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Electronic Supporting Information

A Tetranuclear Calcium Hydride Cluster with a Highly Symmetric $[Ca_4H_6]^{2+}$ Core

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1 General Remarks

All operations were performed under an inert atmosphere of dry argon using standard Schlenk line or glovebox techniques. [D_8]THF was distilled under argon from sodium/benzophenone ketyl prior to use. THF and *n*-pentane were purified using a MB SPS-800 solvent purification system. Hydrogen (99.999%) and Deuterium (99.999%, 99.8% D) purchased from Praxair-Westfalen AG. ^{1}H, ^{11}B{^{1}H} and ^{13}C{^{1}H} 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 and ^{13}C{^{1}H} spectra were referenced internally using the residual solvent resonance and are reported relative to tetramethylsilane. ^{11}B{^{1}H} was referenced externally to $BF_3(OEt_2)$. 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 case for **2**, the results were not satisfactory, possibly due to incomplete combustion and high air- and moisture sensitivity.[1] [$Ca(CH_2Ph)_2(thf)_4$],[2] 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3TACN)[3] and [NEt_3H][$B(C_6H_3$-3,5-$Me_2)_4$][4] were prepared according to literature procedures.

2 Synthetic Procedures and Characterizations

2.1 Synthesis of [(Me$_3$TACN)H][B(C$_6$H$_3$-3,5-Me$_2$)$_4$] (1)

To a stirred suspension of [NEt$_3$H][B(C$_6$H$_3$-3,5-Me$_2$)$_4$] (534 mg, 1.0 mmol) in Et$_2$O (10 mL) was added dropwise Me$_3$TACN (180 mg, 1.05 mmol) at room temperature. After stirring for 1 h, a colorless precipitate formed. The solid was isolated by centrifugation, washed with *n*-pentane (3 x 2 mL) and dried under reduced pressure to give [(Me$_3$TACN)H][B(C$_6$H$_3$-3,5-Me$_2$)$_4$] (**1**) as a colorless solid (588 mg, 0.97 mmol); yield: 97%.

Crystals suitable for single crystal X-ray diffraction were grown by layering of a THF solution with *n*-pentane.

^{1}H NMR (400 MHz, [D$_8$]THF, 25 °C): δ = 2.11 (s, 24 H, ArCH$_3$), 2.17 – 2.32 (m, 21 H, NCH$_3$ + NCH$_2$), 6.37 – 6.43 (m, 4 H, *para*-C$_6$H$_3$), 6.99 – 7.05 (m, 8 H, *ortho*-C$_6$H$_3$), 8.92 (br, 1 H, NH) ppm.

^{13}C{^{1}H} NMR (101 MHz, [D$_8$]THF, 25 °C): δ = 22.26 (ArCH$_3$), 43.25 (NCH$_3$), 51.83 (NCH$_2$), 123.77 (*para*-C$_6$H$_3$), 133.34 (q, $^3J_{BC}$ = 2.7 Hz, *meta*-C$_6$H$_3$), 135.43 (*ortho*-C$_6$H$_3$), 165.75 (q, $^1J_{BC}$ = 49.3 Hz, *ipso*- C$_6$H$_3$) ppm.

^{11}B{^{1}H} NMR (128 MHz, [D$_8$]THF, 25 °C): δ = –6.89 ppm.

Anal. calc. for C$_{41}$H$_{58}$N$_3$B (603.75 g mol^{-1}): C, 81.57; H, 9.68; N, 6.96. Found: C, 81.51; H, 9.56; N, 7.11 %.

2.2 NMR spectra of [(Me$_3$TACN)H][B(C$_6$H$_3$-3,5-Me$_2$)$_4$] (1)

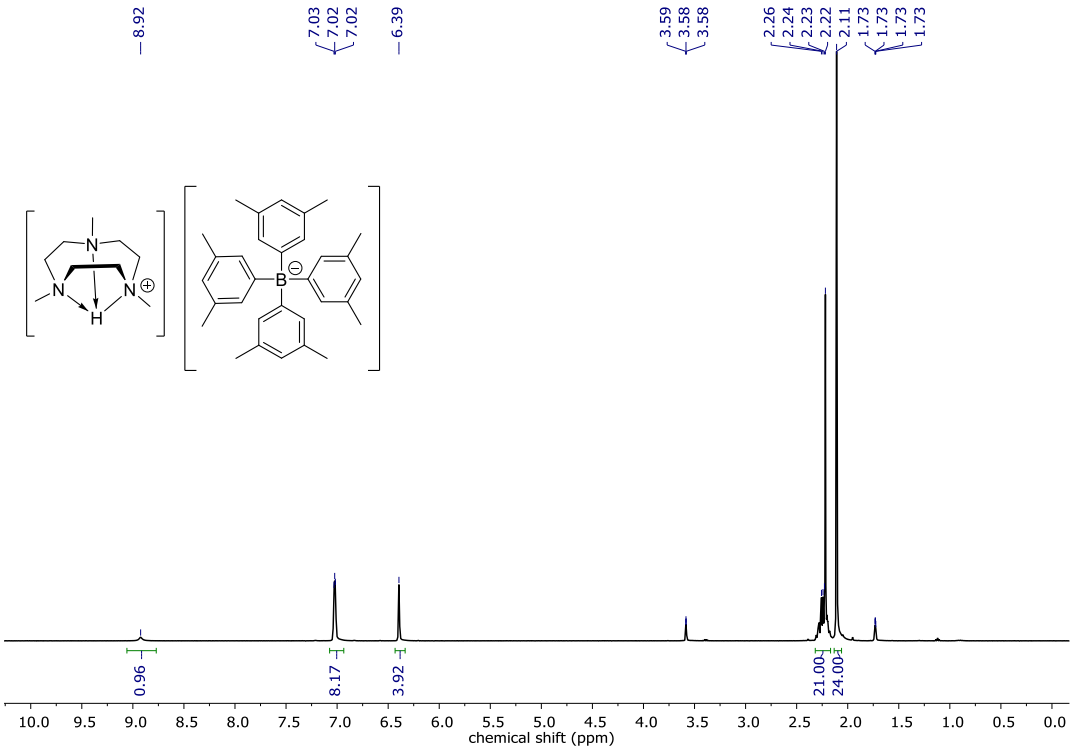


Fig. S1. ^{1}H NMR spectrum (400 MHz, [D$_8$]THF, 25 °C) of [(Me$_3$TACN)H][B(C$_6$H$_3$-3,5-Me$_2$)$_4$] (**1**).

