RESEARCH ARTICLE

A Cationic Barium Hydride Complex Supported by an NNNN-Type Macrocycle

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The dibenzyl complex of barium [(Me$_4$TACD)Ba(CH$_2$Ph)$_2$] was prepared by reacting [Ba(CH$_2$Ph)$_2$] with NNNN-type macrocycle Me$_4$TACD (Me$_4$TACD = 1,4,7,10-tetramethyltetraazacyclododecane) and isolated as yellow crystals. Single crystal X-ray diffraction revealed η^2- and η^3-coordination of the benzyl groups. The benzylbarium cation in [(Me$_4$TACD)Ba-(CH$_2$Ph)(thf)][B(C$_6$H$_3$-3,5-Me$_2$)$_4$] was obtained upon protonolysis of the neutral bariumdibenzyl with the weak Brønsted acid [NEt$_3$H][B(C$_6$H$_3$-3,5-Me$_2$)$_4$] and isolated as colorless crystals.

When the benzylbarium cation was reacted with H$_2$ (1 bar) in THF at room temperature, colorless crystals of the dinuclear hydride complex [(Me$_4$TACD)$_2$Ba$_2$(μ-H)$_2$(thf)$_4$][B(C$_6$H$_3$-3,5-Me$_2$)$_4$]$_2$ precipitated from the reaction mixture and characterized by single crystal X-ray diffraction. The structural motif [Ba$_2$(μ-H)$_2$]$^{2+}$ was compared with that published in the literature. Hydrogenolysis of the dibenzyl [(Me$_4$TACD)Ca(CH$_2$Ph)$_2$] under the same conditions resulted in decomposition.

Introduction

Crystalline barium dihydride [BaH$_2$]$_n$ attracts attention as hydrogen storage and hydride conductance material.[1] More recently, metallic barium was reported to act as an efficient hydrogenation catalysts for olefins, implying formation of surface-confined barium-hydride species.[2] However, discrete molecular barium hydrides still remain scarce.[3] The first example was a remarkable heptanuclear cluster [BaH$_7$(HMDS)$_7$]·2 C$_6$H$_6$ (**A**, HMDS = N(SiMe$_3$)$_2$ in Chart 1), which was formed by reacting [Ba(HMDS)$_2$] with PhSiH$_3$ in benzene.[4] The large ionic radius of the metal (ionic radii for c.n. = 6: 1.14 Å for Ca, 1.32 Å for Sr, 1.49 Å for Ba)[5] and pronounced ionicity of metal-ligand bonds make such molecular species particularly prone to Schlenk-type ligand redistribution.

Dinuclear complexes [(Tp^{Ad,iPr})$_2$Ba$_2$(μ-H)$_2$] (**B**, Tp^{Ad,iPr} = hydrotris(3-adamantyl-5-isopropyl-pyrazolyl)borate) and [(η^5-C$_5$R$_5$)$_2$Ba$_2$(μ-H)$_2$(DABCO)] (**C**, R = C$_6$H$_3$-3,5-^{i}Pr) supported by bulky 5-electron donor ligands of L$_2$X-type were obtained by hydrogenolysis of the corresponding alkyl precursors.[6a,b] Apparently the isolation of low nuclearity barium hydride complexes requires highly sterically demanding ligands to prevent formation of hydride clusters and eventually insoluble [BaH$_2$]$_n$.[1] These molecular barium hydride complexes were reported to catalytically hydrogenate olefins,[4,6,7] but given the activity of activated barium metal itself, it remains to be seen what the actual catalysts are.

Using a macrocyclic polyamine ligand such as NNNN-type macrocycle Me$_4$TACD (Me$_4$TACD = 1,4,7,10-tetramethyltetraazacyclododecane), we have been exploring the possibility to stabilize cationic alkaline earth metal hydrides [MH]$^+$, which do not tend to aggregate due to the positive electric charge.[8–10] Here, a molecular hydride cation of barium stabilized by the macrocyclic polyamine Me$_4$TACD ligand is reported.

