# Supporting Information

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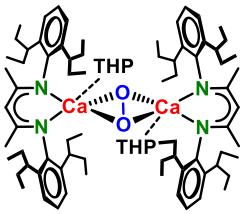
# 1. Materials and Methods

All experiments were conducted in dry glassware under an inert nitrogen or argon atmosphere by applying standard Schlenk techniques or gloveboxes (MBraun) using freshly dried and degassed solvents. Hexanes and pentanes were degassed with nitrogen, dried over a column with activated aluminum oxide (Innovative Technology, Pure Solv 400-4-MD, Solvent Purification System) and then stored under inert atmosphere over molecular sieves (3 Å). Tetrahydropyran (THP) was dried over freshly grounded $CaH_2$, distilled and stored over molecular sieves (3 Å) under inert atmosphere. Deuterated benzene ($C_6D_6$) and deuterated methylcyclohexane ($C_7D_{14}$) were purchased either from Deutero GmbH or Sigma Aldrich, degassed and dried over molecular sieves (3 Å) and stored under an inert atmosphere. $N_2O$ was purchased from Messer N25. The following compounds were prepared according to literature procedures: $[(BDI^*)Ca]_2(N_2)$;[S1] $[(BDI^*)Ca(THP)]_2(N_2)$;[S1] BDI* = $HC[C(Me)N(DIPeP)]_2$, DIPeP = 2,6-($Et_2CH$)-phenyl.

Infrared spectra were acquired on a Bruker Alpha II FT-IR spectrometer equipped with a Platinum ATR diamond from the neat compounds under inert conditions inside a glovebox. All spectra were recorded at room temperature in the range of 400–4000 $cm^{-1}$ with a resolution of 4 $cm^{-1}$ and baseline corrected. Wavenumbers $\tilde{\nu}$ are given in $cm^{-1}$ and intensities of IR bands are described using the following terms: s = strong, m = medium and w = weak. NMR spectra were measured on Bruker Avance III H 400 MHz and Bruker Avance III HD 600 MHz NMR spectrometers. Chemical shifts (δ) are denoted in ppm (parts per million) and coupling constants in Hz (Hertz). $^1H$ and $^{13}C$ NMR spectra were referenced to the solvent residual signal ($SiMe_4$ = 0 ppm). Signal multiplicities are described using common abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet) and br (broad). Elemental analysis was performed with a Hekatech Eurovector EA3000 analyzer. All crystal structures have been measured on a SuperNova (Agilent) diffractometer with dual Cu and Mo microfocus sources and an Atlas S2 detector.

# 2. Synthetic Procedures




**Synthesis of [(BDI*)Ca(THP)]$_2$($\mu_2$-O$_2$) (1).** *Method A:* [(BDI*)Ca](N$_2$) (98 mg, 83.9 µmol) was suspended in precooled hexanes (–25 °C, 4 mL) The suspension was degassed *via* one freeze-pump-thaw cycle and cooled to –85 °C. At this temperature pre-dried pressurized air was added under vigorous stirring. Upon warming to –20 °C, a yellow solution was obtained. The hexanes solution was concentrated to approximately ¼ of its prior volume, filtered, 3 drops of THP were added and cooled to –25 °C. Overnight, [(BDI*)Ca(THP)]$_2$($\mu_2$-O$_2$) was obtained as colorless crystals suitable for X-ray diffraction analysis. The supernatant was decanted and the crystals were washed with cold pentane (–25 °C, 2 x 1 mL) and dried *in vacuo* (crystalline yield: 60 mg, 44.6 µmol, 53%).

*Method B:* [(BDI*)Ca(THP)]$_2$(N$_2$) (96 mg, 71.6 µmol) was suspended in precooled hexanes (–25 °C, 4 mL) The suspension was degassed *via* two freeze-pump-thaw cycles and cooled to –85 °C. At this temperature pre-dried pressurized air was added under vigorous stirring. Upon warming to 0 °C, a yellow solution was obtained. The hexanes solution was concentrated to approximately ¼ of its prior volume, filtered and cooled to –25 °C. Overnight, [(BDI*)Ca(THP)]$_2$($\mu_2$-O$_2$) was obtained as colorless crystals suitable for X-ray diffraction analysis. The supernatant was decanted and the crystals were washed with cold pentane (–25 °C, 2 x 1 mL) and dried *in vacuo* (crystalline yield: 35 mg, 26.0 µmol, 13%).

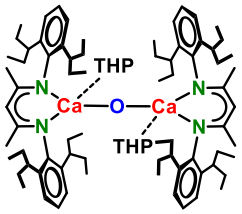
**$^1$H NMR** (600.13 MHz, C$_6$D$_6$, 298K): $\delta$ = 0.76 (t, $^3$J = 7.5 Hz, 12H, C**H$_3$**), 0.88 (t, $^3$J = 7.5 Hz, 12H, C**H$_3$**), 1.32 (m, 12H, THP β-,γ-C**H$_2$**), 1.45 (m, 10H, C**H$_2$**), 1.53–1.68 (m, 24H, C**H$_2$**), 1.71 (s, 12H, C**H$_3$**-backbone), 2.71–2.76 (m, C**H**), 3.52 (m, 8H, THP α-C**H$_2$**), 4.78 (s, 2H, C**H**-backbone), 7.02–7.04 (m, 8H, *meta*-C**H**-arom.), 7.09–7.12 (m, 4H, *para*-C**H**-arom.) ppm.

**$^{13}$C{$^1$H} NMR** (150.92 MHz, C$_6$D$_6$, 298K): $\delta$ = 12.6 (**C**H$_3$), 13.1 (**C**H$_3$), 23.8 (THP γ-**C**H$_2$), 24.7 (**C**H$_3$-backbone), 26.9 (THP β-**C**H$_2$), 27.7 (**C**H$_2$), 29.4 (**C**H$_2$), 42.4 (**C**H), 68.7 (THP α-**C**H$_2$), 93.1 (**C**H-backbone), 123.8 (*para*-**C**-arom.), 124.8 (*meta*-**C**-arom.), 139.4 (*ortho*-**C**-arom.), 148.5 (N-**C**-arom.), 165.3 (**C**N-backbone) ppm.

**FT-IR** (ATR, pure): $\tilde{\nu}$ = 2960 (m), 2928 (m), 2870 (w), 1532 (w), 1514 (w),1456 (m), 1402 (s), 1172 (m), 1040 (m), 923 (m), 871 (m), 782 (m), 751 (m), 645 (m) cm$^{-1}$.

**Elemental analysis** Calculated for C$_{84}$H$_{134}$Ca$_2$N$_4$O$_4$ (M = 1344.18 g/mol): C 75.06, H 10.05, N 4.17; Found: C 75.10, H 9.96, N 4.52.

**Synthesis of [(BDI*)Ca(THP)]$_2$($\mu$-O) (2).** A J-Young NMR tube was charged with crystals of [(BDI*)Ca(THP)]$_2$(N$_2$) (62.0 mg, 46.3 µmol), evacuated and cooled to –70 °C. At this temperature, the atmosphere was backfilled with 1 atm of N$_2$O. Upon warming to 0 °C, a color change from dark brown to off-white was visible. The atmosphere of N$_2$O was removed *in vacuo*. The off-white solid was dissolved in pentane (500 µL), filtered and the clear yellow solution was cooled to –25 °C. Overnight, [(BDI*)Ca(THP)]$_2$($\mu$-O) was obtained as colorless crystals suitable for X-ray diffraction analysis. The supernatant was decanted and the crystals were washed with cold pentane (–25 °C, 2 x 1 mL) and dried *in vacuo* (crystalline yield: 16.6 mg, 12.5 µmol, 27%).




**FT-IR** (ATR, pure): $\tilde{\nu}$ = 2960 (m), 2928 (m), 2870 (m), 1500 (s), 1461 (m),1435 (m), 1388 (s), 1336 (m), 1160 (m), 1032 (m), 959 (w), 824 (m), 775 (m), 570 (w) cm$^{-1}$.

**Melting point:** 105–109 °C (decomp.)

**Elemental analysis** Calculated for $C_{84}H_{134}Ca_2N_4O_3$ (M = 1328.18 g/mol): C 75.96, H 10.17, N 4.22; Found: C 76.20, H 9.96, N 4.13.

Note: Conversion of [(BDI*)Ca(THP)]$_2$(N$_2$) in a hexanes solution led to formation of reported dianionic Ca complex [($^{DIPeP}$BDI$^{2-}$)Ca$^{2+}$(THP)]$_2$ (see **Figure S11**/**S12**).

# 3. Spectroscopic Characterization

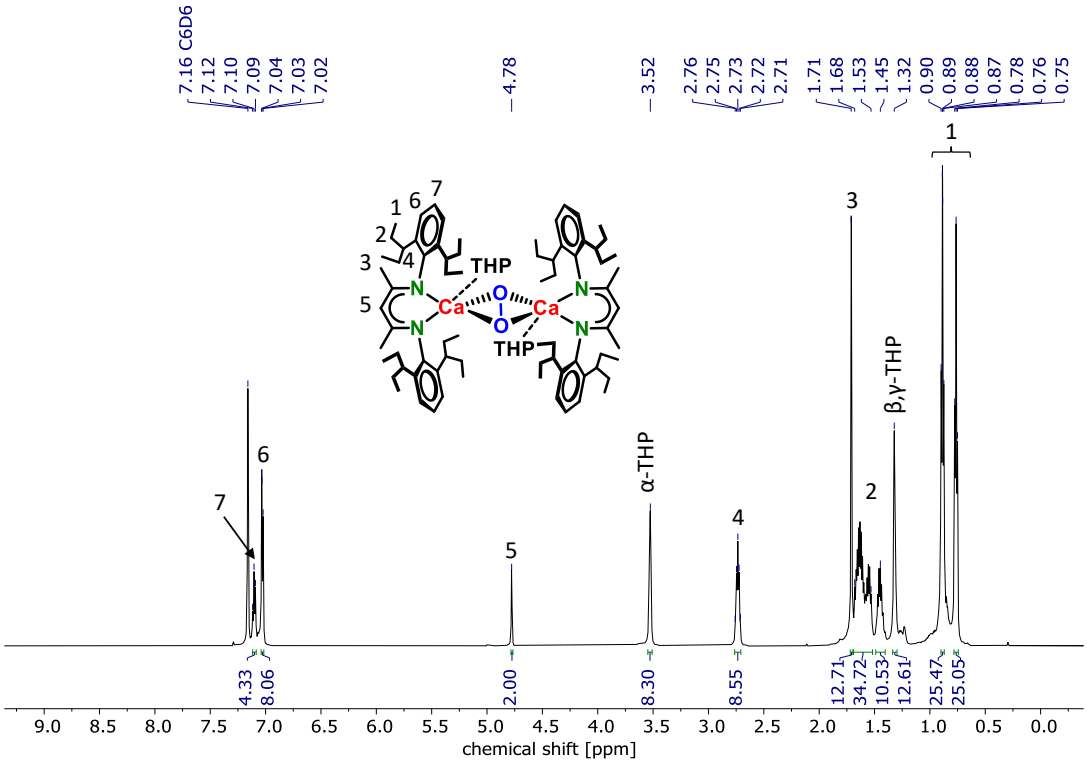



**Figure S1.** $^{1}$H NMR spectrum (600.13 MHz, $C_6D_6$, 298K) of [(BDI*)Ca(THP)]$_2$($\mu_2$-O$_2$) (**1**).

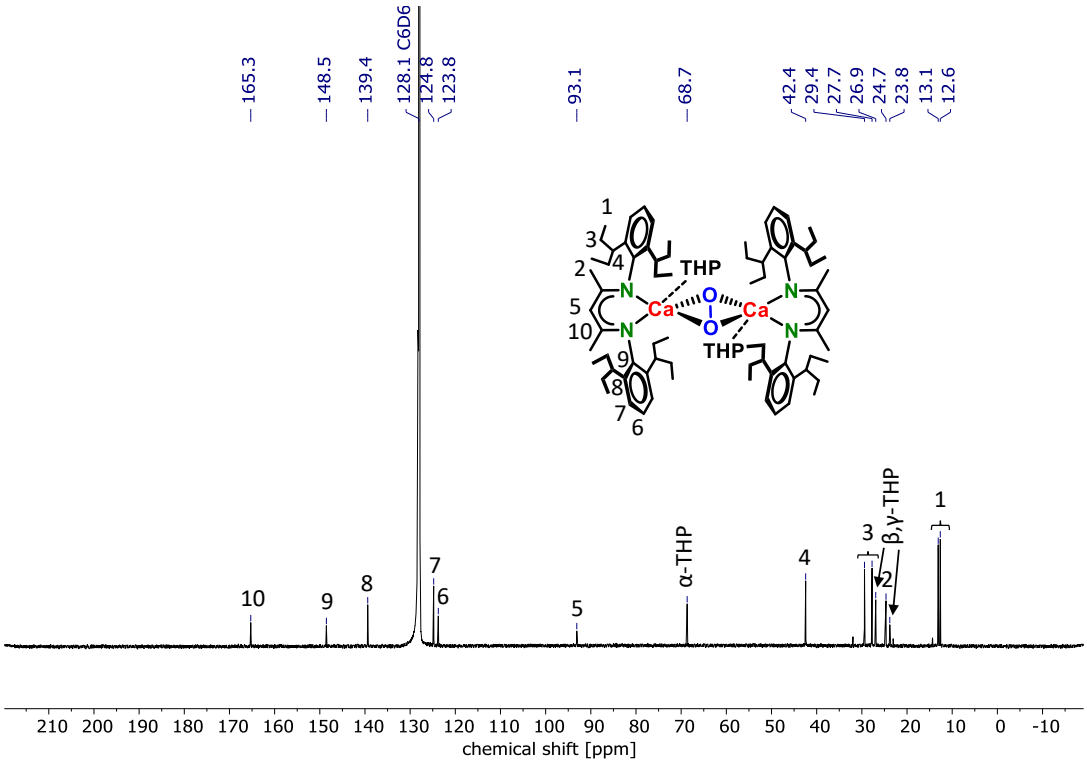



**Figure S2.** $^{13}$C{$^{1}$H} NMR spectrum (150.92 MHz, $C_6D_6$, 298K) of [(BDI*)Ca(THP)]$_2$($\mu_2$-O$_2$) (**1**).

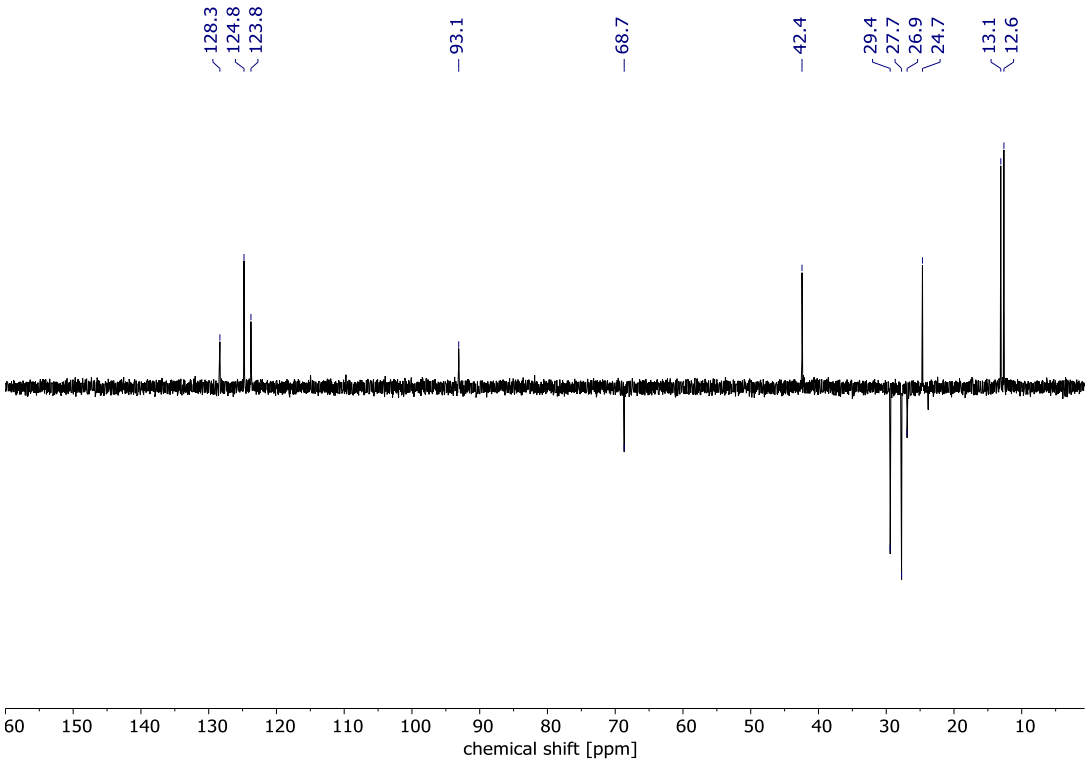



**Figure S3.** $^{13}C$(DEPT 135){$^{1}H$} NMR spectrum (150.92 MHz, $C_6D_6$, 298K) of [(BDI*)Ca(THP)]$_2$($\mu_2$-$O_2$) (**1**).