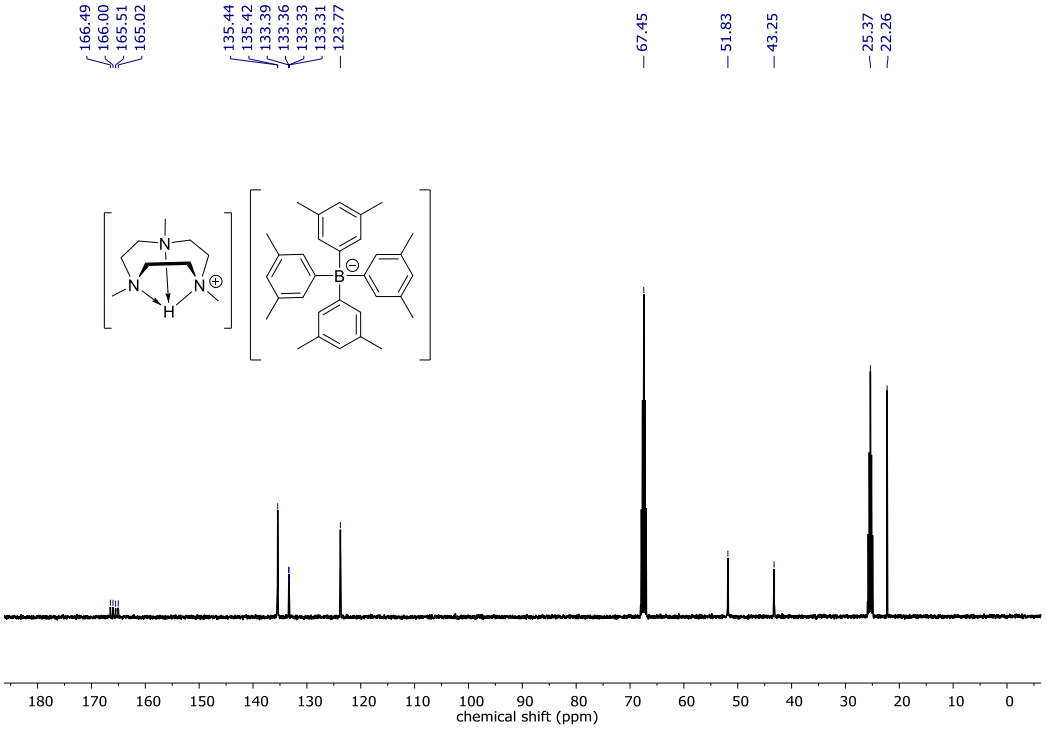


Fig. S2. ^{13}C{^{1}H} NMR (101 MHz, [D$_8$]THF, 25 °C) of [(Me$_3$TACN)H][B(C$_6$H$_3$-3,5-Me$_2$)$_4$] (**1**).

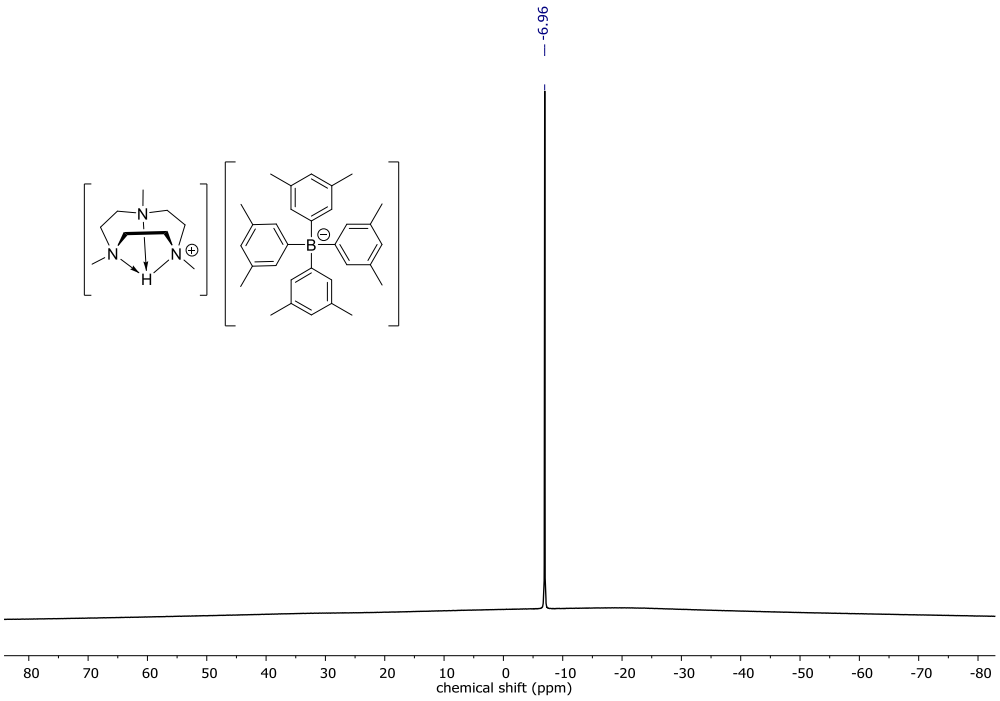


Fig. S3. $^{11}B\{^1H\}$ NMR (128 MHz, [D$_8$]THF, 25 °C) of [(Me$_3$TACN)H][B(C$_6$H$_3$-3,5-Me$_2$)$_4$] (**1**).

2.3 Molecular Structure of [(Me$_3$TACN)H][B(C$_6$H$_3$-3,5-Me$_2$)$_4$] (1)

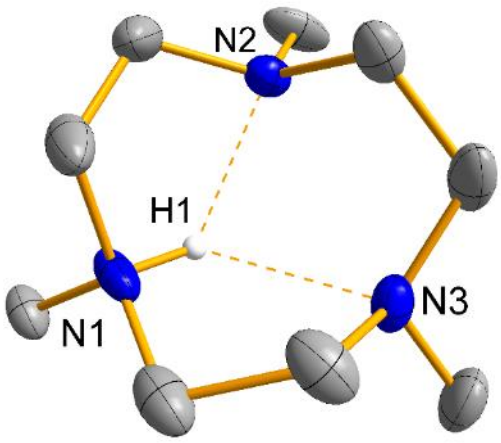


Fig. S4. Molecular structure of [(Me$_3$TACN)H][B(C$_6$H$_3$-3,5-Me$_2$)$_4$] (**1**). Displacement ellipsoids are shown with 50% probability. The borate anion and the hydrogen atoms except for H1 are omitted for clarity.