Results and Discussion

In analogy to the synthesis of [(Me$_4$TACD)M(CH$_2$Ph)$_2$] (M = Ca,[9b] Sr[10]), the isolation of macrocycle supported barium benzyl precursors was attempted starting from the parent dibenzyl [Ba(CH$_2$Ph)$_2$]. Compared to the THF-adduct [Ba(CH$_2$Ph)$_2$(thf)$_{0.5}$] reported in the literature,[11] we observed that THF could be completely removed in vacuo to give the solvent-free compound [Ba(CH$_2$Ph)$_2$]. Addition of Me$_4$TACD to a suspension of [Ba(CH$_2$Ph)$_2$] in THF gave a clear solution, from which after storing at −40 °C for 16 h yellow crystals of the dibenzyl complex [(Me$_4$TACD)Ba(CH$_2$Ph)$_2$] (**1**) were isolated in 92 % yield (Scheme 1).

Single crystal diffraction of **1** revealed a six-coordinate barium center with the typical κ^{4}N-coordination of the macrocycle (Figure 1). In contrast to the seven-coordinate metal center in the strontium homologue [(Me$_4$TACD)Sr-(CH$_2$Ph)$_2$(thf)],[10] no additional THF molecules are coordinated at the barium center. Rather, the solid-state structure of **1** resembles that of the calcium homologue [(Me$_4$TACD)Ca-(CH$_2$Ph)$_2$], although the benzyl ligands in **1** exhibit higher hapticity (η^2 and η^3 for Ba versus two η^1 for Ca). This can be explained by the higher lability of the THF at the significantly larger, less electrophilic barium. The coordination of the benzyl ligands to the metal center in **1** is quite flexible, as indicated by

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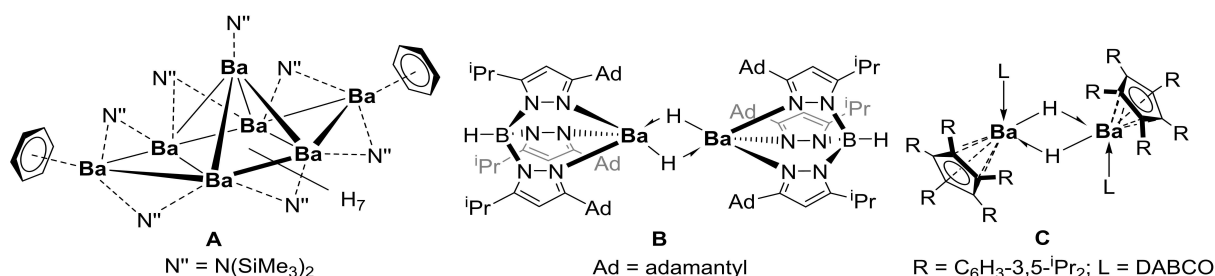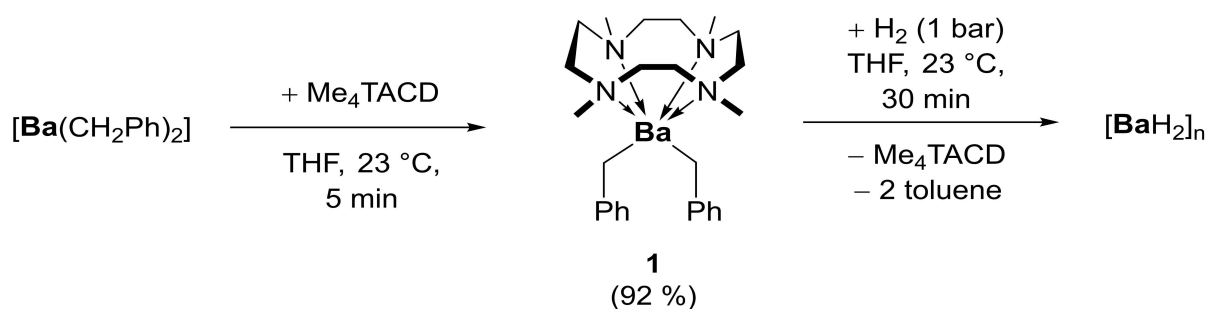jun.okuda@ac.rwth-aachen.de

Chart 1. Isolated barium hydride complexes. For cluster **A** only a schematic representation for the polyhedron formed by the barium centers is shown; the hydride ligands are located in the center of the central square and on each triangular face.