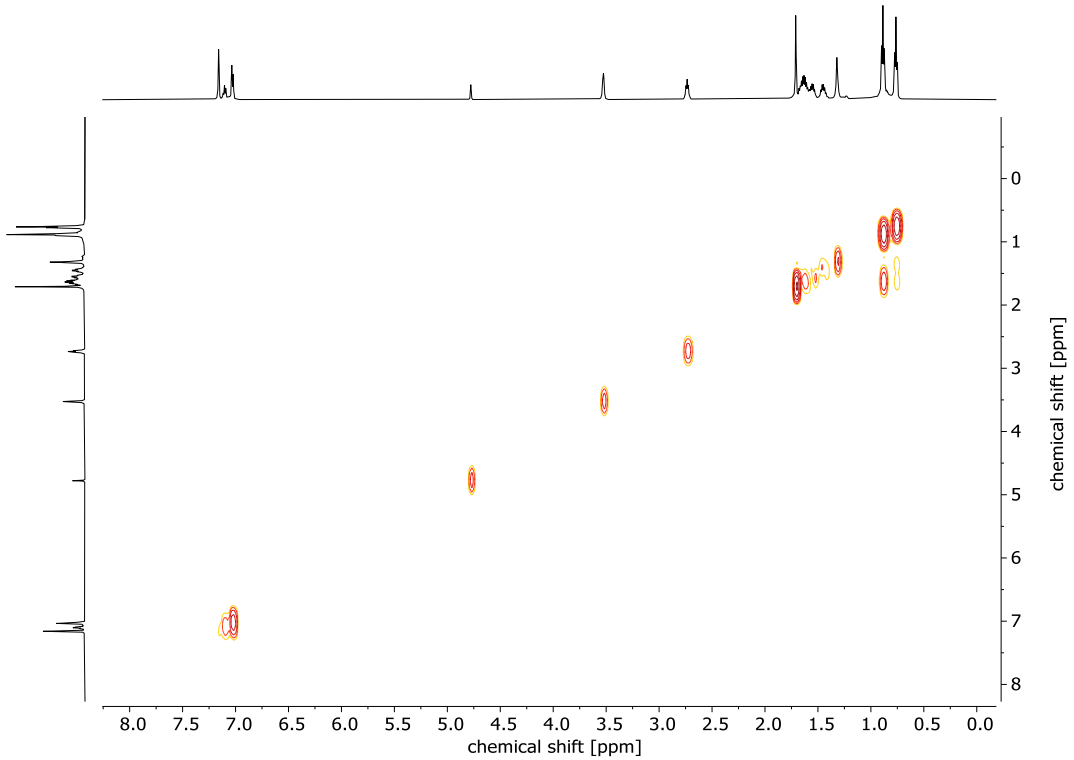



**Figure S4.** $^{1}H$-$^{1}H$ COSY NMR spectrum (600.13 MHz, $C_6D_6$, 298K) of [(BDI*)Ca(THP)]$_2$($\mu_2$-$O_2$) (**1**).

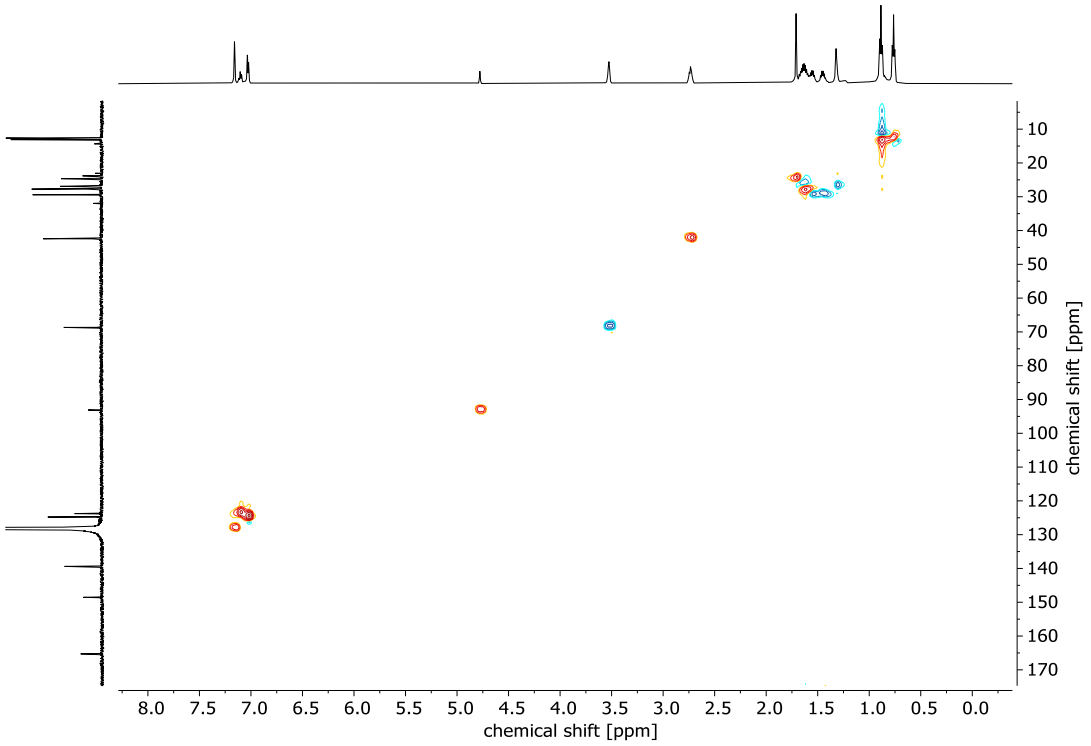



**Figure S5.** $^{1}H$-$^{13}C$ HSQC NMR spectrum (600.13/150.92 MHz, $C_6D_6$, 298K) of $[(BDI^*)Ca(THP)]_2(\mu_2\text{-}O_2)$ (**1**).

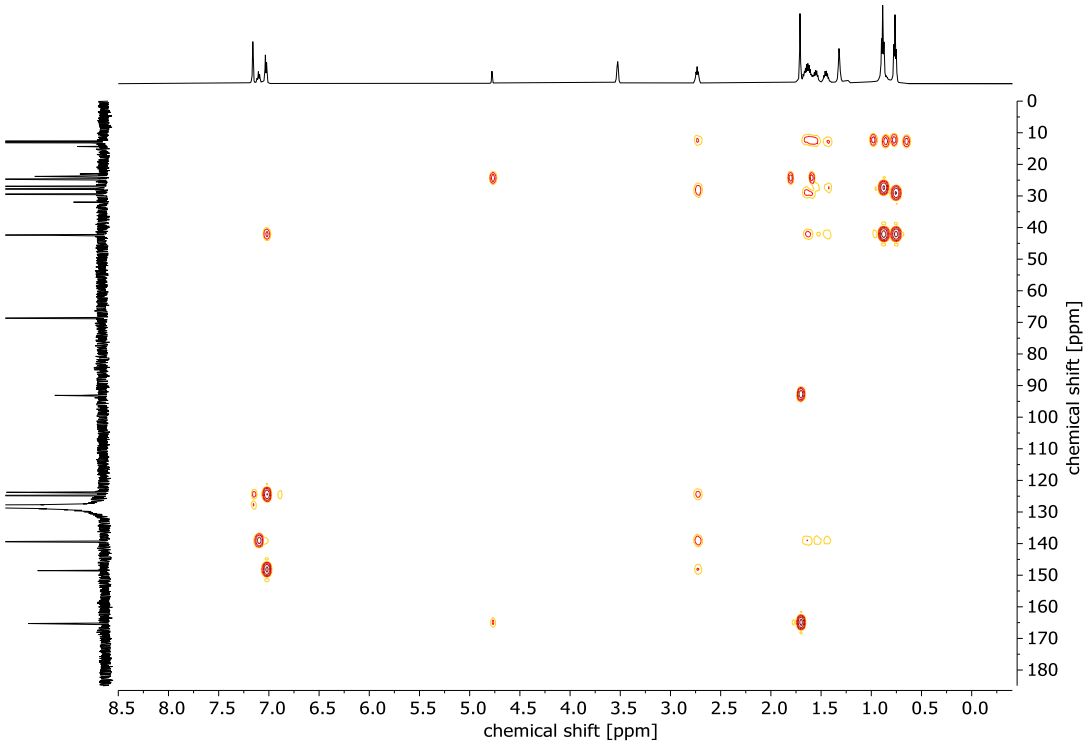



**Figure S6.** $^{1}H$-$^{13}C$ HMBC NMR spectrum (600.13/150.92 MHz, $C_6D_6$, 298K) of $[(BDI^*)Ca(THP)]_2(\mu_2\text{-}O_2)$ (**1**).

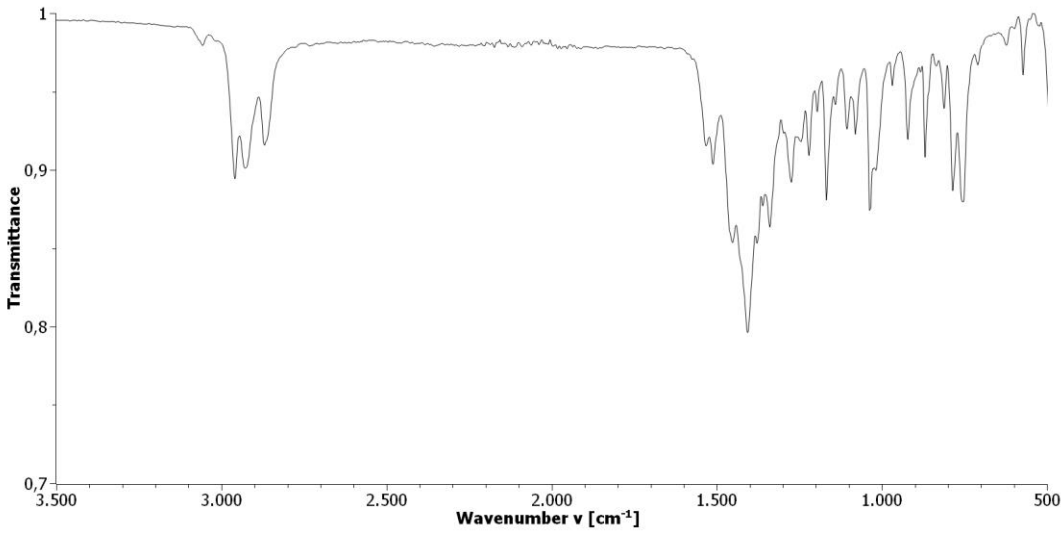



**Figure S7.** FT-IR ATR spectrum of $[(BDI^*)Ca(THP)]_2(\mu_2\text{-}O_2)$ (**1**).

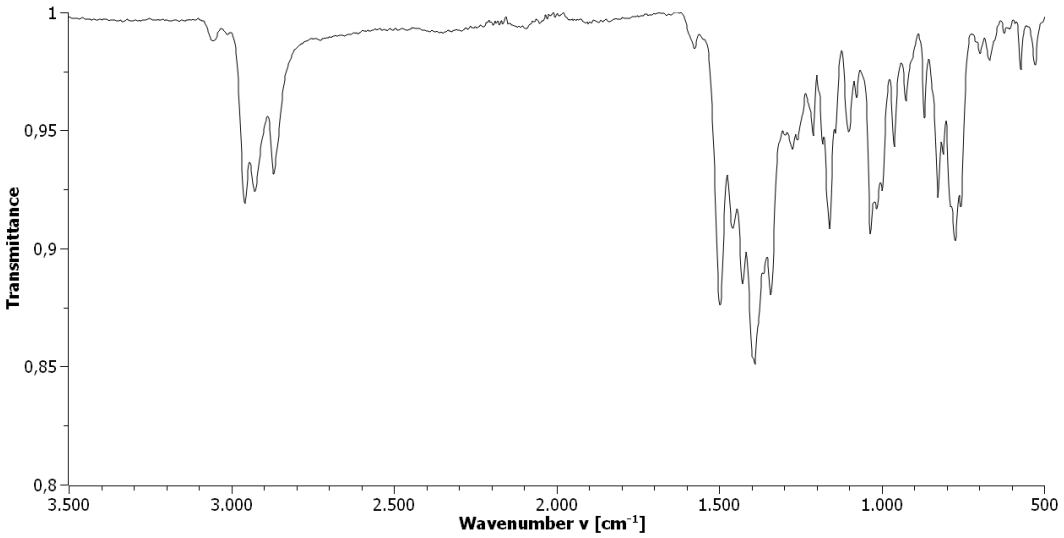



**Figure S8.** FT-IR ATR spectrum of $[(BDI^*)Ca(THP)]_2(\mu\text{-}O)$ (**2**).

# 4. Selected NMR Spectra

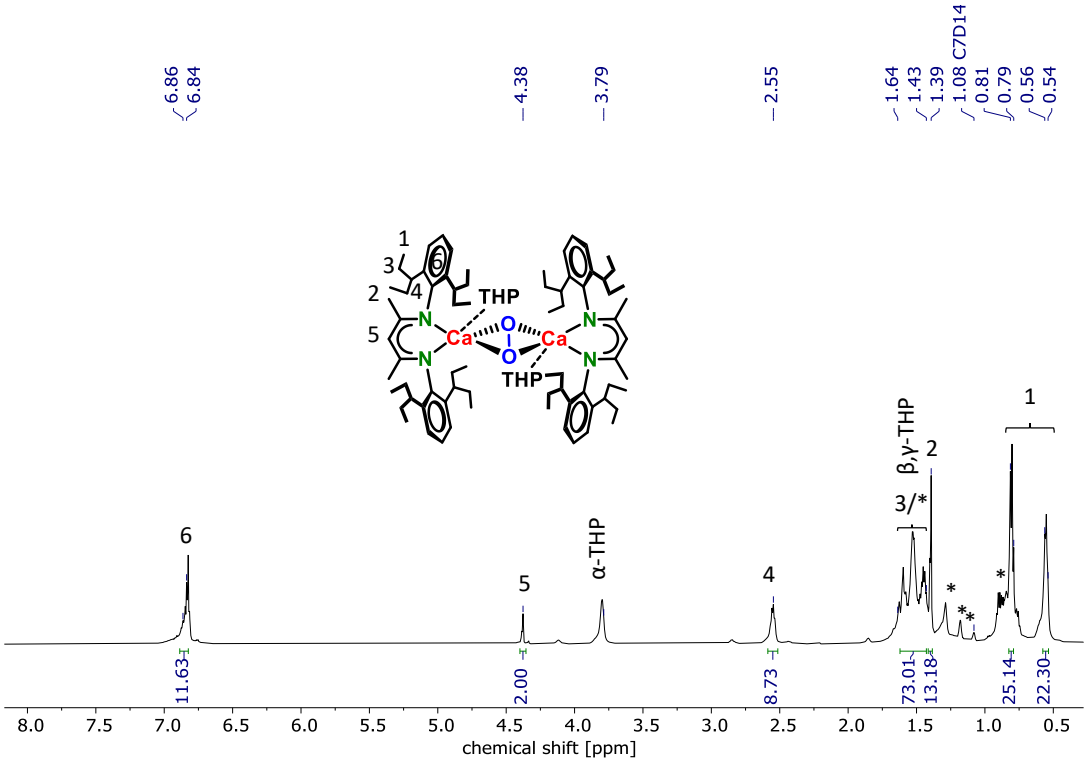



**Figure S9.** $^{1}$H NMR spectrum (600.13 MHz, $C_7D_{14}$, 298K) of the crude reaction product for conversion of a methylcyclohexane solution of $[(BDI^*)Ca(THP)]_2(N_2)$ with dry air showing selective formation of $[(BDI^*)Ca(THP)]_2(\mu_2\text{-}O_2)$ (**1**). Residual methylcyclohexane signals are marked with asterisks.