2.4 Synthesis of $[(Me_3TACN)_4Ca_4(\mu\text{-}H)_6][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]_2$•THF (2)

Method A. In a glass autoclave, a solution of $[Ca(CH_2Ph)_2(thf)_4]$ (50 mg, 0.1 mmol) in THF (1 mL) was added to a solution of $[(Me_3TACN)H][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]$ (**1**) (60 mg, 0.1 mmol) in THF (2 mL) and the reaction mixture was stirred at room temperature for 10 min. The solution was degassed, pressurized with H_2 and heated to 70 °C for 6 h. After 16 h at room temperature, colorless crystals grew. The mother liquor was decanted off, the colorless crystals washed with cold THF (2 mL) and *n*-pentane (2 x 2 mL) and dried under vacuum to give $[(Me_3TACN)_4Ca_4(\mu\text{-}H)_6][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]_2$•THF (19 mg, 11 µmol).

Method B. To a stirred solution of $[(Me_3TACN)H][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]$ (**1**) (60 mg, 0.1 mmol) in THF (2 mL) was added a solution of $[Ca(CH_2Ph)_2(thf)_4]$ (49 mg, 0.1 mmol) in THF (1 mL) and stirred at room temperature for 10 min. $^{n}OctSiH_3$ (30 mg, 0.2 mmol) was added and the solution heated to 70 °C for 6 h. After 16 h at room temperature, colorless crystals precipitated. The mother liquor was decanted off, the colorless crystals washed with cold THF (2 mL) and *n*-pentane (2 x 2 mL) and dried under vacuum to give $[(Me_3TACN)_4Ca_4(\mu\text{-}H)_6][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]_2$•THF (21 mg, 12 µmol).

Insolubility of isolated **2** in $[D_8]$THF prevented from recording of NMR spectra. Single crystals of **2** suitable for XRD were grown from the reaction mixture. $[(Me_3TACN)_4Ca_4(\mu\text{-}D)_6][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]_2$•THF (**$[D_6]$-2**) was prepared analogous using D_2 (reaction time 24 h).

^{1}H NMR (400 MHz, $[D_8]$THF, 25 °C): δ = 4.71 (s, CaH) ppm.

Anal. calc. for $C_{108}H_{178}N_{12}B_2Ca_4O_2$ (1858.63 g mol^{-1}): C, 69.79; H, 9.65; N, 9.04. Found: C, 69.68; H, 9.70; N, 8.70%.

2.5 *In situ* ^{1}H NMR spectra of $[(Me_3TACN)_4Ca_4(\mu\text{-}H)_6][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]_2$•THF (2)

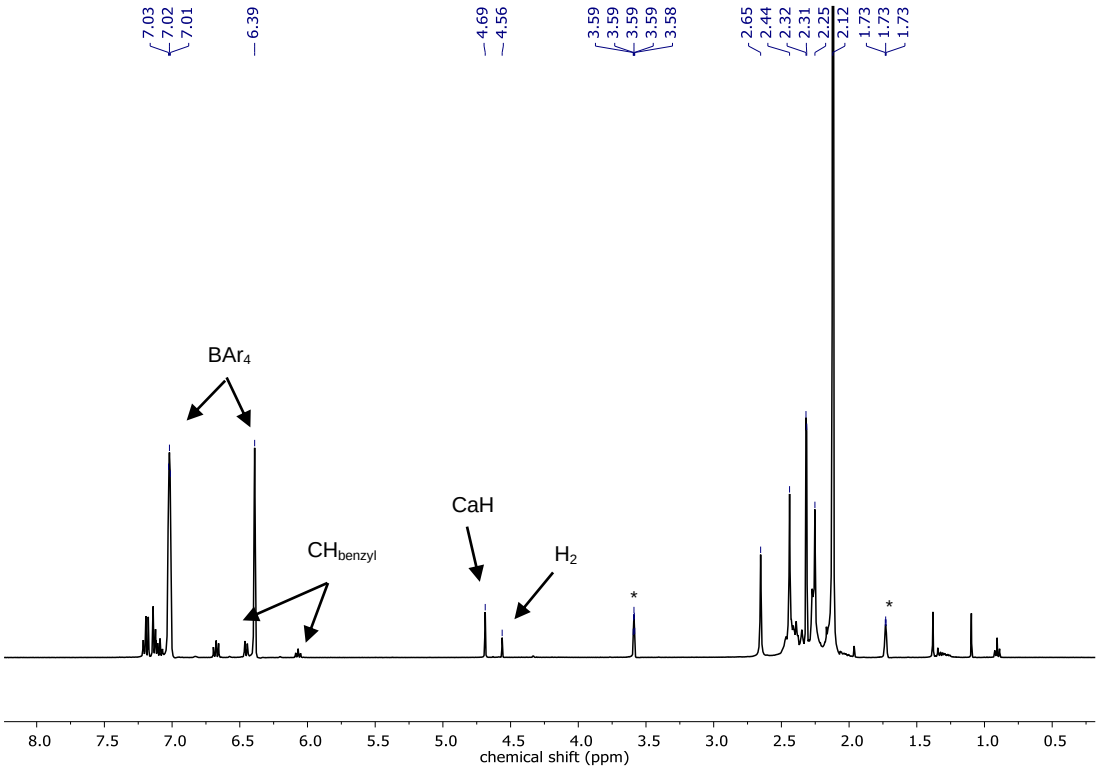


Fig. S5. *In situ* ^{1}H NMR spectrum (400 MHz, [D$_8$]THF (*)) of the synthesis of $[(Me_3TACN)_4Ca_4(\mu\text{-}H)_6][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]_2$•THF (**2**) by hydrogenolysis (t = 4h).