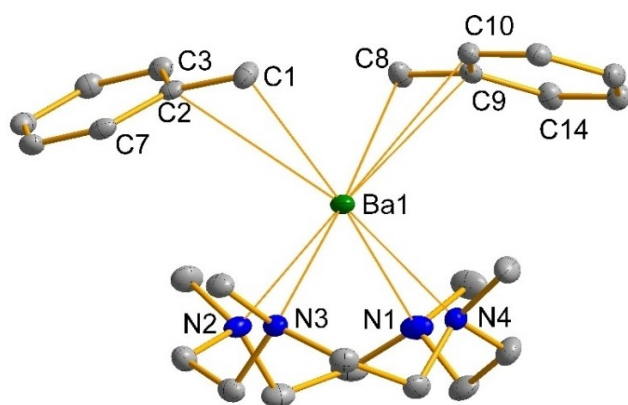**Scheme 1.** Synthesis and hydrogenolysis of a Me$_4$TACD-stabilized barium dibenzyl.

Figure 1. Displacement ellipsoid plot (30 % probability) of one of the two crystallographically independent molecules of **1** in the crystal. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å]: Ba1–N1 2.887(3), Ba1–N2 2.968(3), Ba1–N3 2.858(3), Ba1–N4 2.988(3), Ba1–C1 2.941(4), Ba1–C2 3.410(3), Ba1–C7 3.785(4), Ba1–C8 2.922(4), Ba1–C9 3.155(3), Ba1–C10 3.248(3).

a second crystallographically independent molecule in the unit cell where both benzyl ligands are η^2-coordinated.

Crystalline **1** is sparingly soluble in THF-d_8 and showed only broad resonances in the ^{1}H NMR spectrum (Figure 2). Not unexpectedly, upon hydrogenolysis of a suspension of **1** with H$_2$ (1 bar) in THF, formation of toluene and free Me$_4$TACD was observed, as suggested by the ^{1}H NMR spectrum of the reaction mixture. A very broad resonance at $\delta = 9.4$ ppm (linewidth > 600 Hz) could be assigned to oligomeric [BaH$_2$]$_n$. This

chemical shift is within the reported chemical shift range for barium hydride complexes ($\delta = 7.92$ ppm for **B** and $\delta = 10.39$ ppm for **C**).[6] The chemical shift of solid [BaH$_2$]$_n$ was reported at $\delta = 8.7 \pm 1$ ppm (linewidth = 760 Hz).[12]

The benzylbarium cation [(Me$_4$TACD)Ba(CH$_2$Ph)(thf)][B(C$_6$H$_3$-3,5-Me$_2$)$_4$] (**2**) was obtained upon protonolysis of complex **1** with the weak Brønsted acid [NEt$_3$H][B(C$_6$H$_3$-3,5-Me$_2$)$_4$] in THF and isolated as colorless crystals in 91 % yield (Scheme 2).