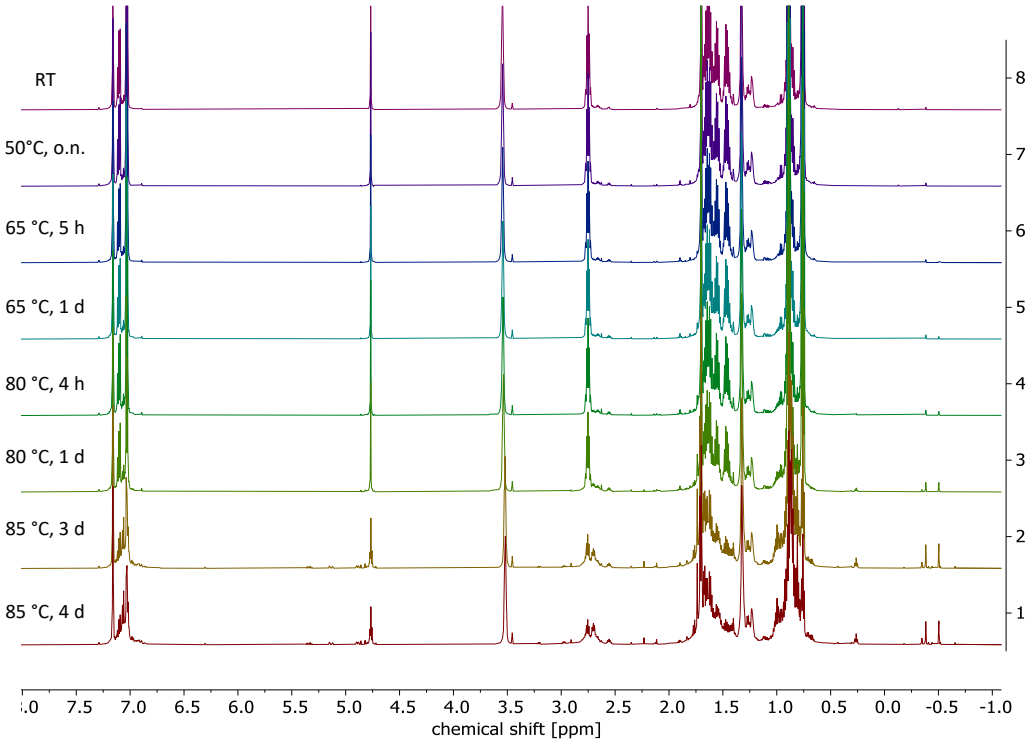



**Figure S10.** Thermal stability of a $C_6D_6$ solution of [(BDI*)Ca(THP)]$_2$($\mu_2$-$O_2$) (**1**) at various temperatures compared to a $^1$H NMR spectrum of [(BDI*)Ca(THP)]$_2$($O_2$) in $C_6D_6$. At 65 °C high-field shifted signals appear around –0.5 ppm. This indicates decomposition by alkyl chain deprotonation.

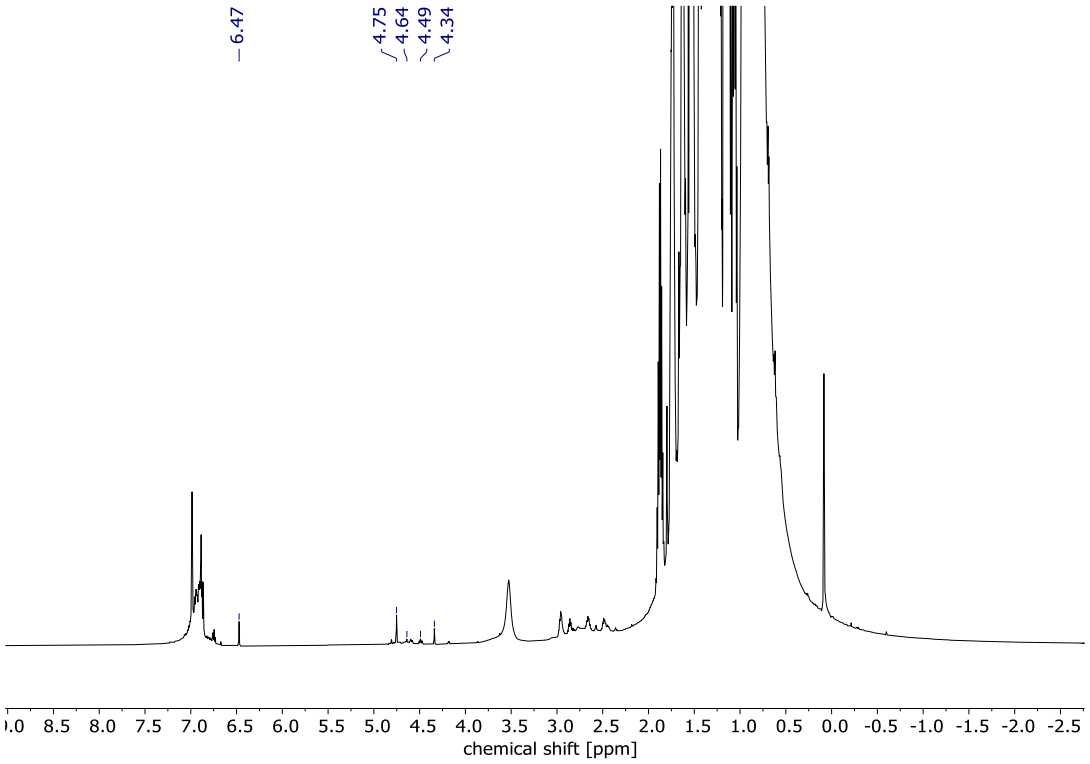



**Figure S11.** No-D NMR spectrum of the reaction between $[(BDI^*)Ca(THP)]_2(N_2)$ and $N_2O$ in hexanes at –70 °C recorded after 5 minutes. Signals in the typical area for the backbone CH moiety between 4.30 to 4.80 ppm show formation of several species. Precipitation of off-white powder was observed. From the mother liquor we isolated a batch of crystals of $[(BDI^*)^{2-}Ca^{2+}(THP)]_2$ as identified by X-ray diffraction and $^1H$ NMR analysis (see **Figure S12**).

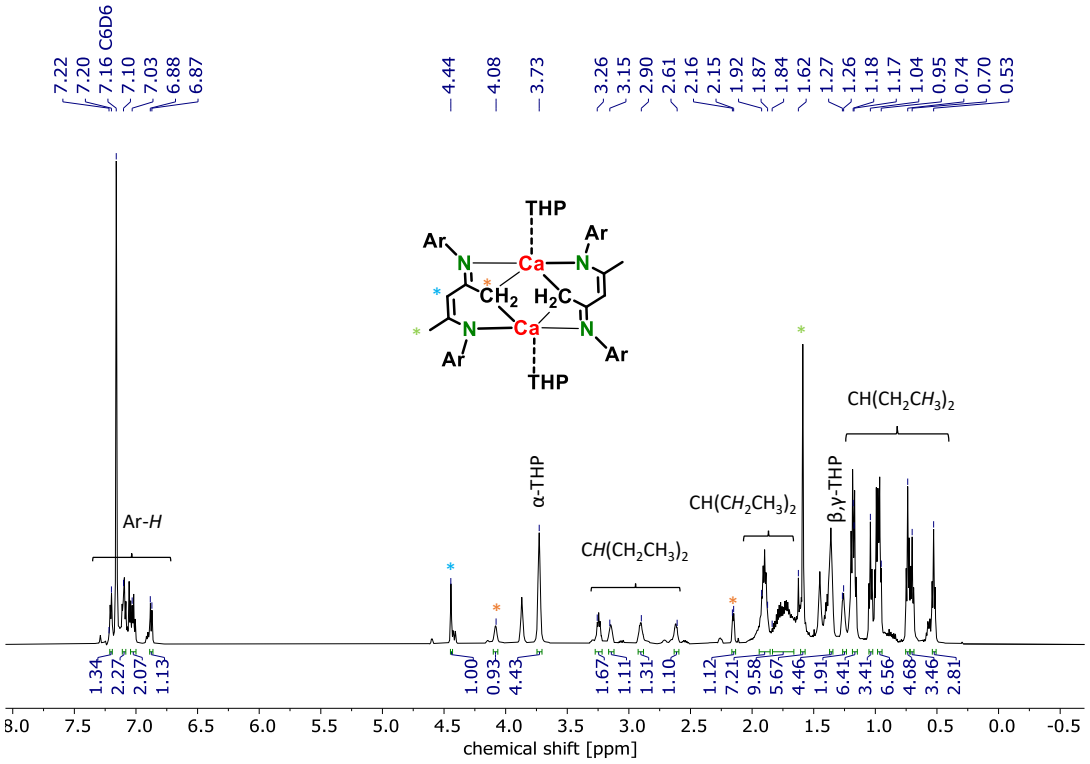



**Figure S12.** $^{1}$H NMR spectrum (600.13 MHz, $C_6D_6$, 298K) of $[(BDI^*)^{2-}Ca^{2+}(THP)]_2$ obtained from the reaction mixture of the reaction of $[(BDI^*)Ca(THP)]_2(N_2)$ in hexanes with $N_2O$ at –70 °C. The $^{1}$H NMR spectrum is in agreement with previous reported NMR data.[S1]

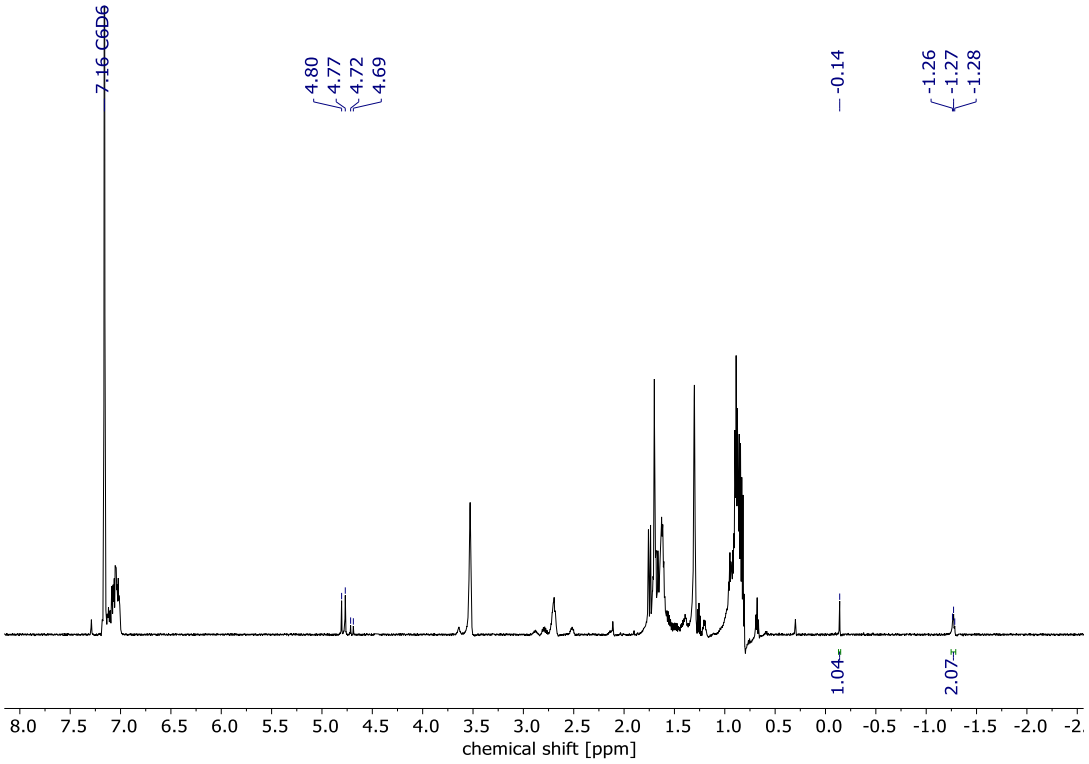



**Figure S13.** $^{1}$H NMR spectrum (600.13 MHz, $C_6D_6$, 298K) of crystalline [(BDI*)Ca(THP)]$_2$($\mu$-O) (**2**) dissolved in $C_6D_6$ showing that this complex is very reactive and not stable in solution. Decomposition is not selective and several signals in the typical area for the backbone methane signals between 4.60 to 4.85 ppm are visible. Signals at negative ppm values indicate C–H activation and deprotonation in the $CHEt_2$ arm. High-field shifted signals at –0.14 and –1.27 ppm in a ratio of 1:2 are present. The singlet may arise from a hydroxide unit and the triplet at –1.27 ppm from a deprotonated $CH_3$-group of the $Et_2CH$-arm bound to a calcium center.

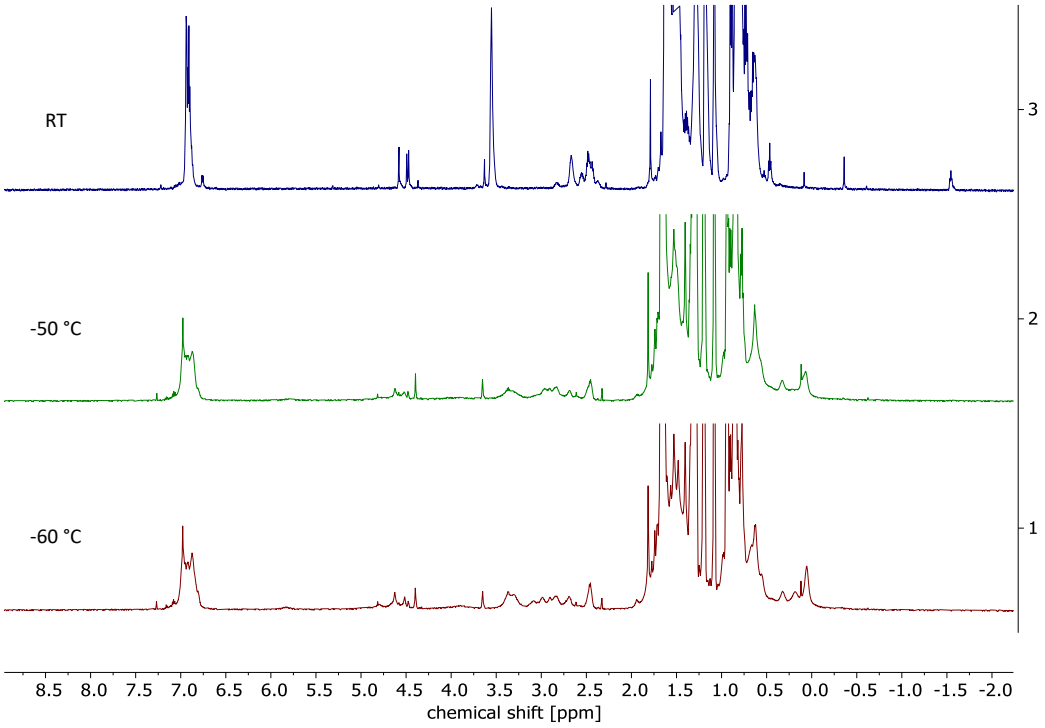



**Figure S14.** Variable temperature $^{1}$H NMR spectra (600.13 MHz, $C_7D_{14}$) of crystalline [(BDI*)Ca(THP)]$_2$($\mu$-O) (**2**) which has been dissolved in $C_7D_{14}$ and was kept at –80 °C. It proves that the bridging oxide is very reactive and not stable in solution. It is likely that immediate C–H activation of the DIPeP arm occurs.