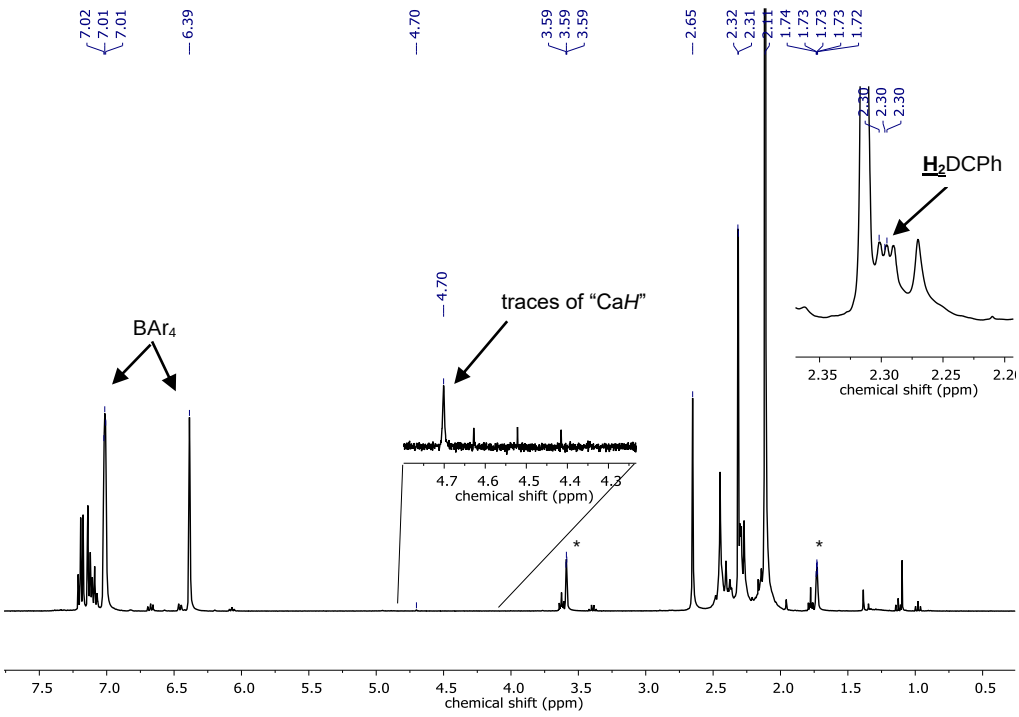


Fig. S6. *In situ* ^{1}H NMR spectrum (400 MHz, [D$_8$]THF (*)) of the synthesis of $[(Me_3TACN)_4Ca_4(\mu\text{-}D)_6][B(C_6H_3\text{-}3,5\text{-}Me_2)_4]_2$•THF (**[D$_6$]-2**) by deuteronolysis (after 18 h).

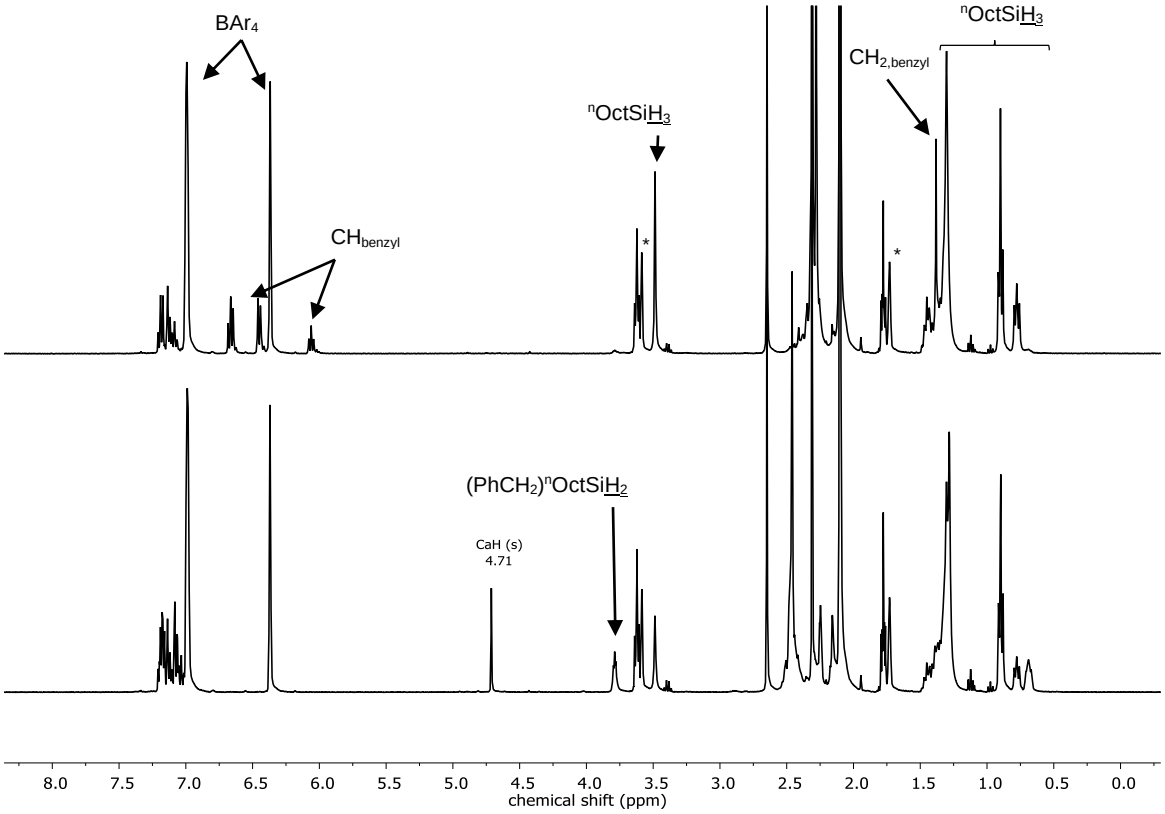


Fig. S7. *In situ* ^{1}H NMR spectrum (400 MHz, [D$_8$]THF (*)) of the synthesis of [(Me$_3$TACN)$_4$Ca$_4$(μ-H)$_6$][B(C$_6$H$_3$-3,5-Me$_2$)$_4$]$_2$•THF (**2**) with ^{n}OctSiH$_3$ (after 6 h).