The ^{1}H NMR spectrum of **2** shows broad resonances for the methylene protons of the Me$_4$TACD ligand, in line with a fluxional coordination of the macrocycle that was previously observed also for the strontium homolog [(Me$_4$TACD)Sr-(CH$_2$Ph)(thf)][B(C$_6$H$_3$-3,5-Me$_2$)$_4$].[10] Compared with the benzylbarium cation of the lighter homologs [(Me$_4$TACD)M-(CH$_2$Ph)(thf)][B(C$_6$H$_3$-3,5-Me$_2$)$_4$] (M = Ca, Sr), the CH$_2$ resonance of the benzyl ligand is shifted downfield to $\delta(^1$H$) = 1.84$ ppm and $\delta(^{13}$C$) = 57.5$ ppm (M = Ca: $\delta(^1$H$) = 1.47$ ppm and $\delta(^{13}$C$) = 42.9$ ppm; M = Sr: $\delta(^1$H$) = 1.46$ ppm and $\delta(^{13}$C$) = 46.8$ ppm).[10] This may indicate a higher hapticity of the benzyl ligand at the barium center. Mulvey et al. elaborated on the influence of the alkali metal cation on the coordination mode of the benzyl ligand, showing that a downfield shift of the resonance in the ^{1}H NMR spectra is caused by higher hapticity.[13] For **2**, the observed downfield shift hints at a higher hapticity for the benzyl ligand compared to the cationic benzyl complexes of the lighter congeners with η^1-coordination. As in the case of the lighter homologues, one THF molecule is coordinated to the metal center of **2** and cannot be removed *in vacuo*. Despite several attempts, no single crystals could be obtained.
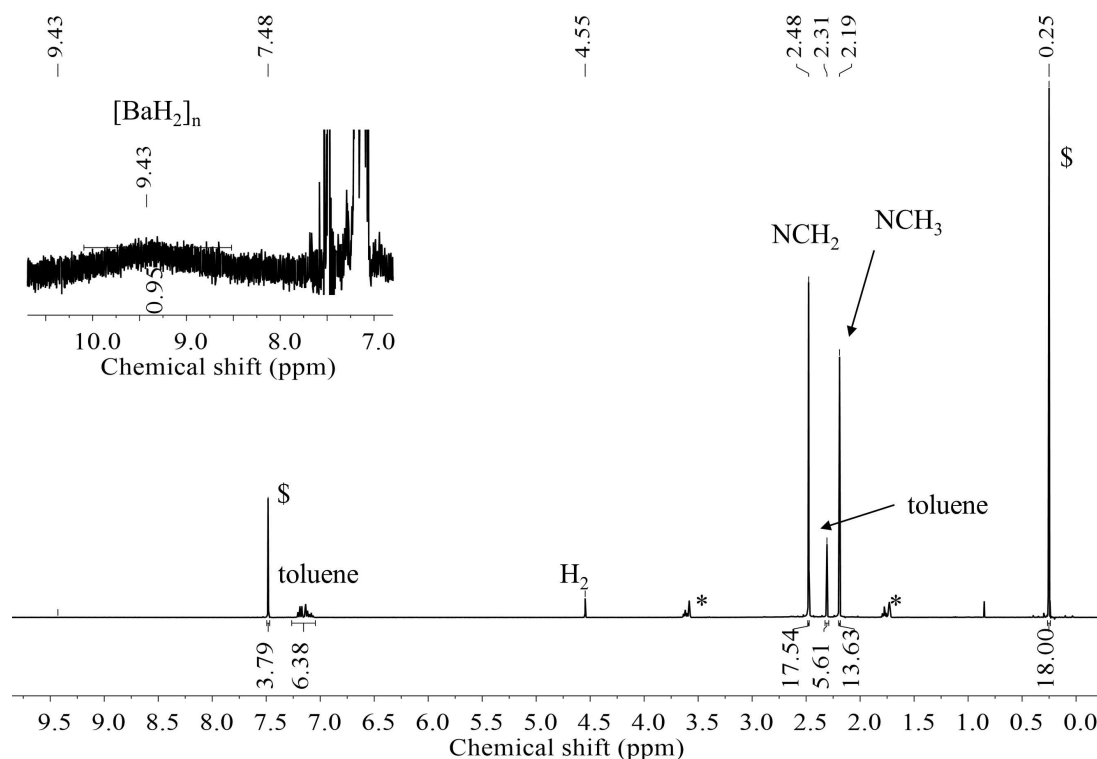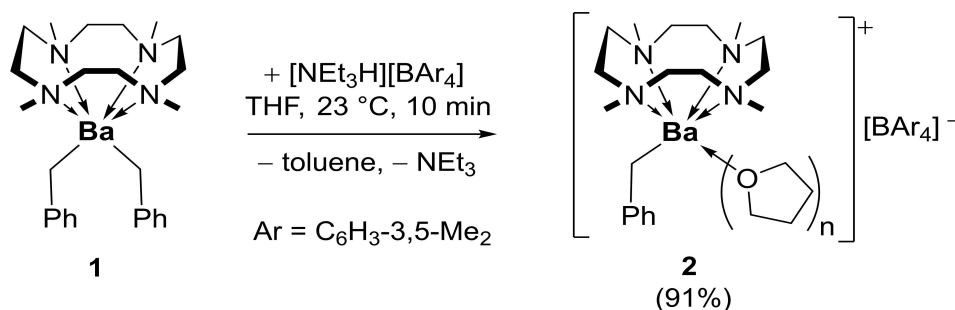
Figure 2. ^1H NMR spectrum (400 MHz, THF-d_8, 23 °C) of the reaction mixture of **1** with H_2 (1 bar) with 1,4-$(SiMe_3)_2$–C_6H_4 ($) as internal standard. (*) denotes residual proton resonances of THF-d_8.