# 5. Crystallographic Data

Suitable single crystals of compounds **1**-**2** were embedded in protective perfluoropolyalkylether oil (viscosity 1800 cSt; ABCR GmbH) on a microscope slide and a single specimen was selected and subsequently transferred to the cold nitrogen gas stream of the diffractometer.

The intensity data was collected at 100 K using Cu$K_\alpha$ radiation ($\lambda$ = 1.54184 Å) on an Agilent SuperNova dual radiation diffractometer with microfocus X-ray sources and mirror optics. The measured data were processed with the CrysAlisPro software package.[S2] Data were corrected for Lorentz and polarization effects, and an empirical absorption correction using spherical harmonics as well as a numerical absorption correction based on gaussian integration over a multifaceted crystal model were applied. Using Olex2,[S3] the structures were solved by dual-space methods (SHELXT)[S4] and refined by full-matrix least-squares procedures on $F^2$ using SHELXL.[S5] All non-hydrogen atoms were refined with anisotropic displacement parameters. Most H-atoms were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2$U_{eq}$ (CH or $CH_2$) or 1.5$U_{eq}$ ($CH_3$) of its parent C-atom. The hydrogen atoms H3 in the ligand backbone of both compounds deviated significantly from the calculated position. Therefore, these H atoms were placed in the positions indicated by a difference electron density map and their positions were refined together with an isotropic displacement parameter.

In case of [(BDI*)Ca(THP)]$_2$($\mu_2$-$O_2$) (**1**), a similar situation was observed. The asymmetric unit contained only half of the molecule and the co-crystalized hexane was disordered. Both half-molecules of the solvent were disordered about inversion centers. One of the moieties was modeled as disordered *n*-hexane, using similarity restraints (SADI, SIMU). The second moiety seemed to be a mixture of different hexane isomers with *n*-hexane as the dominant species (an isomeric mixture of hexanes was used for crystallization). However, attempts to build a suitable disorder model failed in this case. Therefore, a solvent mask[S7] was calculated for this solvent moiety using Olex2[S3] and 50.9 electrons were found in a volume of 228.5 $A^3$ (10.1% of the unit cell) in one void. This is consistent with the presence of one hexane per formula unit which accounts for 50 electrons per unit cell.

The asymmetric unit of compound [(BDI*)Ca(THP)]$_2$($\mu$-O) (**2**) contained half of the molecule and two half-molecules of *n*-pentane, which were disordered about inversion centers. This disorder was modeled with the help of similarity restraints (SADI) and rigid bond restraints (RIGU).[S6]

The crystal structure data has been deposited with the Cambridge Crystallographic Data Centre. CCDC 2427514-2427515 contain the supplementary crystallographic data for the complexes. This data

can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystallographic and refinement data are summarized in **Table S1**.

**Table S1.** Crystal data and structure refinement for compounds **1-2**.

| Compound | [(BDI*)Ca(THP)]$_2$($\mu_2$-O$_2$)·2hexane (**1**) | [(BDI*)Ca(THP)]$_2$($\mu$-O)·2(*n*-pentane) (**2**) |
|---|---|---|
| Identification code | hasj211028b | hasj220112b |
| Empirical formula | $C_{96}H_{162}Ca_2N_4O_4$ | $C_{94}H_{158}Ca_2N_4O_3$ |
| Formula weight | 1516.45 | 1472.39 |
| Temperature/K | 100.0(4) | 100.0(6) |
| Crystal system | triclinic | triclinic |
| Space group | P-1 | P-1 |
| a/Å | 12.8220(3) | 12.7723(3) |
| b/Å | 12.8590(2) | 12.8615(3) |
| c/Å | 16.6221(3) | 16.5534(3) |
| α/° | 71.9328(16) | 71.5478(17) |
| β/° | 71.5933(19) | 72.2458(17) |
| γ/° | 62.498(2) | 62.332(2) |
| Volume/Å$^3$ | 2262.16(10) | 2243.75(9) |
| Z | 1 | 1 |
| $\rho_{calc}$g/cm$^3$ | 1.113 | 1.090 |
| μ/mm$^{-1}$ | 1.470 | 1.460 |
| F(000) | 838.0 | 814.0 |
| Crystal size/mm$^3$ | 0.308 × 0.193 × 0.161 | 0.263 × 0.22 × 0.13 |
| Radiation | Cu Kα (λ = 1.54184) | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 5.714 to 145.368 | 5.73 to 148.788 |
| Index ranges | -13 ≤ h ≤ 15, -15 ≤ k ≤ 15, -20 ≤ l ≤ 20 | -15 ≤ h ≤ 15, -16 ≤ k ≤ 15, -20 ≤ l ≤ 20 |
| Reflections collected | 34013 | 32978 |
| Independent reflections | 8804 [$R_{int}$ = 0.0233, $R_{sigma}$ = 0.0199] | 8939 [$R_{int}$ = 0.0267, $R_{sigma}$ = 0.0230] |
| Data/restraints/parameters | 8804/75/485 | 8939/49/529 |
| Goodness-of-fit on F$^2$ | 1.061 | 1.034 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0320, w$R_2$ = 0.0819 | $R_1$ = 0.0419, w$R_2$ = 0.1129 |
| Final R indexes [all data] | $R_1$ = 0.0335, w$R_2$ = 0.0833 | $R_1$ = 0.0479, w$R_2$ = 0.1177 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.52/-0.54 | 0.71/-0.33 |
| CCDC number | 2427515 | 2427514 |

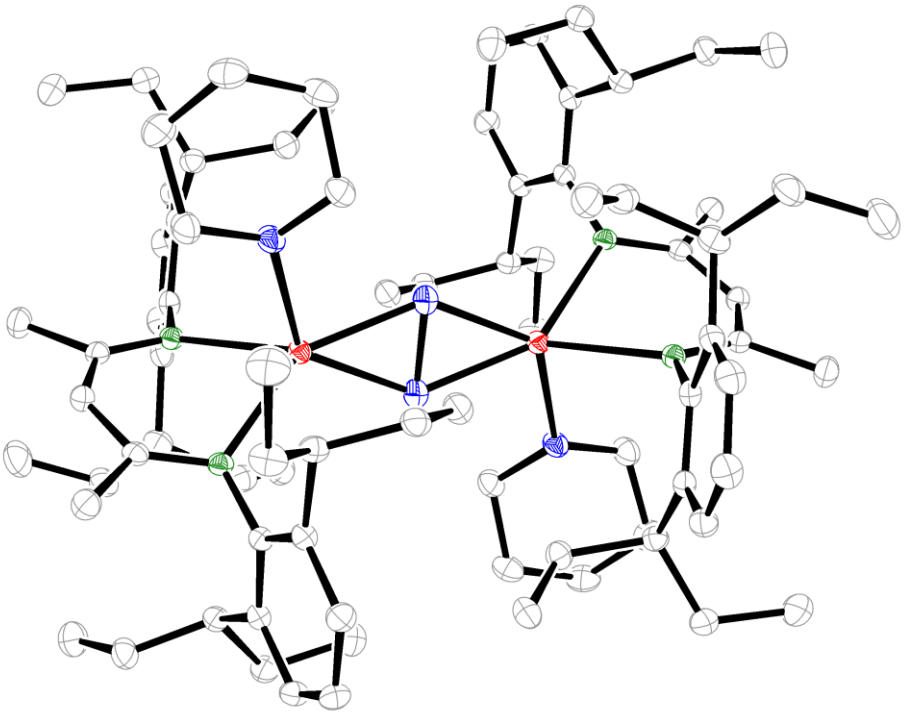


**Figure S15.** Solid state structure of [(BDI)Ca(THP)]$_2$($\mu_2$-O$_2$) (**1**). Ellipsoids represent 50% probability. Hydrogen atoms have been omitted for clarity.

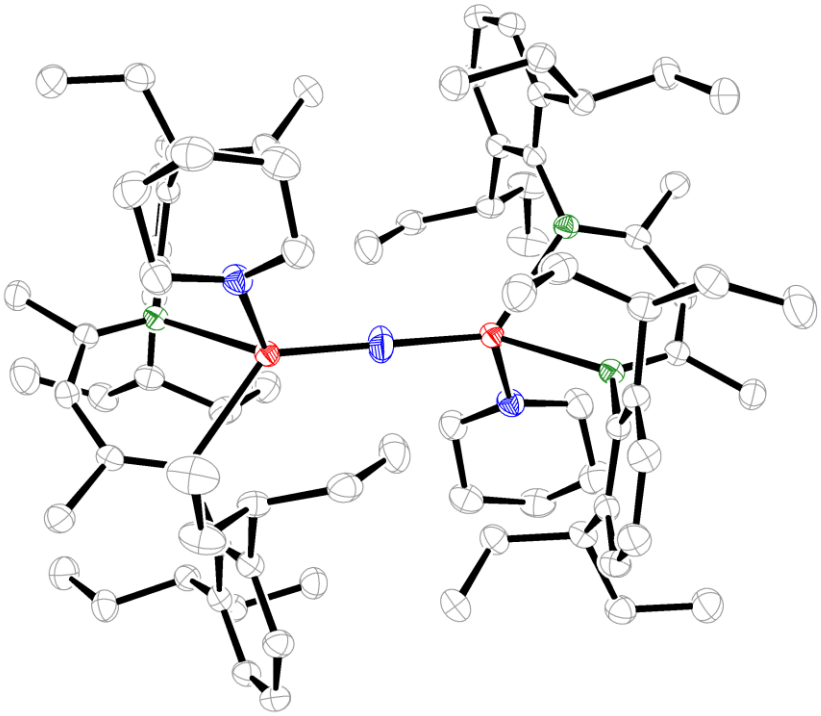


**Figure S16.** Solid state structure of [(BDI*)Ca(THP)]$_2$($\mu$-O) (**2**). Ellipsoids represent 50% probability. Hydrogen atoms have been omitted for clarity.

# 6. Computational Details

All calculations were carried out using Gaussian 16A.[S8] All methods were used as implemented. All structures were fully optimized at a B3PW91-GD3BJ/def2svp level of theory which includes Grimme D3 dispersion correction using Becke–Johnson dampening (GD3BJ).[S9–S13] All structures were characterized as true minima (Nimag = 0) or as transition states (Nimag = 1) by frequency calculations on the same level of theory. Energies were determined at a B3PW91-GD3BJ/def2tzvp level of theory. The same level of theory was used for the NPA charge calculations with NBO.[S14] All structures were evaluated using Molecule 2.3.[S15] QTAIM analysis was carried out using AIMAll (v17) with the wave functions obtained at the B3PW91-GD3BJ/def2tzvp level of theory.[S16,S17]

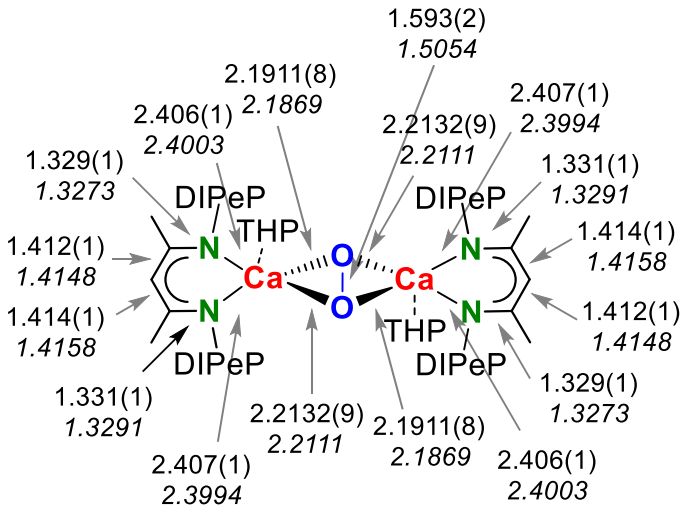



**Figure S17.** Comparison of calculated bond distances (in italic) with those in the crystal structure given in Å for complex [(BDI*)Ca(THP)]$_2$($\mu_2$-O$_2$) (**1**).

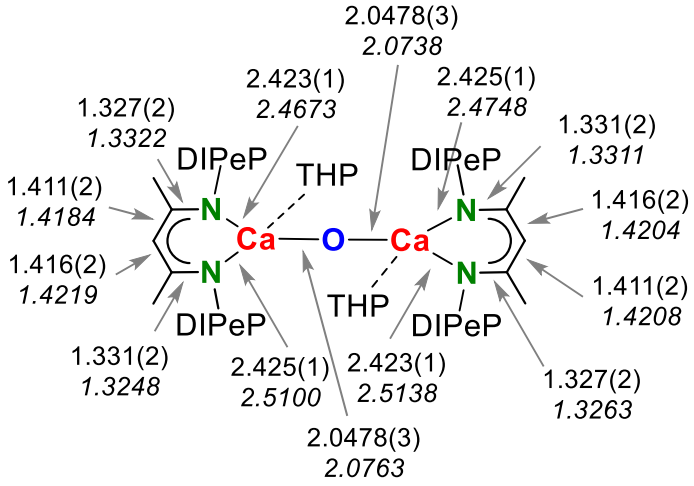



**Figure S18.** Comparison of calculated bond distances (in italic) with those in the crystal structure given in Å for complex [(BDI*)Ca(THP)]$_2$($\mu$-O) (**2**).

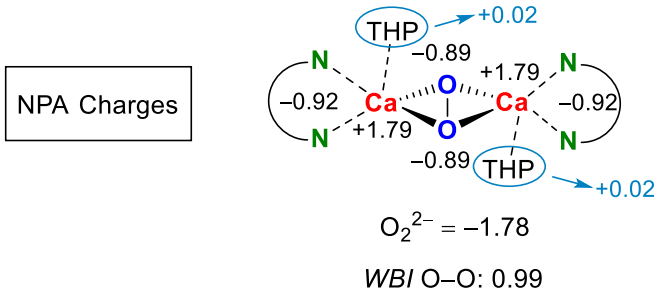



**Figure S19.** NPA charges for selected atoms or groups and Wiberg Bond Index (WBI) in the peroxide dianion $O_2^{2-}$ for complex $[(BDI^*)Ca(THP)]_2(\mu_2\text{-}O_2)$ (**1**).