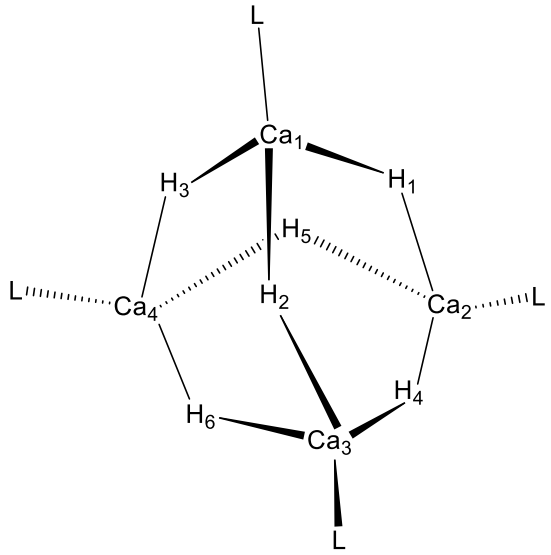
3 Crystal structure determinations

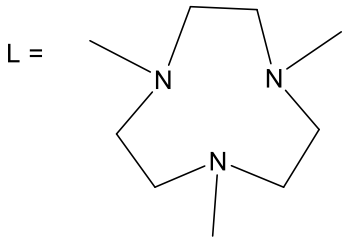
X-ray diffraction data of **1** and **2** were collected at on an Eulerian 4-circle diffractometer STOE STADIVARI in ω-scan mode at 100 K with Mo radiation (**1**) or with Cu radiation (**2**). Using the program system Olex2,[5] the structures of **1** and **2** were solved by direct methods with the program SHELXT.[6] **2** crystallizes in the tetragonal space group $P\bar{4}2_1c$ (no. 114) with crystallographic site symmetry $\bar{4}$ relating all four metal atoms of the cationic fragments (around Wyckoff position 2*a*), a C_2 axis through H1 (Wyckoff position 4*c*), and a C_2 axis through the molecular anion (with the boron atom B1 on Wyckoff position 4*d*). All refinements were carried out against F^2 using SHELXL[7] with anisotropic displacement parameters, except for the disordered carbon and oxygen atoms C26, C27, C28, C29 and O1 of the non-coordinated molecules of THF in **2** that were refined with isotropic displacement parameters. In the refinement, distance restraints were applied in the refinement (DFIX in the program SHELXL). All hydrogen atoms in **2** were included in calculated positions and treated as riding throughout the refinement. Only the hydrides within the central $Ca_4H_6^{2+}$ fragment in **2** were located in a Fourier difference map and were refined with isotropic displacement parameters. In **1**, all hydrogen atoms were located in a Difference Fourier map and refined in their positions. The hydrogen atom of the NH group was disordered and refined with 55 % multiplicity for H1 (connected to N1) and with 45% multiplicity for H2 (connected to N2). Refinement results are given in Table S1. Graphical representations were performed with the program DIAMOND.[8] CCDC-1961706 and CCDC-1961707 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1: Crystallographic data of **1** and **2**.

	1	**2**
formula	$C_9H_{22}N_3$, $C_{32}H_{36}B$	$C_{18}H_{45}Ca_2N_6$, $C_{32}H_{36}B$, $2(C_4H_8O)$
Fw /g·mol^{-1}	603.71	1001.38
cryst. color, habit	colorless, block	colorless block
crystal size / mm	0.20 × 0.22 × 0.26	0.15 × 0.18 × 0.23
crystal system	monoclinic	tetragonal
space group	$P2_1/n$	$P\bar{4}2_1c$
a / Å	13.0798(5)	18.88272(18)
b / Å	14.2813(8)	
c / Å	19.7342(8)	16.61907(16)
β / °	3598.0(3)	
V / Å^3	3598.0(3)	5925.65(13)
Z	4	4
d_{calc}/Mg·m^{-3}	1.114	1.122
μ(MoKα)/mm^{-1}	0.064	
μ(CuKα)/mm^{-1}		1.996
F(000)	1320	2192
θ range / °	2.14, 30.63	3.31, 71.99
index ranges	-18≤h≤14; -20≤k≤18; -27≤l≤27	-17≤h≤22; -22≤k≤23; -19≤l≤20
refln.	18176	61098
independ. reflns (R_{int})	9555 (0.0390)	5788 (0.0582)
observed reflns	5565	5590
data/ restr./ param.	9555 / 0 / 584	5788 / 12 / 322
R_1, $wR2$ [$I > 2\sigma(I)$]	0.0733, 0.1726	0.0511, 0.1394
R_1, $wR2$ (all data)	0.1248, 0.1849	0.0527, 0.1419
GooF on F^2	1.075	1.043
largest diff. peak, hole/ e·Å^3	0.268, -0.218	0.623, -0.360
CCDC number	1961706	1961707

4 DFT Calculations





All calculations were carried out at the DFT level of theory using the hybrid functional B3PW91[9] with the Gaussian 09 suite of programs.[10] The calcium atom was represented with a large-core Stuttgart-Dresden relativistic effective core potential associated with adapted basis sets.[11] All the other atoms carbon, hydrogen and nitrogen were described with a 6-31G(d), double-zeta quality basis set.[11] Geometry optimizations were computed without any symmetry constraints but the results show nearly perfect T_d symmetry of the cluster. Nearly identical results were obtained if the calculations were performed with constrained geometry. The enthalpy was determined at T = 298 K in the gas phase and the density was analyzed using the NBO method.[12]

Natural Charge

Ca_1 = 0.89444 **Ca_2** = 0.89449 **Ca_3** = 0.89454 **Ca_4** = 0.89448
H_1= -0.48141 **H_2**= -0.48128 **H_3**= -0.48132 **H_4** = -0.48139 **H_5**= -0.48140 **H_6** = -0.48133

Wiberg Bond Indexes

Average Ca-Ca = 0.1028
Average Ca-N = 0.1144

Ca_1-H_2 = 0.3372	Ca_1-H_1 = 0.3363	Ca_1-H_3 = 0.3355
Ca_2-H_1 = 0.3355	Ca_2-H_4 = 0.3364	Ca_2-H_5 = 0.3372
Ca_3-H_2 = 0.3372	Ca_3-H_4 = 0.3354	Ca_3-H_6 = 0.3364
Ca_4-H_3 = 0.3364	Ca_4-H_5 = 0.3372	Ca_4-H_6 = 0.3354

Listing of main Natural Bonding Orbital's

(1.71174) BD(1) Ca_1-H_1
(13.69%) Ca_1 s(24.34%)p(40.37%)d(35.29%)
(86.31%) H_1 s(100.00%)

(1.71224) BD(1) Ca_1-H_2
(13.73%) Ca_1 s(24.50%)p(40.31%)d(35.19%)
(86.27%) H_2 s(100.00%)

(1.71110) BD(1) Ca_1-H_3
(13.67%) Ca_1 s(24.40%)p(40.24%)d(35.36%)
(86.33%) H_3 s(100.00%)

(1.71191) BD(1) Ca_2-H_4
(13.70%) Ca_2 s(22.89%)p(40.81%)d(36.30%)
(86.30%) H_4 s(100.00%)

(1.71252) BD(1) Ca_2-H_5
(13.73%) Ca_2 s(23.04%)p(40.77%)d(36.19%)
(86.27%) H_5 s(100.00%)

(1.71201) BD(1) Ca_3-H_6
(13.70%) Ca_3 s(21.59%)p(41.18%)d(37.23%)
(86.30%) H_6 s(100.00%)

Donor–acceptor interactions by Second Order Perturbation Theory Analysis of Fock Matrix in the NBO Basis