Scheme 2. Synthesis of cationic barium benzyl **2**.

When **2** was reacted with H_2 (1 bar) in THF, colorless crystals precipitated from the reaction mixture, which were identified by single crystal X-ray diffraction as the dinuclear hydride complex $[(Me_4TACD)_2Ba_2(\mu-H)_2(thf)_4][B(C_6H_3-3,5-Me_2)_4]_2$ (**3**) (Scheme 3). NMR spectroscopic analysis of **3** was prevented by insolubility in all aprotic solvents. Attempts to redissolve crystals of **3** in THF-d_8 by heating the mixture to 40 °C were unsuccessful. Although the formation of free Me_4TACD suggested decomposition of compound **3** due to its thermal sensitivity, no resonances of $[BaH_2]_n$ were observed.

The molecular structure of **3** was established by X-ray diffraction on a single crystal and shows a dinuclear cation of C_i-symmetry. Both barium centers are eight-coordinate with approximate square anti-prismatic coordination geometry (Figure 3).

Two THF ligands are coordinated to the barium cation in addition to the κ^4-Me_4TACD macrocycle and the bridging hydride ligands. Compared to the Me_4TACD hydride complexes of calcium[9] and strontium,[10] the higher coordination number for the barium center in **3** is consistent with its higher ionic radius. Due to a significant amount (25%) of a co-crystallized OH-bridged species, the metal-hydride bond lengths in **3** will not be discussed. We have pointed out that structural analysis of heavy alkaline metal hydrides often suffer from difficulties arising from the exceedingly high sensitivity to moisture and that discussions on metal-hydrogen bond distances should be treated with some care.[14]

The electron-density based interaction of X-rays with matter adds to these difficulties.[15] The cation in **3** and the neutral complexes **B** and **C** (Chart 1) share the $[Ba_2(\mu-H)_2]$ motif. All of
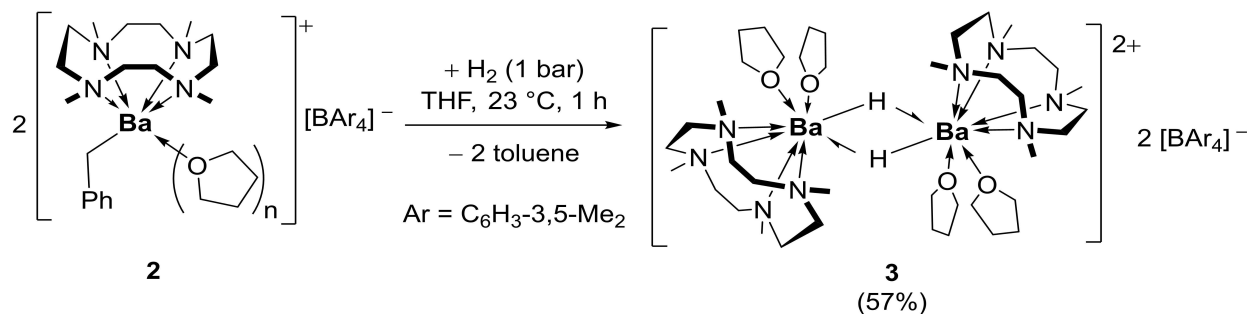
Scheme 3. Synthesis of Me$_4$TACD stabilized barium hydride complex **3**.
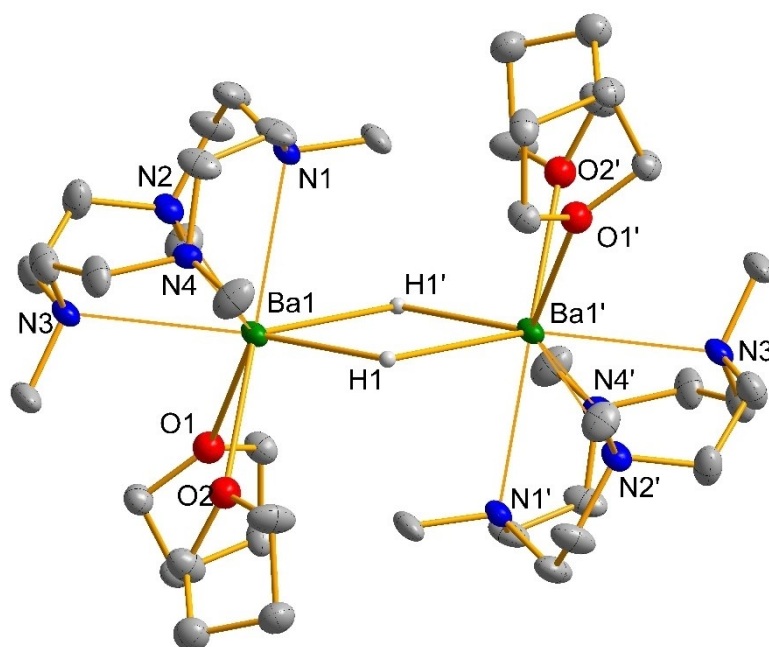