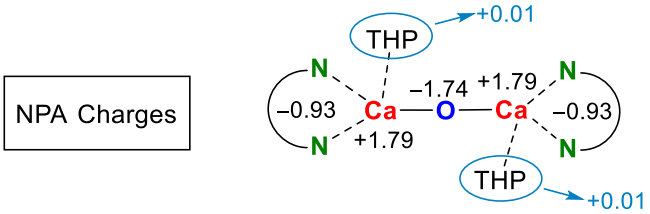



**Figure S20.** NPA charges for selected atoms or groups for complex $[(BDI^*)Ca(THP)]_2(\mu\text{-}O)$ (**2**).

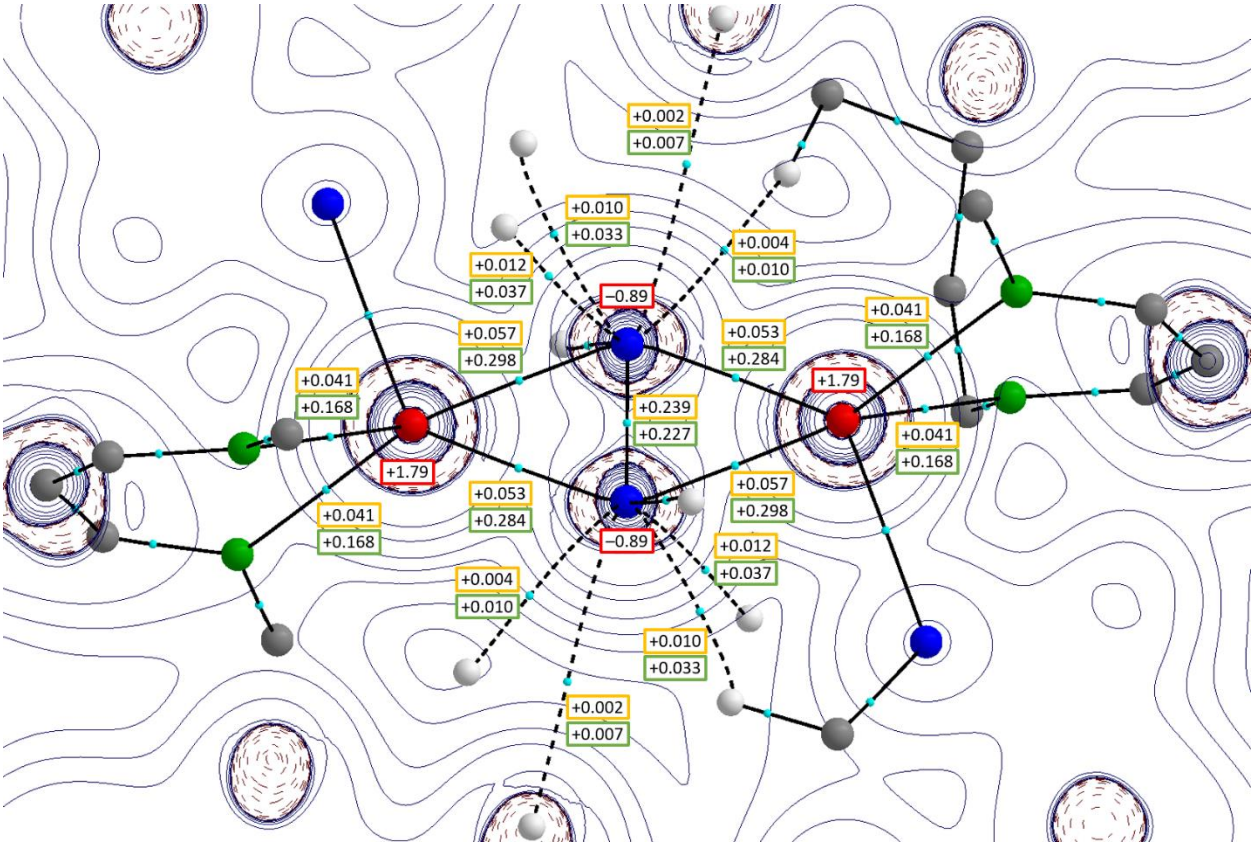



**Figure S21.** Contour plots of the Laplacian of [(BDI*)Ca(THP)]$_2$($\mu_2$-O$_2$) (**1**) showing areas of electron density concentration (dashed lines) and depletion (solid lines). The BCP's are shown in blue. The electron density $\rho$(**r**) in e·B$^{-3}$ (orange box) and the Laplacian $\nabla^2\rho$(**r**) in e·B$^{-5}$ (green box) in the BCPs (blue) are given. NPA charges are given in red boxes. In addition, weak O···H–C bonding interactions of the $O_2^{2-}$ dianion with organic fragments of the BDI* ligand are displayed.

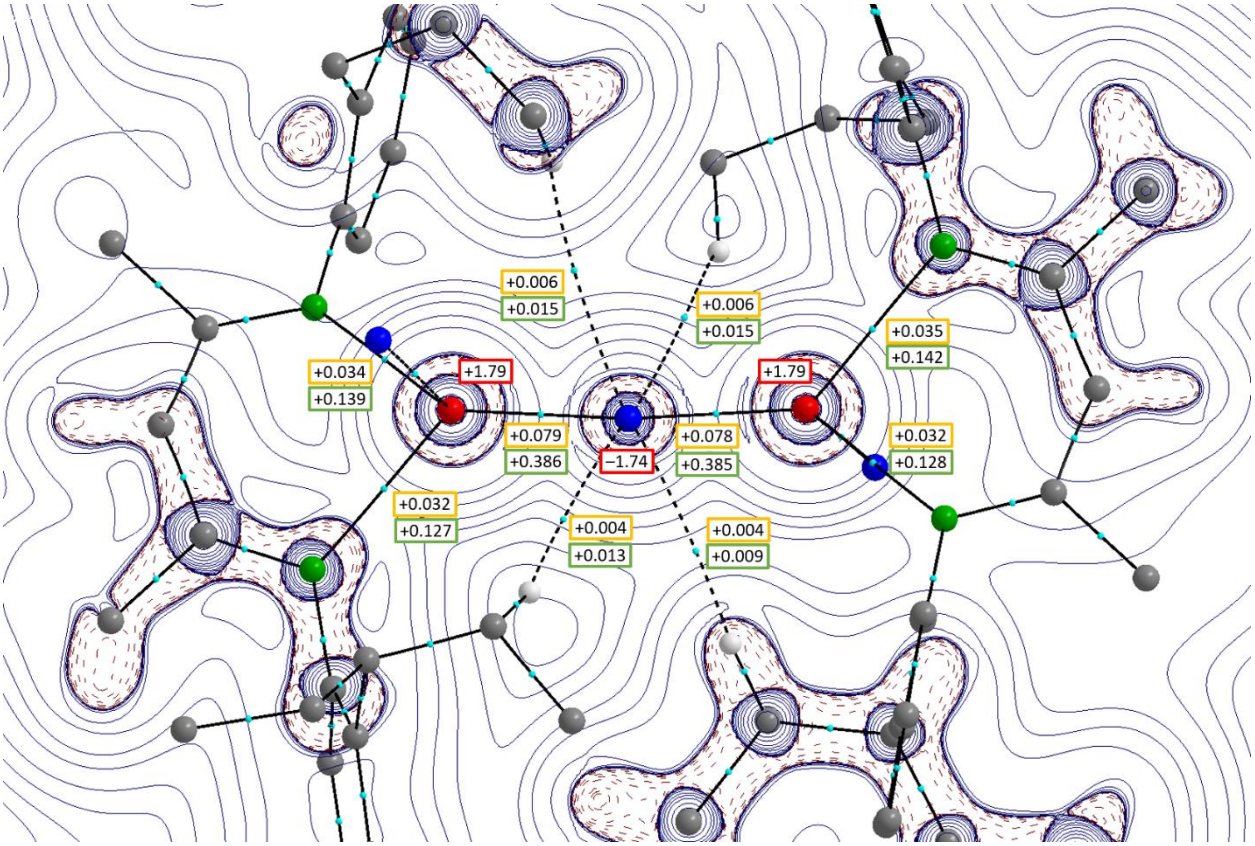



**Figure S22.** Contour plots of the Laplacian of [(BDI*)Ca(THP)]$_2$($\mu$-O) (**2**) showing areas of electron density concentration (dashed lines) and depletion (solid lines). The BCP's are shown in blue. The electron density $\rho(\mathbf{r})$ in e·B$^{-3}$ (yellow box) and the Laplacian $\nabla^2\rho(\mathbf{r})$ in e·B$^{-5}$ (green box) in the BCPs (blue) are given. NPA charges are given in red boxes. In addition, weak O···H–C bonding interactions of the $O^{2-}$ dianion with organic fragments of the BDI* ligand are displayed.

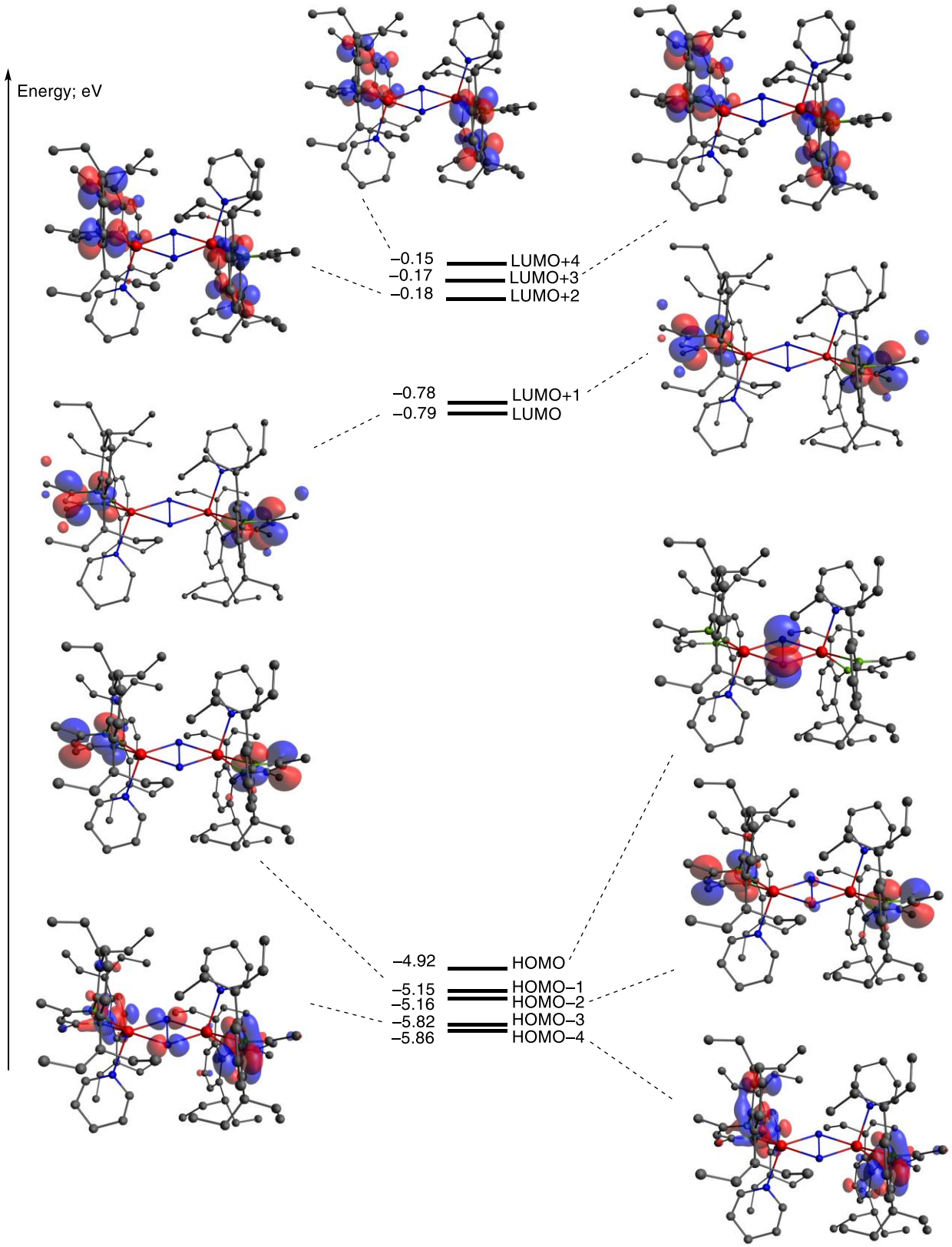



**Figure S23.** Molecular Orbital Diagram of [(BDI*)Ca(THP)]$_2$($\mu_2$-O$_2$) (**1**) calculated at the B3PW91-GD3BJ/def2tzvp//B3PW91-GD3BJ/def2svp level of theory.

**Table S2.** Selected MO's for [(BDI*)Ca(THP)]$_2$($\mu_2$-O$_2$) (**1**) with most prominent contributions, computed at the B3PW91-GD3BJ/def2tzvp//B3PW91-GD3BJ/def2svp level of theory.

| | |
|---|---|
| **LUMO+4** | C175-p=0.0635, C61-p=0.0631, C179-p=0.0614, C181-p=0.0612, C65-p=0.0610, C67-p=0.0607, C174-p=0.0579, C60-p=0.0575, C20-p=0.0549, C134-p=0.0548, C26-p=0.0514, C140-p=0.0513, C24-p=0.0242, C138-p=0.0241, C19-p=0.0229, C133-p=0.0228 |
| **LUMO+3** | C134-p=0.0691, C140-p=0.0668, C20-p=0.0668, C26-p=0.0646, C138-p=0.0561, C24-p=0.0537, C133-p=0.0531, C19-p=0.0509, C61-p=0.0455, C175-p=0.0437, C67-p=0.0414, C181-p=0.0397, C65-p=0.0393, C179-p=0.0379, C60-p=0.0373, C174-p=0.0360 |
| **LUMO+2** | C24-p=0.0732, C138-p=0.0706, C19-p=0.0689, C133-p=0.0665, C26-p=0.0579, C20-p=0.0578, C140-p=0.0554, C134-p=0.0553, C175-p=0.0452, C61-p=0.0436, C181-p=0.0410, C67-p=0.0395, C179-p=0.0302, C65-p=0.0289, C174-p=0.0286, C60-p=0.0274 |
| **LUMO+1** | C127-p=0.1270, C13-p=0.1265, C124-p=0.1147, C10-p=0.1143, N119-p=0.0677, N5-p=0.0675, N118-p=0.0630, N4-p=0.0628, Ca2-d=0.0127, Ca1-d=0.0126, H131-s=0.0118, H17-s=0.0118, C125-d=0.0112, C11-d=0.0111 |
| **LUMO** | C13-p=0.1257, C127-p=0.1252, C10-p=0.1148, C124-p=0.1144, N5-p=0.0674, N119-p=0.0672, N4-p=0.0622, N118-p=0.0620, Ca1-d=0.0136, Ca2-d=0.0136, H17-s=0.0117, H131-s=0.0117, C11-d=0.0111, C125-d=0.0111 |
| **HOMO** | O2-p=0.4563, O1-p=0.4563, Ca2-d=0.0125, Ca1-d=0.0125 |
| **HOMO–1** | C125-p=0.1972, C11-p=0.1960, N119-p=0.1076, N5-p=0.1069, N118-p=0.1068, N4-p=0.1061 |
| **HOMO–2** | C11-p=0.1905, C125-p=0.1892, N5-p=0.1050, N119-p=0.1043, N4-p=0.1021, N118-p=0.1014, O1-p=0.0139 O2-p=0.0139 |
| **HOMO–3** | O2-p=0.0984, O1-p=0.0984, N5-p=0.0588, N119-p=0.0587, C63-p=0.0579, C177-p=0.0579, C59-p=0.0537, C173-p=0.0536, C67-p=0.0294, C181-p=0.0293, C60-p=0.0289, C174-p=0.0289, N4-p=0.0185, N118-p=0.0185, C18-p=0.0162, C132-p=0.0162, C22-p=0.0151, C136-p=0.0151, N5-s=0.0141, N119-s=0.0141 |
| **HOMO–4** | N119-p=0.0565, N5-p=0.0565, C177-p=0.0531, C63-p=0.0531, C173-p=0.0509, C59-p=0.0509, C132-p=0.0372, C18-p=0.0372, C136-p=0.0371, C22-p=0.0370, N118-p=0.0369, N4-p=0.0369, C181-p=0.0288, C67-p=0.0288, C174-p=0.0272, C60-p=0.0272, C140-p=0.0199, C26-p=0.0199, C133-p=0.0191, C19-p=0.0191, N119-s=0.0142, N5-s=0.0142 |