Donor NBO Bond **Ca_1–H** to Acceptor NBO at **Ca**

Ca_1-H_1 to Ca_2 = 322.04 kcal/mol	**Ca_1-H_2 to Ca_3 = 365.9 kcal/mol**	**Ca_1-H_3 to Ca_4 = 412.32 kcal/mol**
Ca_1-H_1 to Ca_3 = 110.51 kcal/mol	Ca_1-H_2 to Ca_2 = 53.67 kcal/mol	Ca_1-H_3 to Ca_2 = 59.06 kcal/mol
Ca_1-H_1 to Ca_4 = 119.23 kcal/mol	Ca_1-H_2 to Ca_4 = 124.28 kcal/mol	Ca_1-H_3 to Ca_3 = 88.61 kcal/mol

Donor NBO Bond **Ca_2–H** to Acceptor NBO at **Ca**

Ca_2-H_4 to Ca_3 =395.64 kcal/mol	**Ca_2-H_5 to Ca_4 = 384.84 kcal/mol**
Ca_2-H_4 to Ca_1 =19.65 kcal/mol	Ca_2-H_5 to Ca_1 = 22.81 kcal/mol
Ca_2-H_4 to Ca_4 =109.3 kcal/mol	Ca_2-H_5 to Ca_3 =78.18 kcal/mol

Donor NBO Bond **Ca_3–H** to Acceptor NBO at **Ca**

Ca_3-H_6 to Ca_4 =394.44 kcal/mol
Ca_3-H_6 to Ca_1 = 17.8 kcal/mol
Ca_3-H_6 to Ca_2 = 19.19 kcal/mol

Donor-acceptor interactions between calcium and ligand

- Average ligand to Ca through one-center core pair (CR) at N = 18.67 kcal/mol
- average ligand to Ca through one-center valence lone pair (LP) at N = 63.72 kcal/mol
- average ligand to Ca through N-C bond (BD) = 69.22 kcal/mol

Cartesian coordinates of the optimized structure of $[(Me_3TACN)_4Ca_4(\mu\text{-}H)_6]^{2+}$

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scf done: -2229.411178

Ca	11.232298	8.504329	9.751675
Ca	8.501968	7.645183	6.875480
Ca	7.647687	10.386110	9.743303
Ca	10.383881	11.229620	6.867871
N	12.814219	9.310260	11.625611
N	13.566033	7.434169	9.479545
N	11.580826	6.634577	11.507570
N	9.304432	6.056176	5.005837
N	7.432564	5.312626	7.158805
N	6.629168	7.289503	5.124005
N	6.061413	9.590484	11.618402
N	5.314877	11.454900	9.459867
N	7.294921	12.265430	11.488338
N	9.584765	12.808600	4.988244
N	11.452905	13.563919	7.140059
N	12.260172	11.575597	5.118181
H	9.439086	9.447936	10.713569
H	10.109168	7.152036	8.361827
H	11.731479	10.108870	8.264241
H	9.443707	9.434916	5.905697
H	7.152276	8.773503	8.263539
H	8.773812	11.730898	8.348548
C	14.226650	8.962610	11.360860
C	12.636658	10.763538	11.715556
C	12.261758	8.653862	12.823031
C	13.741262	7.180818	8.045520
C	13.713899	6.187087	10.259054
C	14.465726	8.514750	9.918978
C	10.254920	6.089219	11.816225
C	12.377980	5.643415	10.763913
C	12.246976	7.128313	12.731859
C	8.957545	4.644796	5.277126
C	10.757499	6.233660	4.912606
C	8.645732	6.603322	3.807260
C	7.181866	5.142501	8.593923
C	6.184054	5.161626	6.382141
C	8.512562	4.411483	6.720825
C	6.083367	8.614265	4.811258
C	5.639467	6.495506	5.872928
C	7.120363	6.618382	3.901439
C	4.649718	9.936791	11.348051
C	6.238570	8.137748	11.717029
C	6.610917	10.253649	12.813444
C	5.142871	11.700326	8.024061
C	5.165086	12.706303	10.232092
C	4.414254	10.376632	9.903122
C	8.620136	12.812290	11.797373
C	6.499759	13.252679	10.737413
C	6.625646	11.778603	12.713697
C	9.931463	14.221432	5.252010
C	8.131851	12.630957	4.893049
C	10.245673	12.254119	3.794249
C	11.700916	13.741408	8.574743
C	12.702890	13.710687	6.364982
C	10.373895	14.462824	6.695177
C	12.806824	10.249314	4.813444
C	13.248535	12.374036	5.864129
C	11.770830	12.239781	3.891069
H	14.399341	6.354376	11.094750
H	14.190506	5.407309	9.649603
H	12.567749	4.739083	11.368799
H	11.769987	5.333786	9.904150
H	11.743449	6.738483	13.626909
H	13.265517	6.732937	12.781615
H	12.807708	8.949962	13.736320
H	11.231476	9.015766	12.931998
H	14.878490	9.823546	11.562330
H	14.551669	8.187725	12.060988
H	15.526823	8.229935	9.806258
H	14.286252	9.363539	9.246995
H	14.768368	6.865095	7.799362
H	13.046866	6.398321	7.726048
H	13.505620	8.090462	7.484177
H	10.310997	5.186291	12.446055
H	9.662376	6.845995	12.338351
H	9.737983	5.838014	10.884592
H	13.024014	11.234179	10.807397
H	11.569395	10.997338	11.786766
H	13.155728	11.194289	12.587471
H	3.997263	9.077051	11.552650
H	4.322936	10.715599	12.042976
H	3.353405	10.660678	9.786170
H	4.595483	9.524145	9.236290
H	4.690104	13.482710	9.617103
H	4.477489	12.543713	11.066948
H	6.308454	14.160198	11.337025
H	7.109934	13.557792	9.877585
H	7.126677	12.173710	13.607832
H	5.606908	12.174029	12.758375
H	6.062844	9.962564	13.727078
H	7.640991	9.892534	12.926892
H	9.139588	13.058206	10.865719
H	8.562528	13.718744	12.421980
H	9.211171	12.058381	12.325328
H	5.379866	10.787658	7.468235
H	4.116278	12.014556	7.773892
H	5.837904	12.481136	7.701884
H	7.305610	7.904302	11.792485
H	5.717076	7.711955	12.589935
H	5.853640	7.662014	10.810491
H	12.166243	13.258300	3.841199
H	12.164058	11.734958	2.998236
H	9.884372	11.223569	3.685798
H	9.952850	12.798369	2.878884
H	10.709006	14.545296	4.554314
H	9.071319	14.872981	5.046221
H	9.522598	14.284308	7.364244
H	10.658192	15.524125	6.807313
H	13.480359	14.188218	6.976653
H	12.538716	14.394918	5.527679
H	13.555232	11.767459	6.725937
H	14.154993	12.563042	5.262176
H	12.015800	14.768884	8.820434
H	10.789161	13.506753	9.133058
H	12.482151	13.047452	8.898243
H	13.054960	9.733764	5.746672
H	12.051978	9.655853	4.289564
H	13.711904	10.304622	4.186635
H	7.898261	11.563590	4.822776
H	7.657737	13.019911	5.798714
H	7.704474	13.148554	4.018597
H	6.724991	5.599608	3.856758
H	6.728615	7.118168	3.005132
H	9.007368	7.633120	3.693026
H	8.940104	6.053340	2.895840
H	5.331588	7.107057	6.730801
H	4.733877	6.303323	5.270677
H	6.349827	4.472891	5.548852
H	5.405403	4.687438	6.994895
H	9.362589	4.593853	7.390476
H	8.228237	3.350778	6.838374
H	8.092385	5.380652	9.152779
H	6.399582	5.837647	8.912248
H	6.867126	4.116129	8.844360
H	8.181290	4.316766	4.579923
H	9.818162	3.992235	5.076597
H	11.186860	5.711106	4.042085
H	10.990922	7.300677	4.836652
H	11.229786	5.850106	5.821526
H	6.838926	9.204484	4.284755
H	5.178831	8.555803	4.183950
H	5.834631	9.135115	5.741386