Figure 3. Displacement ellipsoid plot (30 % probability) of the dinuclear cation of **3** in the crystal; hydrogen atoms except the hydride ligands are omitted for clarity. Selected interatomic distances [Å]: Ba1···Ba1′ 4.3752(9), Ba1–N1 2.963(4), Ba1–N2 2.939(4), Ba1–N3 3.003(4), Ba1–N4 2.969(4), Ba1–O1 2.903(3), Ba1–O2 2.869(3). Unprimed and primed atoms are related by the symmetry operation 2-x, 1-y, 1-z.

them have been characterized by X-ray diffraction; in view of the necessarily limited precision of hydrogen coordinates in the presence of such dominant scattering centers as barium, a closer look at the treatment of intensity data and refinement procedures seems appropriate. For this purpose, published structure models and the underlying diffraction data for **B** and **C** were obtained from the CCDC.[16]

For both **B** and **C**, data were originally collected to a slightly higher resolution than the commonly accepted minimum (sinθ/λ = 0.6) but truncated during refinement; ca 1300 reflections for **B** and ca 3900 for **C** were thus omitted. In addition, the original authors decided to exclude individual intensities from the refinement which did not agree with their structure models (42 reflections were affected in the case of **B**, 149 in the case of **C**). Our diffraction data for **3** extended to a similar resolution as those of **B** and **C**, and we did not exclude any individual intensities from the least-squares refinement. To what extent do

such decisions concerning the treatment of intensity data influence the reported structure models, in particular the most relevant and presumably less precise hydride positions?

The intensity data for **C** and **3** are rather robust with respect to alternative refinement strategies. Re-refinement of **C** with all available intensity data and, *vice versa*, tentative data truncation for **3** to the required minimum resolution led to minor variations in the resulting [Ba$_2$(μ-H)$_2$]$^{2+}$ core which remained within the standard uncertainties suggested by the published models. In contrast, the structure model for **B** strongly depends on data handling. Without omission of individual reflections, refinement converges for significantly more unsymmetric hydride bridges. If the additional reflections at slightly higher resolution are also included, the lowest agreement factors are reached for an entirely different geometry. A graphical synopsis of these results is provided in Figure 4.
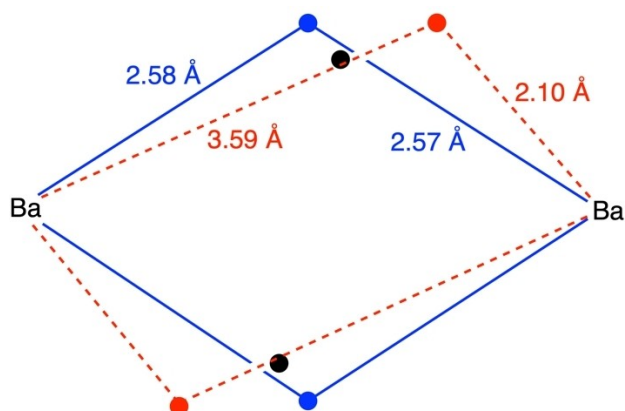
Figure 4. Convergence geometry obtained by alternative refinement strategies using the published diffraction data of **B**. The H atoms in the [Ba$_2$(μ-H)$_2$] core have been depicted as spheres, their radius denoting the standard uncertainty of the published structure model. Blue spheres indicate the geometry of the published model, black spheres result from a structure model in which no individual reflections were omitted from the refinement, red spheres were obtained from a structure model using all available data, i.e. without resolution-based truncation.