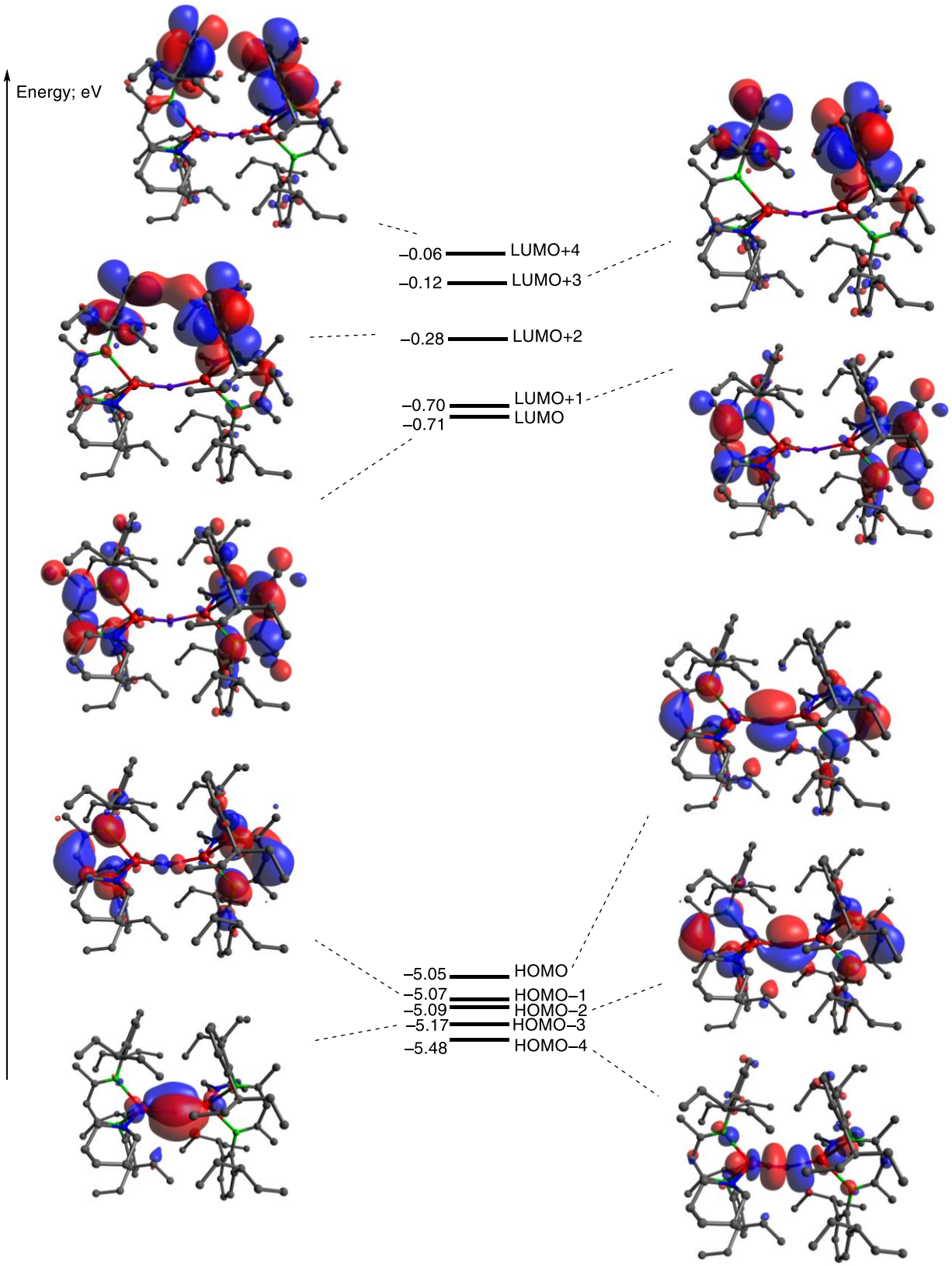



**Figure S24.** Molecular Orbital Diagram of [(BDI*)Ca(THP)]$_2$($\mu$-O) (**2**) calculated at the B3PW91-GD3BJ/def2tzvp//B3PW91-GD3BJ/def2svp level of theory.

**Table S3.** Selected MO's for [(BDI*)Ca(THP)]$_2$($\mu$-O) (**2**) with most prominent contributions, computed at the B3PW91-GD3BJ/def2tzvp//B3PW91-GD3BJ/def2svp level of theory.

| | |
|---|---|
| **LUMO+4** | C176-p=0.1312, C63-p=0.1311, C172-p=0.1295, C59-p=0.1294, C61-p=0.0425, C174-p=0.0425, C67-p=0.0334, C180-p=0.0334, C178-p=0.0269, C65-p=0.0269, C173-p=0.0163, C60-p=0.0162 |
| **LUMO+3** | C61-p=0.1057, C174-p=0.1056, C67-p=0.0954, C180-p=0.0954, C60-p=0.0938, C173-p=0.0936, C65-p=0.0913, C178-p=0.0911, C59-d=0.0102, C172-d=0.0102 |
| **LUMO+2** | C178-p=0.1106, C65-p=0.1106, C173-p=0.0975, C60-p=0.0974, C180-p=0.0810, C67-p=0.0809, C174-p=0.0786, C61-p=0.0785, C123-p=0.0113, C10-p=0.0112 |
| **LUMO+1** | C126-p=0.1236, C13-p=0.1232, C123-p=0.1108, C10-p=0.1104, N118-p=0.0680, N5-p=0.0678, N117-p=0.0620, N4-p=0.0618, C124-d=0.0109, C11-d=0.0109, H128-s=0.0103, H15-s=0.0103 |
| **LUMO** | C13-p=0.1202, C126-p=0.1198, C10-p=0.1058, C123-p=0.1054, N5-p=0.0660, N118-p=0.0658, N4-p=0.0599, N117-p=0.0597, C11-d=0.0104, C124-d=0.0104 |
| **HOMO** | O2-p=0.4797, C124-p=0.0784, C11-p=0.0769, N117-p=0.0483, N4-p=0.0475, N118-p=0.0410, N5-p=0.0403, Ca115-d=0.0200, Ca1-d=0.0200 |
| **HOMO–1** | C11-p=0.1926, C124-p=0.1921, N4-p=0.1087, N117-p=0.1084, N5-p=0.0992, N118-p=0.0989, O2-p=0.0193 |
| **HOMO–2** | O2-p=0.3418, C11-p=0.1191, C124-p=0.1181, N4-p=0.0670, N117-p=0.0664, N5-p=0.0612, N118-p=0.0607, Ca1-d=0.0203, Ca115-d=0.0203 |
| **HOMO–3** | O2-p=0.8480, Ca1-d=0.0394, Ca2-d=0.0394 |
| **HOMO–4** | O2-p=0.7788, Ca2-d=0.0562, Ca1-d=0.0562, N5-p=0.0108, N118-p=0.0108 |

**NLMO analysis for the Ca–($O_2$)–Ca and Ca–O–Ca moieties in complexes 1 and 2**

Using the Natural-Localized-Molecular-Orbital (NLMO) method (**Table S4** and **Table S5**) shows that the bonding orbital O–O in Ca peroxide **1** is predominately comprised of O orbitals. For Ca peroxide **1** as well as for Ca oxide **2**, all lone-pairs are predominately located on the O orbitals.

**Table S4.** NLMOs for [(BDI*)Ca(THP)]$_2$($\mu_2$-$O_2$) (**1**) including the O valence electrons. Contributions of non-metals are neglectable.

| | |
|---|---|
| **(2.00000) $e^-$ 98.9781% lonepair O1** | **98.979% O1 s (90.34%), p 0.11 (9.65%)**, d 0.00 (0.01%) f 0.00 ( 0.00%)<br>0.015% O2 s (16.16%), p 4.26 (68.87%), d 0.88 (14.19%), f 0.05 (0.78%)<br>0.429% Ca1 s (89.13%), p 0.01 (0.85%), d 0.11 (10.02%)<br>0.428% Ca2 s (88.63%), p 0.01 (0.79%), d 0.12 (10.58%) |
| **(2.00000) $e^-$ 98.3554% lonepair O1** | **98.355% O1 s (0.76%), p 99.99 (99.21%)**, d 0.03 (0.03%), f 0.00 (0.00%)<br>0.061% O2 s (0.05%), p 99.99 (58.06%), d 99.99 (40.75%), f 21.77 (1.14%)<br>0.326% Ca1 s (1.38%), p 1.38 (1.90%), d 70.24 (96.72%)<br>0.263% Ca2 s (1.26%), p 2.35 (2.96%), d 76.18 (95.78%) |
| **(2.00000) $e^-$ 97.1776% lonepair O1** | **97.178% O1 s (0.03%), p 99.99 (99.93%)**, d 1.44 (0.04%), f 0.03 (0.00%)<br>0.124% O2 s (0.07%), p 99.99 (81.56%), d 99.99 (17.78%), f 8.58 (0.59%)<br>1.179% Ca1 s (0.46%), p 15.11 (6.94%), d 99.99 (92.60%)<br>1.012% Ca2 s (5.87%), p 0.68 (3.98%), d 15.37 (90.15%) |
| **(2.00000) $e^-$ 98.9780% lonepair O2** | 0.015% O1 s (16.17%), p 4.26 (68.86%), d 0.88 (14.19%), f 0.05 (0.78%)<br>**98.979% O2 s (90.34%), p 0.11 (9.65%)**, d 0.00 (0.01%), f 0.00 (0.00%)<br>0.428% Ca1 s (88.63%), p 0.01 (0.79%), d 0.12 (10.58%)<br>0.429% Ca2 s (89.12%), p 0.01 (0.85%), d 0.11 (10.02%) |
| **(2.00000) $e^-$ 98.3554% lonepair O2** | 0.061% O1 s (0.05%), p 99.99 (58.05%), d 99.99 (40.75%), f 21.83 (1.14%)<br>**98.355% O2 s (0.76%), p 99.99 (99.21%)**, d 0.03 (0.03%), f 0.00 (0.00%)<br>0.263% Ca1 s (1.25%), p 2.36 (2.96%), d 76.34 (95.79%)<br>0.326% Ca2 s (1.38%), p 1.38 (1.90%), d 70.28 (96.72%) |
| **(2.00000) $e^-$ 97.1774% lonepair O2** | 0.124% O1 s (0.07%), p 99.99 (81.56%), d 99.99 (17.78%), f 8.55 (0.59%)<br>**97.177% O2 s (0.03%), p 99.99 (99.93%)**, d 1.44 (0.04%), f 0.03 (0.00%)<br>1.012% Ca1 s (5.87%), p 0.68 (3.98%), d 15.37 (90.15%)<br>1.180% Ca2 s (0.46%), p 15.12 (6.94%), d 99.99 (92.60%) |
| **(2.00000) $e^-$ 98.8294% Bonding orbital O1–O2** | **49.417% O1 s (9.26%), p 9.78 (90.56%)**, d 0.02 (0.17%), f 0.00 (0.01%)<br>**49.417% O2 s (9.26%), p 9.78 (90.56%)**, d 0.02 (0.17%), f 0.00 (0.01%)<br>0.430% Ca1 s (37.59%), p 0.49 (18.50%), d 1.17 (43.91%)<br>0.430% Ca2 s (37.59%), p 0.49 (18.50%), d 1.17 (43.91%) |

**Table S5.** NLMOs for [(BDI*)Ca(THP)]$_2$($\mu$-O) (**2**) including the O valence electrons. Contributions of non-metals are neglectable.

| | |
|---|---|
| **(2.00000) $e^-$** | **99.186% O2 s (99.77%)**, p 0.00 (0.22%), d 0.00 (0.01%), f 0.00 (0.00%) |
| **99.1862%** | 0.365% Ca1 s (60.42%), p 0.03 (1.88%), d 0.62 (37.70%) |
| **lonepair O2** | 0.365% Ca2 s (60.42%), p 0.03 (1.88%), d 0.62 (37.70%) |
| **(2.00000) $e^-$** | **96.782% O2** s (0.00%), **p 1.00 (100.00%)**, d 0.00 (0.00%), f 0.00 (0.00%) |
| **96.7813%** | 0.969% Ca1 s (0.75%), p 6.38 (4.79%), d 99.99 (94.45%) |
| **lonepair O2** | 0.969% Ca2 s (0.75%), p 6.38 (4.79%), d 99.99 (94.45%) |
| **(2.00000) $e^-$** | **96.274% O2** s (0.22%), **p 99.99 (99.78%)**, d 0.02 (0.00%), f 0.00 (0.00%) |
| **96.2735%** | 0.937% Ca1 s (0.98%), p 0.90 (0.88%), d 99.99 (98.15%) |
| **lonepair O2** | 0.937% Ca2 s (0.98%), p 0.90 (0.88%), d 99.99 (98.14%) |
| **(2.00000) $e^-$** | **94.501% O2** s (0.00%), **p 1.00 (100.00%)**, d 0.00 (0.00%), f 0.00 (0.00%) |
| **94.5008%** | 2.318% Ca1 s (0.24%), p 31.49 (7.58%), d 99.99 (92.18%) |
| **lonepair O2** | 2.318% Ca2 s (0.24%), p 31.51 (7.58%), d 99.99 (92.18%) |

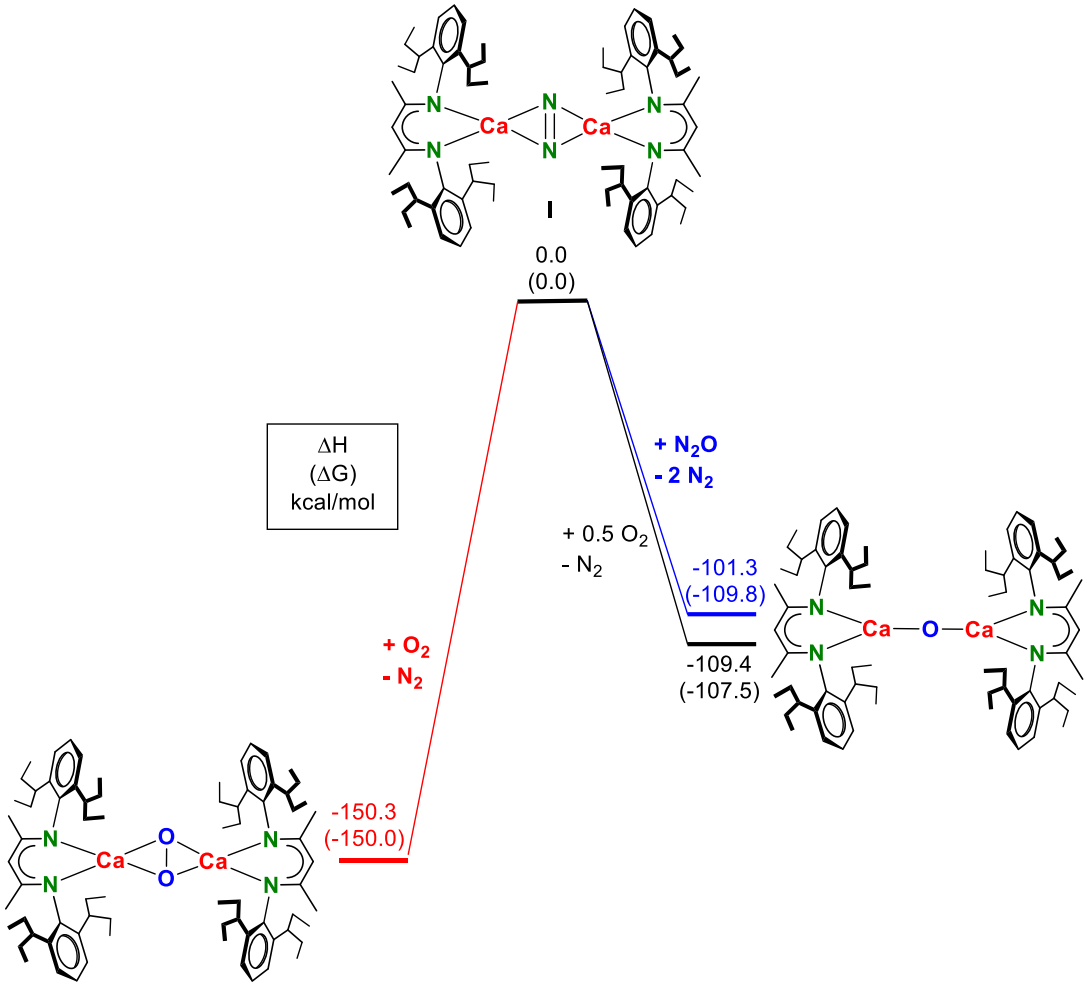



**Figure S25.** Energy profile (B3PW91/def2tzvp//def2svp) for the reaction of ether-free $[(BDI^*)Ca]_2(N_2)$ with $O_2$ (red), 0.5 $O_2$ (black), and $N_2O$ (blue) which shows extremely exothermic conversions to the ether-free Ca peroxide complex $[(BDI^*)Ca]_2(\mu_2\text{-}O_2)$ and to the ether-free Ca oxide complex $[(BDI^*)Ca]_2(\mu\text{-}O)$, respectively. ΔH and ΔG(298 K) (between brackets) are given in kcal $mol^{-1}$.