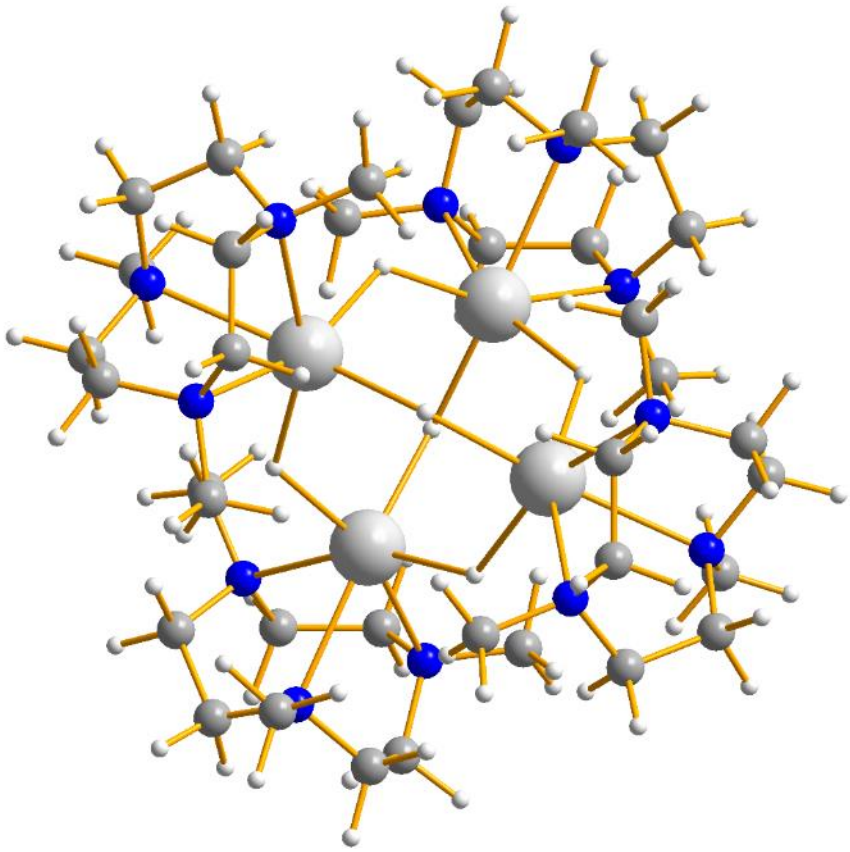
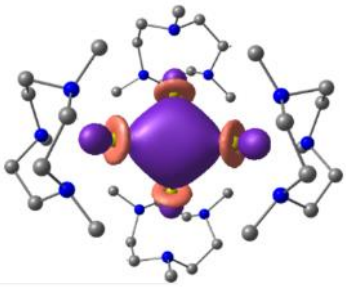
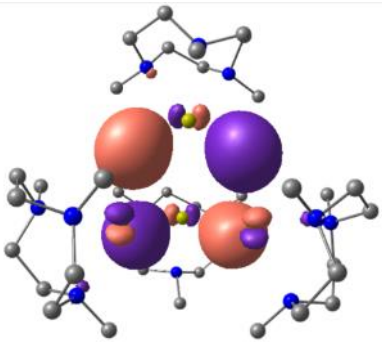


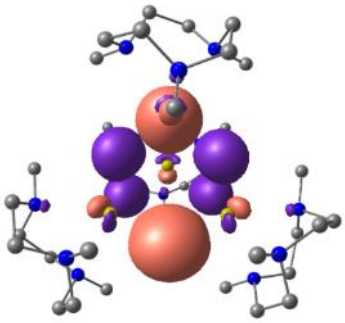
Fig. S8. DIAMOND representation of the optimized molecular structure of $[(Me_3TACN)_4Ca_4(\mu\text{-}H)_6]^{2+}$.

Molecular Orbitals of $[(Me_3TACN)_4Ca_4(\mu\text{-}H)_6]^{2+}$

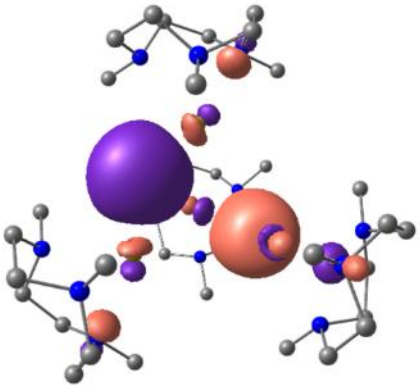




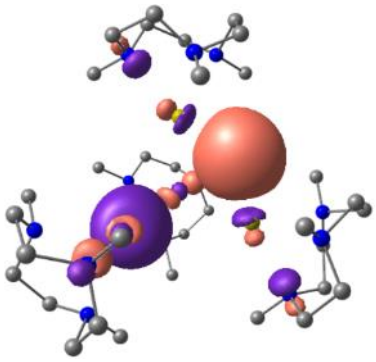
HOMO (E = -9.78 eV)