This clear correlation between the data handling and a structure model shows that the resulting structural parameters should be interpreted with care. Like in this example, the geometry of the hydride coordination may be affected by the treatment of the X-ray data; more reliable neutron data are usually not available.

Conclusion

In conclusion, the first example of a cationic barium hydride [(Me$_4$TACD)$_2$Ba$_2$(μ-H)$_2$(thf)$_4$][B(C$_6$H$_3$-3,5-Me$_2$)$_4$]$_2$ (**3**) has been presented. Low solubility in organic solvents and limitations in the crystallographic refinement did not allow a detailed structural discussion, but the large ionic radius of barium is clearly manifest in the high coordination number 8, as compared with 6 or 7 for the calcium homologs [(Me$_4$TACD)$_2$Ca$_2$(μ-H)$_2$(thf)$_n$] (n = 0, 1).[9] Notably, despite some efforts, the strontium homolog with the 12-membered macrocycle remains elusive.[10] In contrast, for both calcium and strontium the 15-membered N,N,N,N,N-type macrocycle allowed stabilization of the [M$_2$(μ-H)$_2$]$^{2+}$ core.[17] As attempts to stabilize the [Ba$_2$(μ-H)$_2$]$^{2+}$ core using the 18-membered N,N,N,N,N,N-type macrocycle remained inconclusive,[17c] one can assume that coordination of a large metal ion requires specific conformational constraints of the macrocycle at a large, polarizable ("soft") metal ion. To prevent ligand dissociation and subsequent on-set of the Schlenk equilibrium to give larger aggregates, specific ligand design becomes crucial, in particular when molecular hydrides of the heavy alkaline earth metals are to be employed in homogeneous catalysis.[3b,c,18]

Supplementary data

CCDC-2208015 and 2208016 contain the supplementary crystallographic data for **1** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Experimental Section

General Remarks. All operations were performed under an inert atmosphere of dry argon using standard Schlenk line or glovebox techniques. THF-d$_8$, THF, benzene and n-pentane were distilled under argon from sodium/benzophenone ketyl prior to use. Hydrogen (99.999%) and deuterium (99.8%) were purchased from Praxair-Westfalen AG. Commercially available reagents were dried over CaH$_2$ and distilled, or in case of solids, sublimed before use. ^{1}H, ^{2}H, ^{11}B{^{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. Chemical shifts for ^{1}H, ^{2}H and ^{13}C {^{1}H} NMR spectra were referenced internally using the residual solvent resonance and are reported relative to tetramethylsilane. ^{11}B{^{1}H} and ^{29}Si{^{1}H} NMR spectra were referenced externally to BF$_3$(OEt$_2$) and SiMe$_4$. The resonances in the ^{1}H and ^{13}C{^{1}H} NMR spectra were assigned on the basis of two-dimensional NMR experiments (COSY, HSQC, HMBC). Elemental analyses were performed on an Elementar vario EL instrument. In several instances, the carbon values were not satisfactory, possibly due to incomplete combustion as the result of carbonate or carbide formation as well as high air- and moisture sensitivity.[19] 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane Me$_4$TACD,[20] [K-(CH$_2$Ph)],[21] [NEt$_3$H][B(C$_6$H$_3$-3,5-Me$_2$)$_4$],[9b] and [Ba(CH$_2$Ph)$_2$][11] were prepared using literature procedures.

