 (CH$_2$), 68.27 (THF), 122.50 (*para*-Ph), 126.19 (*meta*-Ph), 137.27 (*ortho*-Ph), 162.40 (*ipso*-Ph) ppm. ^{29}Si{^{1}H} NMR (THF-d_8, 79.5 MHz): δ −8.06 (Ca*Si*) ppm. Anal. Calcd for

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$C_{59}H_{108}N_{12}Ca_3O_2Si$: C, 60.78; H, 9.34; N, 14.42; Ca, 10.31. Found: C, 57.82; H, 9.06; N, 14.34; Ca, 10.30%.

*$[Ca_3D_2(Me_3TACD)_3](SiPh_3)\cdot 2THF$ (**4b**).* A degassed solution of $[Ca(Me_3TACD)SiPh_3]$ (**2**) (51 mg, 0.1 mmol) in THF (2 mL) was charged with D_2 (1 bar) in a glass autoclave and stirred for 15 min at 60 °C. The reaction mixture was layered with hexane (1 mL) and cooled to −30 °C. Single crystals grew within 12 h. After the supernatant was removed, the crystals were washed with pentane, and the solvent was removed under reduced pressure. After it dried in vacuo, $[Ca_3D_2(Me_3TACD)_3](SiPh_3)\cdot 2THF$ (**4b**) (39 mg, 0.032 mmol, 97%) was isolated as red crystals.

^1H NMR (THF-d_8, 400.1 MHz): δ 1.78 (m, 8H, THF), 2.16−2.38 (br, 16H, CH_2), 2.24 (s, 9H, CH_3), 2.56 (s, 18H, CH_3), 2.60−2.90 (br, 24H, CH_2), 2.92−3.20 (br, 8H, CH_2), 3.62 (m, 8H, THF), 6.62−6.72 (m, 3H, *para*-Ph), 6.78−6.88 (m, 6H, *meta*-Ph), 7.30−7.39 (m, 6H, *ortho*-Ph) ppm. $^{13}C\{^1H\}$ NMR (THF-d_8, 100.6 MHz): δ 26.43 (THF), 44.24 (CH_3), 46.05 (CH_3), 51.15 (CH_2), 54.13 (CH_2), 55.21 (CH_2), 58.96 (CH_2), 68.27 (THF), 122.50 (*para*-Ph), 126.18 (*meta*-Ph), 137.26 (*ortho*-Ph), 162.38 (*ipso*-Ph) ppm. $^{29}Si\{^1H\}$ NMR (THF-d_8, 79.5 MHz): δ −8.06 (Ca*Si*) ppm. ^2H NMR (THF-d_8, 61.1 MHz): δ 4.09 (s, 2D, Ca*D*) ppm. Anal. Calcd for $C_{59}H_{106}D_2N_{12}Ca_3O_2Si$: C, 60.68; H, 9.49; N, 14.39; Ca, 10.29. Found: C, 58.32; H, 9.23; N, 14.28; Ca, 10.23%.

X-ray Crystal Structure Determination. X-ray diffraction data were collected at −173 °C on a Bruker D8 goniometer with APEX CCD area-detector in ω-scan mode. Mo Kα radiation (multilayer optics, λ = 0.710 73 Å) from an Incoatec microsource was used. The programs SAINT+[28] and SADABS[29] were used for unit cell determination and absorption correction. The structure was solved by direct methods using SIR-92;[30] the refinement was carried out against F^2 with SHELXL-2013.[31] The Me_3TACD fragment and the anionic $(SiPh_3)^-$ fragment, as well as the THF molecules, are disordered. The disorder could be well modeled with split positions. The metal atoms Ca and Si were refined with anisotropic displacement parameters; all other atoms were refined with isotropic displacement parameters except for the hydrogen atoms that were placed in calculated positions. The positions of both hydrides H1 and H2 were located in a difference Fourier synthesis as the highest residual peaks with 0.52 and 0.59 e·Å^{-3} and were fixed in this position.

■ ASSOCIATED CONTENT

Supporting Information

^1H, ^2H, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra of **2**, **3**, **4a**/**4b** and X-ray crystallographic details and data for **4a**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00527. CCDC 1052284 contains crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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