**XYZ Coordinates**

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[(BDI*)Ca(THP)]$_2$($\mu_2$-O$_2$) (**1**)

| | | | |
|---|---|---|---|
| Ca | 1.940832 | -0.285437 | -0.648594 |
| O | 0.207470 | -0.236416 | 0.683849 |
| O | 1.933491 | -0.449351 | -3.038589 |
| N | 3.924277 | 1.057063 | -0.504751 |
| N | 3.533123 | -2.063314 | -0.392937 |
| C | 6.232015 | 1.586952 | -1.125273 |
| H | 5.911845 | 2.430039 | -1.751286 |
| H | 7.109492 | 1.110091 | -1.578277 |
| H | 6.529518 | 2.019134 | -0.159558 |
| C | 5.100833 | 0.604906 | -0.926420 |
| C | 5.415677 | -0.746466 | -1.207856 |
| H | 6.409934 | -0.885721 | -1.633606 |
| C | 4.753148 | -1.959320 | -0.905121 |
| C | 5.536470 | -3.209211 | -1.254167 |
| H | 5.237087 | -4.071314 | -0.645477 |
| H | 6.618261 | -3.051582 | -1.154722 |
| H | 5.333897 | -3.467549 | -2.307125 |
| C | 3.830471 | 2.425371 | -0.138670 |
| C | 3.361603 | 3.385563 | -1.067646 |
| C | 3.310546 | 4.729681 | -0.679236 |
| H | 2.980592 | 5.481081 | -1.398656 |
| C | 3.677122 | 5.128346 | 0.601895 |
| H | 3.632494 | 6.182806 | 0.884205 |
| C | 4.093397 | 4.171831 | 1.523735 |
| H | 4.369308 | 4.484244 | 2.532739 |
| C | 4.177844 | 2.819819 | 1.177322 |
| C | 2.853541 | 2.962249 | -2.431065 |
| H | 3.264723 | 1.959851 | -2.624595 |
| C | 1.319890 | 2.802639 | -2.409168 |
| H | 1.019186 | 2.307980 | -3.345700 |
| H | 1.026542 | 2.102104 | -1.610513 |
| C | 0.513015 | 4.079057 | -2.239011 |
| H | 0.615368 | 4.758316 | -3.099774 |
| H | 0.804205 | 4.632769 | -1.336181 |
| H | -0.554283 | 3.847375 | -2.130102 |
| C | 3.306762 | 3.863840 | -3.583517 |
| H | 2.822916 | 3.496743 | -4.506115 |
| H | 2.919383 | 4.886217 | -3.444534 |
| C | 4.813396 | 3.915466 | -3.781517 |
| H | 5.087014 | 4.553711 | -4.635803 |
| H | 5.225340 | 2.911007 | -3.970317 |
| H | 5.316384 | 4.319684 | -2.889270 |
| C | 4.556686 | 1.776892 | 2.208663 |
| H | 4.936062 | 0.903040 | 1.660099 |
| C | 3.301875 | 1.282508 | 2.954411 |
| H | 2.568238 | 0.930493 | 2.209786 |
| H | 3.589291 | 0.397661 | 3.542107 |
| C | 2.635498 | 2.297132 | 3.871217 |
| H | 3.311418 | 2.631899 | 4.672879 |
| H | 1.751798 | 1.860079 | 4.357378 |
| H | 2.302463 | 3.186739 | 3.318066 |
| C | 5.658937 | 2.211524 | 3.178752 |
| H | 5.333813 | 3.085546 | 3.766674 |
| H | 5.794650 | 1.400889 | 3.915134 |
| C | 6.990670 | 2.519402 | 2.511403 |
| H | 7.750571 | 2.819401 | 3.249300 |
| H | 6.891075 | 3.339471 | 1.783175 |
| H | 7.378737 | 1.639140 | 1.975564 |
| C | 3.132679 | -3.292006 | 0.186837 |
| C | 2.379962 | -4.250296 | -0.526946 |
| C | 2.066021 | -5.463126 | 0.099162 |
| H | 1.491346 | -6.212768 | -0.450429 |
| C | 2.468161 | -5.733446 | 1.402177 |
| H | 2.221276 | -6.690571 | 1.867385 |
| C | 3.157788 | -4.759501 | 2.120821 |
| H | 3.443448 | -4.954682 | 3.157236 |
| C | 3.480173 | -3.529710 | 1.542625 |
| C | 1.908696 | -4.010773 | -1.948628 |
| H | 2.230194 | -2.994470 | -2.231470 |
| C | 0.374833 | -4.063999 | -2.028765 |
| H | 0.057713 | -3.920696 | -3.074584 |
| H | 0.040723 | -5.080442 | -1.757302 |
| C | -0.314569 | -3.044529 | -1.140621 |
| H | -0.187739 | -2.012402 | -1.497670 |
| H | 0.081081 | -3.082196 | -0.118495 |
| H | -1.396703 | -3.225085 | -1.077660 |
| C | 2.577060 | -4.999536 | -2.918676 |
| H | 3.662698 | -4.987454 | -2.732342 |
| H | 2.246266 | -6.021957 | -2.666581 |
| C | 2.314872 | -4.734352 | -4.395306 |
| H | 2.860360 | -5.450659 | -5.028738 |
| H | 2.642350 | -3.723552 | -4.686544 |
| H | 1.247804 | -4.818971 | -4.650335 |
| C | 4.228409 | -2.471659 | 2.327482 |
| H | 4.038740 | -1.515245 | 1.812179 |
| C | 3.736877 | -2.326158 | 3.772047 |
| H | 4.006766 | -3.226370 | 4.352116 |
| H | 4.305030 | -1.505339 | 4.240389 |
| C | 2.244973 | -2.056635 | 3.907612 |
| H | 1.923217 | -1.234323 | 3.251063 |
| H | 1.980591 | -1.788919 | 4.941739 |
| H | 1.652001 | -2.936950 | 3.627693 |
| C | 5.748253 | -2.718627 | 2.275946 |
| H | 5.998781 | -3.518668 | 2.995590 |
| H | 6.013572 | -3.119741 | 1.288035 |
| C | 6.589049 | -1.477951 | 2.537842 |
| H | 7.664284 | -1.714463 | 2.540511 |
| H | 6.353340 | -1.009589 | 3.505688 |
| H | 6.414976 | -0.729242 | 1.749634 |
| C | 3.119185 | -0.734324 | -3.775822 |
| H | 3.155394 | -1.821211 | -3.977567 |
| H | 3.962915 | -0.493774 | -3.114421 |

| | | | |
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| C | 3.165464 | 0.044111 | -5.076500 |
| H | 4.083883 | -0.226090 | -5.621898 |
| H | 3.231379 | 1.120586 | -4.848024 |
| C | 1.918254 | -0.237599 | -5.909191 |
| H | 1.925929 | -1.294638 | -6.231761 |
| H | 1.910916 | 0.371533 | -6.826733 |
| C | 0.671014 | 0.030492 | -5.072677 |
| H | 0.581215 | 1.109403 | -4.871129 |
| H | -0.244210 | -0.268173 | -5.607632 |
| C | 0.728346 | -0.717884 | -3.753755 |
| H | -0.084631 | -0.426971 | -3.075075 |
| H | 0.662897 | -1.807750 | -3.928067 |
| Ca | -1.940839 | 0.285413 | 0.648616 |
| O | -0.207518 | 0.236261 | -0.683892 |
| O | -1.933487 | 0.449162 | 3.038630 |
| N | -3.924313 | -1.057040 | 0.504730 |
| N | -3.533077 | 2.063359 | 0.392960 |
| C | -6.232095 | -1.586851 | 1.125129 |
| H | -5.911986 | -2.429954 | 1.751153 |
| H | -7.109587 | -1.109972 | 1.578083 |
| H | -6.529544 | -2.019016 | 0.159389 |
| C | -5.100867 | -0.604843 | 0.926364 |
| C | -5.415675 | 0.746530 | 1.207824 |
| H | -6.409947 | 0.885808 | 1.633533 |
| C | -4.753110 | 1.959374 | 0.905128 |
| C | -5.536427 | 3.209271 | 1.254168 |
| H | -5.237062 | 4.071362 | 0.645453 |
| H | -6.618224 | 3.051642 | 1.154756 |
| H | -5.333824 | 3.467627 | 2.307115 |
| C | -3.830556 | -2.425338 | 0.138605 |
| C | -3.361745 | -3.385578 | 1.067555 |
| C | -3.310743 | -4.729686 | 0.679099 |
| H | -2.980801 | -5.481124 | 1.398488 |
| C | -3.677340 | -5.128298 | -0.602043 |
| H | -3.632751 | -6.182752 | -0.884385 |
| C | -4.093567 | -4.171735 | -1.523854 |
| H | -4.369486 | -4.484097 | -2.532871 |
| C | -4.177942 | -2.819728 | -1.177401 |
| C | -2.853597 | -2.962325 | 2.430960 |
| H | -3.264663 | -1.959883 | 2.624508 |
| C | -1.319938 | -2.802884 | 2.409004 |
| H | -1.019154 | -2.308157 | 3.345477 |
| H | -1.026545 | -2.102466 | 1.610259 |
| C | -0.513217 | -4.079421 | 2.238980 |
| H | -0.615623 | -4.758553 | 3.099836 |
| H | -0.804495 | -4.633219 | 1.336233 |
| H | 0.554101 | -3.847873 | 2.130007 |
| C | -3.306854 | -3.863877 | 3.583432 |
| H | -2.822924 | -3.496830 | 4.506006 |
| H | -2.919576 | -4.886290 | 3.444425 |
| C | -4.813480 | -3.915372 | 3.781520 |
| H | -5.087099 | -4.553595 | 4.635821 |
| H | -5.225325 | -2.910879 | 3.970352 |
| H | -5.316556 | -4.319543 | 2.889301 |
| C | -4.556715 | -1.776746 | -2.208713 |
| H | -4.936108 | -0.902913 | -1.660132 |
| C | -3.301852 | -1.282336 | -2.954363 |
| H | -2.568265 | -0.930344 | -2.209677 |
| H | -3.589222 | -0.397468 | -3.542048 |
| C | -2.635402 | -2.296922 | -3.871158 |
| H | -3.311251 | -2.631651 | -4.672897 |
| H | -1.751659 | -1.859841 | -4.357218 |
| H | -2.302414 | -3.186554 | -3.318021 |
| C | -5.658925 | -2.211321 | -3.178873 |
| H | -5.333784 | -3.085315 | -3.766828 |
| H | -5.794606 | -1.400647 | -3.915216 |
| C | -6.990684 | -2.519221 | -2.511584 |
| H | -7.750567 | -2.819176 | -3.249520 |
| H | -6.891118 | -3.339328 | -1.783394 |
| H | -7.378759 | -1.638984 | -1.975709 |
| C | -3.132609 | 3.292057 | -0.186777 |
| C | -2.379881 | 4.250316 | 0.527037 |
| C | -2.065882 | 5.463145 | -0.099044 |
| H | -1.491190 | 6.212756 | 0.450573 |
| C | -2.467974 | 5.733493 | -1.402068 |
| H | -2.221046 | 6.690614 | -1.867260 |
| C | -3.157626 | 4.759583 | -2.120734 |
| H | -3.443263 | 4.954791 | -3.157152 |
| C | -3.480071 | 3.529798 | -1.542560 |
| C | -1.908637 | 4.010748 | 1.948713 |
| H | -2.230204 | 2.994465 | 2.231550 |
| C | -0.374760 | 4.063871 | 2.028820 |
| H | -0.057625 | 3.920561 | 3.074633 |
| H | -0.040597 | 5.080289 | 1.757331 |
| C | 0.314570 | 3.044350 | 1.140681 |
| H | 0.187684 | 2.012235 | 1.497738 |
| H | -0.081089 | 3.082032 | 0.118556 |
| H | 1.396713 | 3.224844 | 1.077708 |
| C | -2.576930 | 4.999554 | 2.918776 |
| H | -3.662573 | 4.987547 | 2.732453 |
| H | -2.246065 | 6.021953 | 2.666680 |
| C | -2.314759 | 4.734344 | 4.395407 |
| H | -2.860163 | 5.450705 | 5.028849 |
| H | -2.642344 | 3.723579 | 4.686644 |
| H | -1.247679 | 4.818848 | 4.650427 |
| C | -4.228355 | 2.471788 | -2.327428 |
| H | -4.038736 | 1.515367 | -1.812120 |
| C | -3.736815 | 2.326269 | -3.771985 |
| H | -4.006678 | 3.226490 | -4.352051 |
| H | -4.304979 | 1.505470 | -4.240345 |
| C | -2.244913 | 2.056722 | -3.907535 |
| H | -1.923175 | 1.234418 | -3.250966 |
| H | -1.980531 | 1.788979 | -4.941653 |
| H | -1.651931 | 2.937035 | -3.627632 |
| C | -5.748186 | 2.718833 | -2.275894 |
| H | -5.998677 | 3.518901 | -2.995520 |

| | | | |
|---|---|---|---|
| H | -6.013481 | 3.119938 | -1.287975 |
| C | -6.589048 | 1.478208 | -2.537796 |
| H | -7.664272 | 1.714776 | -2.540427 |
| H | -6.353395 | 1.009857 | -3.505659 |
| H | -6.414989 | 0.729467 | -1.749615 |
| C | -3.119172 | 0.734155 | 3.775871 |
| H | -3.155343 | 1.821036 | 3.977651 |
| H | -3.962911 | 0.493658 | 3.114462 |
| C | -3.165479 | -0.044317 | 5.076525 |
| H | -4.083887 | 0.225903 | 5.621932 |
| H | -3.231434 | -1.120783 | 4.848020 |
| C | -1.918259 | 0.237321 | 5.909226 |
| H | -1.925892 | 1.294349 | 6.231831 |
| H | -1.910945 | -0.371843 | 6.826748 |
| C | -0.671029 | -0.030793 | 5.072702 |
| H | -0.581276 | -1.109701 | 4.871114 |
| H | 0.244208 | 0.267811 | 5.607666 |
| C | -0.728336 | 0.717634 | 3.753808 |
| H | 0.084638 | 0.426718 | 3.075124 |
| H | -0.662847 | 1.807493 | 3.928163 |