[(Me$_4$TACD)Ba(CH$_2$Ph)$_2$] (1). To a suspension of [Ba(CH$_2$Ph)$_2$] (128 mg, 0.40 mmol) in THF (1 mL) was added dropwise a solution of Me$_4$TACD (128 mg, 0.56 mmol) in THF (1 mL). The resulting red solution was stirred for 5 min until a precipitate started to form and then stored at −40 °C. After 16 h light orange microcrystals formed, which were isolated, washed with n-pentane (3×1 mL), and dried *in vacuo* to give [(Me$_4$TACD)Ba(CH$_2$Ph)$_2$] as yellow microcrystals (202 mg, 0.37 mmol); yield: 92%. Single crystals suitable for X-ray diffraction were obtained when a diluted solution of [Ba(CH$_2$Ph)$_2$] was layered with a solution of Me$_4$TACD and stored at −40 °C. Anal. calc. for C$_{26}$H$_{42}$BaN$_4$ (547.98 g mol^{-1}): C, 56.99; H, 7.73; N, 10.22. Found: C, 55.66; H, 7.40; N, 10.99%. Poor solubility in common organic solvents precluded NMR spectroscopic analysis.

[(Me$_4$TACD)Ba(CH$_2$Ph)(thf)][B(C$_6$H$_3$-3,5-Me$_2$)$_4$] (2). A solution of [(Me$_4$TACD)Ba(CH$_2$Ph)$_2$] (55 mg, 0.10 mmol) and [NEt$_3$H][B(C$_6$H$_3$-3,5-Me$_2$)$_4$] (53 mg, 0.10 mmol) in THF (1 mL) was stirred for 5 min at room temperature, filtered, layered with n-pentane and stored at −40 °C. Within 72 h light orange crystals formed, which were isolated, washed with n-pentane (3×2 mL), and dried under reduced pressure to give [(Me$_4$TACD)Ba(thf)(CH$_2$Ph)][B(C$_6$H$_3$-3,5-Me$_2$)$_4$] as yellow microcrystals (88 mg, 0.09 mmol); yield: 91%. ^{1}H NMR (400 MHz, 23 °C, THF-d$_8$): δ 1.74–1.80 (m, 4 H, THF), 1.84 (s, 2 H, Ba–CH$_2$), 1.90–2.96 (br. s, 16 H, NCH$_2$), 2.08 (s, 24 H, Ar–CH$_3$), 2.26 (s, 12 H, NCH$_3$), 3.60–3.64 (m, 4 H, THF), 5.64–5.68 (m, 1 H, *para*-Ph), 5.86–5.90 (m, 2 H, *meta*-Ph), 6.35 (s, 4 H, *para*-C$_6$H$_3$), 6.55–6.59 (m, 2 H, *ortho*-Ph), 6.94–6.98 (m, 8 H, *ortho*-C$_6$H$_3$) ppm. ^{13}C {^{1}H} (101 MHz, 23 °C, THF-d$_8$): δ 22.5 (Ar–CH$_3$), 26.6 (THF), 44.7 (NCH$_3$), 54.7 (br. NCH$_2$), 57.5 (Ba–CH$_2$), 68.4 (THF), 107.4 (*para*-Ph), 115.9 (*meta*-Ph), 123.6 (*para*-C$_6$H$_3$), 131.6 (*ortho*-Ph), 133.0 (*meta*-C$_6$H$_3$), 135.7 (*ortho*-

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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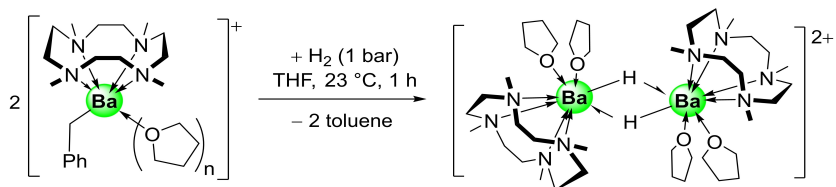
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A Cationic Barium Hydride Complex Supported by an NNNN-Type Macrocycle