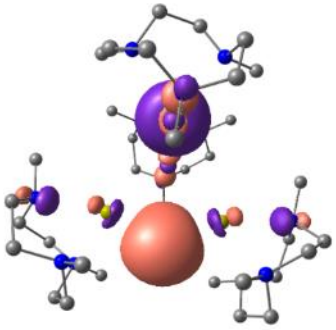
HOMO$_{-1}$ (E = -9.78 eV)



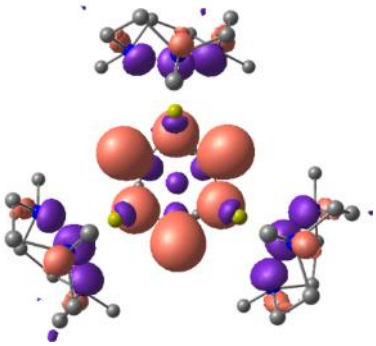
HOMO$_{-2}$ (E = -10.16 eV)



HOMO$_{-3}$ (E = -10.16 eV)

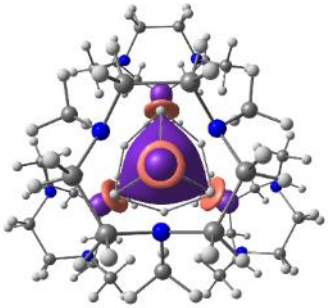


HOMO$_{-4}$ (E = -10.16 eV)

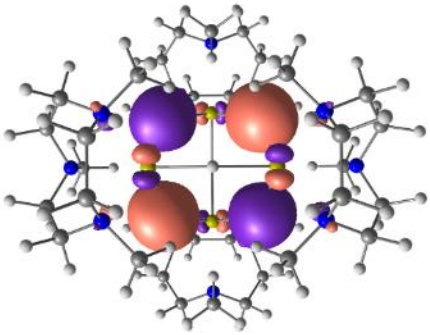


HOMO$_{-5}$ (E = -10.84 eV)

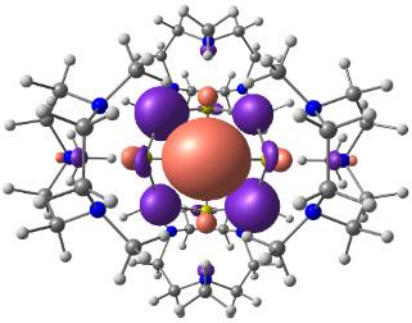
Molecular Orbitals of T_d symmetric $[(Me_3TACN)_4Ca_4(\mu\text{-}H)_6]^{2+}$



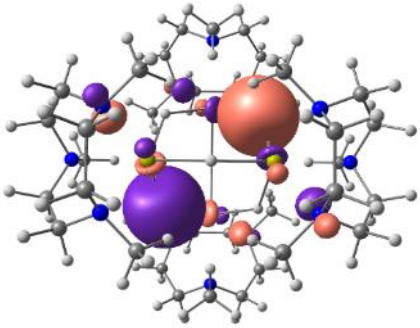
LUMO (E = -4.11 eV)



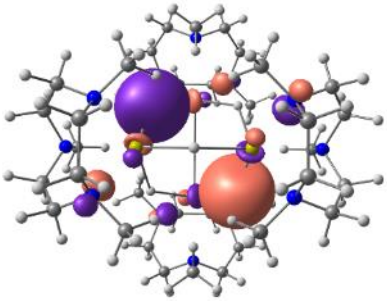
HOMO (E = -9.72 eV)



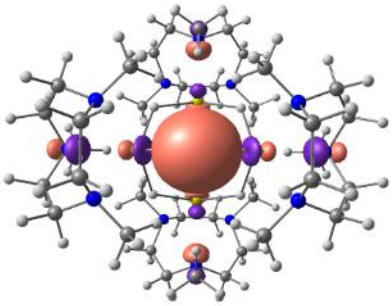
$HOMO_{-1}$ (E = -9.72 eV)



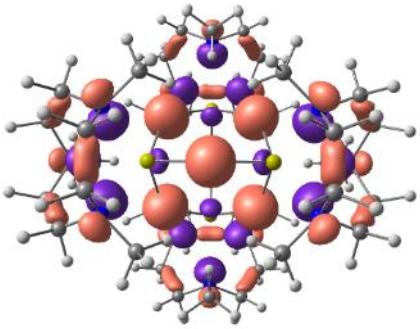
$HOMO_{-2}$ (E = -10.06 eV)



$HOMO_{-3}$ (E = -10.06 eV)



$HOMO_{-4}$ (E = -10.06 eV)



$HOMO_{-5}$ (E = -10.77 eV)

5 References

1 a) V. Leich, T. P. Spaniol, L. Maron, J. Okuda, *Angew. Chem. Int. Ed.* **2016**, *55*, 4794-4797; b) A. Causero, G. Ballmann, J. Pahl, H. Zijlstra, C. Farber, S. Harder, *Organometallics* **2016**, *35*, 3350-3360; c) A. S. S. Wilson, M. S. Hill, M. F. Mahon, *Organometallics* **2018**, *38*, 351-360; d) M. S. Hill, M. F. Mahon, A. S. S. Wilson, C. Dinoi, L. Maron, E. Richards, *Chem. Commun.* **2019**, *55*, 5732-5735.

2 K. Izod, P. G. Waddell, *Organometallics* **2015**, *34*, 2726-2730.

3 N. J. Schoenfeldt, A. W. Korinda, J. M. Notestein, *Chem. Commun.* **2010**, *46*, 1640-1642.

4 D. Schuhknecht, C. Lhotzky, T. P. Spaniol, L. Maron, J. Okuda, *Angew. Chem. Int. Ed.* **2017**, *56*, 12367-12371.

5 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341.

6 G. M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3-8.

7 G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.

8 K. Brandenburg, *Diamond Version 4.6.0*, Crystal Impact GbR, Bonn, 2019.

9 a) J. P. Perdew, Y. Wang, *Phys. Rev. B* **1992**, *45*, 13244; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

10 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratman, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowswi, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. Martin, D. J. Fox, T. Keith, M. A. AlLaham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Jonhson, W. Chen, M. W. J. Wong, L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 09; D.01 ed. Pittsburgh PA* **2009.**

11 J.-P. Blaudeau, M. P. McGrath, L. A. Curtiss, L. Radom, *J. Chem. Phys.* **1997**, *107*, 5016.

12 A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.,* **1988**, *88*, 899.