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[(BDI*)Ca(THP)]$_2$($\mu$-O) (**2**)

| | | | |
|---|---|---|---|
| Ca | 1.965107 | 0.134945 | -0.704167 |
| O | 0.004351 | 0.027793 | -0.029715 |
| O | 1.853110 | 0.320745 | -3.177903 |
| N | 3.779716 | -1.530893 | -0.564027 |
| N | 3.815204 | 1.790893 | -0.336408 |
| C | 5.933290 | -2.200810 | -1.546091 |
| H | 6.373947 | -2.677267 | -0.657938 |
| H | 6.747719 | -1.767874 | -2.140164 |
| H | 5.458563 | -3.006416 | -2.121103 |
| C | 4.922829 | -1.146932 | -1.130306 |
| C | 5.352347 | 0.182127 | -1.377434 |
| H | 6.310882 | 0.212619 | -1.898375 |
| C | 4.958833 | 1.470952 | -0.923728 |
| C | 6.020457 | 2.525227 | -1.201652 |
| H | 6.074146 | 2.713274 | -2.286172 |
| H | 7.013280 | 2.169451 | -0.891789 |
| H | 5.812744 | 3.477544 | -0.700172 |
| C | 3.663576 | -2.908359 | -0.219569 |
| C | 4.171623 | -3.363375 | 1.029770 |
| C | 4.090100 | -4.726441 | 1.340205 |
| H | 4.490033 | -5.083643 | 2.291806 |
| C | 3.528111 | -5.642069 | 0.456370 |
| H | 3.488580 | -6.704132 | 0.711467 |
| C | 3.013228 | -5.190025 | -0.753636 |
| H | 2.574795 | -5.911775 | -1.446140 |
| C | 3.058352 | -3.836119 | -1.111600 |
| C | 2.429018 | -3.375162 | -2.418009 |
| H | 2.900244 | -2.412374 | -2.673386 |
| C | 0.922520 | -3.073160 | -2.222873 |
| H | 0.792535 | -2.414683 | -1.345801 |
| H | 0.578928 | -2.482571 | -3.088284 |
| C | 0.007248 | -4.280609 | -2.060656 |
| H | -0.059024 | -4.879432 | -2.982544 |
| H | -1.013709 | -3.962381 | -1.803458 |
| H | 0.348590 | -4.944567 | -1.253701 |
| C | 2.653635 | -4.314501 | -3.614957 |
| H | 2.192952 | -5.297047 | -3.420851 |
| H | 2.087971 | -3.901125 | -4.469490 |
| C | 4.105244 | -4.519238 | -4.029494 |
| H | 4.177150 | -5.183122 | -4.905585 |
| H | 4.696482 | -4.976510 | -3.220770 |
| H | 4.588952 | -3.566341 | -4.298784 |
| C | 4.759125 | -2.385002 | 2.038320 |
| H | 5.123483 | -1.516702 | 1.467419 |
| C | 5.953762 | -2.922204 | 2.843460 |
| H | 6.228115 | -2.148128 | 3.581902 |
| H | 5.654092 | -3.796692 | 3.444989 |
| C | 7.184183 | -3.280056 | 2.018794 |
| H | 8.004060 | -3.636159 | 2.662482 |
| H | 7.560505 | -2.408173 | 1.459763 |
| H | 6.966704 | -4.076854 | 1.290281 |
| C | 3.658394 | -1.826974 | 2.971120 |
| H | 4.086155 | -0.971764 | 3.521888 |
| H | 2.855804 | -1.410889 | 2.338829 |
| C | 3.052167 | -2.806500 | 3.970104 |
| H | 3.798814 | -3.184593 | 4.686040 |
| H | 2.597566 | -3.674085 | 3.468921 |
| H | 2.261324 | -2.317497 | 4.559994 |
| C | 3.632943 | 3.084315 | 0.228315 |
| C | 3.931586 | 3.287549 | 1.607433 |
| C | 3.670369 | 4.535202 | 2.185023 |
| H | 3.904440 | 4.692918 | 3.240938 |
| C | 3.129629 | 5.583689 | 1.446713 |
| H | 2.927486 | 6.548181 | 1.919676 |
| C | 2.870718 | 5.393133 | 0.094918 |
| H | 2.469464 | 6.222536 | -0.494086 |
| C | 3.122062 | 4.168493 | -0.538616 |
| C | 4.626780 | 2.216839 | 2.439277 |
| H | 4.441916 | 1.249181 | 1.942549 |
| C | 6.152826 | 2.466289 | 2.421845 |
| H | 6.462046 | 2.674365 | 1.387637 |
| H | 6.358281 | 3.397415 | 2.980901 |
| C | 7.013899 | 1.332481 | 2.968409 |
| H | 8.084307 | 1.570526 | 2.863921 |
| H | 6.829979 | 0.394801 | 2.419875 |
| H | 6.830808 | 1.136654 | 4.036149 |
| C | 4.118077 | 2.110792 | 3.886540 |
| H | 4.672217 | 1.295677 | 4.380126 |
| H | 4.395916 | 3.021860 | 4.446559 |
| C | 2.626987 | 1.851470 | 4.037016 |
| H | 2.326984 | 0.944753 | 3.490121 |
| H | 2.027344 | 2.684152 | 3.642695 |
| H | 2.354278 | 1.712224 | 5.095470 |

| | | | |
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| C | 2.906659 | 4.088082 | -2.044853 |
| H | 3.072738 | 3.039383 | -2.341221 |
| C | 1.482223 | 4.482267 | -2.481213 |
| H | 1.368593 | 5.577736 | -2.387797 |
| H | 1.379969 | 4.274644 | -3.560092 |
| C | 0.358168 | 3.801426 | -1.720187 |
| H | 0.411092 | 2.703017 | -1.783762 |
| H | -0.628923 | 4.106251 | -2.098252 |
| H | 0.394123 | 4.064757 | -0.655661 |
| C | 3.950436 | 4.963438 | -2.777744 |
| H | 3.721032 | 6.023619 | -2.569821 |
| H | 4.941109 | 4.788611 | -2.333086 |
| C | 4.043457 | 4.754765 | -4.285908 |
| H | 4.820254 | 5.402002 | -4.722901 |
| H | 3.100171 | 4.987728 | -4.803493 |
| H | 4.310221 | 3.714111 | -4.533577 |
| C | 2.963414 | 0.620350 | -4.026014 |
| H | 3.867685 | 0.428169 | -3.428987 |
| H | 2.936684 | 1.699506 | -4.271369 |
| C | 2.936683 | -0.200063 | -5.305402 |
| H | 3.795550 | 0.091058 | -5.932424 |
| H | 3.071119 | -1.265934 | -5.055008 |
| C | 1.615409 | 0.001833 | -6.044586 |
| H | 1.554949 | -0.651806 | -6.929571 |
| H | 1.559862 | 1.040650 | -6.418647 |
| C | 0.447756 | -0.262670 | -5.095825 |
| H | -0.515375 | -0.007199 | -5.565664 |
| H | 0.405950 | -1.336173 | -4.848440 |
| C | 0.590586 | 0.540761 | -3.812093 |
| H | 0.487164 | 1.621328 | -4.027146 |
| H | -0.168669 | 0.270388 | -3.064607 |
| Ca | -1.922628 | 0.110350 | 0.732355 |
| O | -1.831738 | 0.047320 | 3.268946 |
| N | -3.737350 | -1.556325 | 0.501175 |
| N | -3.789261 | 1.762230 | 0.406474 |
| C | -5.875031 | -2.274640 | 1.483682 |
| H | -6.339854 | -2.692843 | 0.578639 |
| H | -6.672639 | -1.874222 | 2.121817 |
| H | -5.392478 | -3.116576 | 1.996623 |
| C | -4.868119 | -1.202628 | 1.107936 |
| C | -5.288462 | 0.113577 | 1.437053 |
| H | -6.228109 | 0.117683 | 1.991887 |
| C | -4.908066 | 1.421164 | 1.031724 |
| C | -5.933504 | 2.475879 | 1.422915 |
| H | -5.848697 | 2.684094 | 2.502483 |
| H | -6.957013 | 2.117946 | 1.245064 |
| H | -5.789260 | 3.422654 | 0.889180 |
| C | -3.629167 | -2.913532 | 0.079223 |
| C | -4.158951 | -3.300722 | -1.184025 |
| C | -4.083611 | -4.644793 | -1.569777 |
| H | -4.500071 | -4.949217 | -2.532472 |
| C | -3.507295 | -5.607633 | -0.747908 |
| H | -3.473179 | -6.654167 | -1.061314 |
| C | -2.971890 | -5.221834 | 0.475688 |
| H | -2.522334 | -5.980126 | 1.120254 |
| C | -3.009345 | -3.889353 | 0.907718 |
| C | -2.352188 | -3.505292 | 2.224981 |
| H | -2.806066 | -2.553047 | 2.543276 |
| C | -0.846268 | -3.209125 | 2.015781 |
| H | -0.728602 | -2.493504 | 1.182561 |
| H | -0.474149 | -2.685995 | 2.912133 |
| C | 0.050374 | -4.412142 | 1.750915 |
| H | 0.120052 | -5.079401 | 2.624299 |
| H | 1.072344 | -4.088114 | 1.505582 |
| H | -0.309218 | -5.008971 | 0.900802 |
| C | -2.563851 | -4.508387 | 3.371812 |
| H | -2.111807 | -5.480950 | 3.116900 |
| H | -1.983080 | -4.146153 | 4.239252 |
| C | -4.009755 | -4.729475 | 3.797493 |
| H | -4.071181 | -5.438585 | 4.638230 |
| H | -4.615445 | -5.141018 | 2.975051 |
| H | -4.485342 | -3.790525 | 4.124081 |
| C | -4.761287 | -2.272431 | -2.131595 |
| H | -5.107883 | -1.430140 | -1.512637 |
| C | -5.975471 | -2.765878 | -2.935763 |
| H | -6.262573 | -1.955943 | -3.629398 |
| H | -5.692022 | -3.610352 | -3.585948 |
| C | -7.189344 | -3.161337 | -2.103856 |
| H | -8.024078 | -3.482344 | -2.746922 |
| H | -7.550689 | -2.317838 | -1.493692 |
| H | -6.959371 | -3.994494 | -1.421276 |
| C | -3.676501 | -1.677771 | -3.060581 |
| H | -4.111285 | -0.796541 | -3.562133 |
| H | -2.858557 | -1.295243 | -2.426998 |
| C | -3.096655 | -2.611538 | -4.117466 |
| H | -3.860574 | -2.954735 | -4.832824 |
| H | -2.632744 | -3.502257 | -3.668064 |
| H | -2.318291 | -2.096469 | -4.701613 |
| C | -3.646828 | 3.076230 | -0.120698 |
| C | -3.997921 | 3.319970 | -1.479832 |
| C | -3.794388 | 4.594978 | -2.019665 |
| H | -4.072628 | 4.784017 | -3.059518 |
| C | -3.255693 | 5.631404 | -1.263738 |
| H | -3.099160 | 6.618297 | -1.706824 |
| C | -2.940485 | 5.398460 | 0.068918 |
| H | -2.542279 | 6.218076 | 0.673247 |
| C | -3.139496 | 4.145979 | 0.665603 |
| C | -4.688886 | 2.260498 | -2.327833 |
| H | -4.457134 | 1.281013 | -1.875967 |
| C | -6.219347 | 2.462983 | -2.245494 |
| H | -6.497756 | 2.587893 | -1.188722 |
| H | -6.468545 | 3.424893 | -2.729628 |
| C | -7.069346 | 1.347123 | -2.843198 |
| H | -8.141005 | 1.546109 | -2.684263 |
| H | -6.841090 | 0.378322 | -2.371240 |
| H | -6.920413 | 1.234435 | -3.928114 |

C -4.220650 2.231921 -3.792111
H -4.759971 1.420175 -4.307192
H -4.543219 3.156077 -4.304558
C -2.725596 2.030146 -3.988302
H -2.391975 1.093629 -3.516649
H -2.142233 2.847981 -3.540828
H -2.469428 1.978912 -5.058637
C -2.861965 4.022570 2.158235
H -3.123801 2.995080 2.459892
C -1.373445 4.241095 2.477823
H -1.070834 5.233134 2.099974
H -1.235734 4.287288 3.571780
C -0.465586 3.171191 1.896249
H -0.618715 2.204037 2.396356
H 0.598159 3.427859 2.003448
H -0.652753 3.022539 0.823488
C -3.757237 4.989291 2.965861
H -3.377181 6.018407 2.840307
H -4.767020 4.994372 2.525485
C -3.867831 4.671423 4.453468
H -4.506165 5.406788 4.968149
H -2.889381 4.682309 4.958914
H -4.315037 3.677535 4.620054
C -2.932312 0.479630 4.073127
H -3.816573 0.459915 3.418628
H -2.750051 1.526335 4.385451
C -3.122516 -0.401588 5.296910
H -3.962691 -0.006746 5.891662
H -3.411876 -1.414551 4.969686
C -1.838983 -0.463357 6.121756
H -1.943553 -1.167631 6.962607
H -1.641293 0.528868 6.567297
C -0.669377 -0.862123 5.224017
H 0.289592 -0.793547 5.762757
H -0.783310 -1.912334 4.908477
C -0.599202 0.026773 3.991365
H -0.345387 1.062117 4.288801
H 0.164576 -0.312943 3.278116

3
$N_2O$
N 0.000000 -0.000000 0.073822
N 0.000000 -0.000000 1.223327
O -0.000000 0.000000 -1.135006

2
N2
N 0.000000 0.000000 0.545362
N 0.000000 -0.000000 -0.545362

195
[(BDI*)Ca]$_2$($\mu$-O) THP free
Ca -1.858044 0.211990 0.767126
O -0.000033 -0.023645 0.000430
N -3.627262 -1.304311 1.191353
N -3.659348 1.756414 0.518850
C -5.565915 -1.901350 2.557934
H -6.060740 -2.561704 1.832229
H -6.336368 -1.425771 3.177002
H -4.942237 -2.551402 3.187512
C -4.709105 -0.880368 1.844859
C -5.158951 0.458287 1.922273
H -6.055267 0.586929 2.531021
C -4.761706 1.636286 1.241221
C -5.695208 2.816950 1.406984
H -5.573198 3.247075 2.414174
H -6.744453 2.505613 1.310084
H -5.485222 3.609206 0.677385
C -3.457349 -2.694888 0.978201
C -4.183796 -3.329907 -0.064207
C -4.003736 -4.698495 -0.277664
H -4.567514 -5.196540 -1.068945
C -3.120374 -5.440838 0.502602
H -2.997697 -6.512177 0.327473
C -2.389708 -4.806538 1.500160
H -1.697369 -5.391287 2.108212
C -2.532691 -3.435742 1.751649
C -1.680342 -2.763637 2.812062
H -2.188363 -1.816780 3.068782
C -0.283780 -2.391168 2.265228
H -0.359366 -1.699980 1.405078
H 0.246753 -1.821245 3.049499
C 0.588914 -3.549099 1.805336
H 0.868104 -4.224293 2.628210
H 1.518566 -3.176883 1.351557
H 0.083237 -4.147502 1.036479
C -1.579171 -3.562129 4.117457
H -1.063061 -4.519306 3.936870
H -0.920056 -3.001840 4.803101
C -2.917842 -3.823058 4.790993
H -2.794263 -4.383524 5.730458
H -3.584685 -4.406976 4.137872
H -3.431647 -2.878511 5.032875
C -5.054655 -2.504611 -0.992190
H -5.387960 -1.620220 -0.428875
C -6.313136 -3.213088 -1.498626
H -6.803781 -2.543812 -2.226556
H -6.043037 -4.115218 -2.071568
C -7.301827 -3.583776 -0.403342
H -8.188507 -4.090006 -0.815144
H -7.651247 -2.688565 0.135305
H -6.844083 -4.261051 0.334701
C -4.198182 -1.957090 -2.150615
H -4.754353 -1.137447 -2.626720
H -3.297430 -1.497027 -1.712357
C -3.789939 -2.962928 -3.215891

| | | | |
|---|---|---|---|
| H | -4.655599 | -3.311586 | -3.799652 |
| H | -3.300322 | -3.844386 | -2.778742 |
| H | -3.078726 | -2.509197 | -3.922991 |
| C | -3.355270 | 2.908501 | -0.237017 |
| C | -3.572899 | 2.873472 | -1.638842 |
| C | -3.158920 | 3.956663 | -2.417467 |
| H | -3.330425 | 3.937132 | -3.496029 |
| C | -2.529553 | 5.059126 | -1.842188 |
| H | -2.202555 | 5.893847 | -2.466463 |
| C | -2.324073 | 5.089670 | -0.466802 |
| H | -1.835926 | 5.957184 | -0.015170 |
| C | -2.736387 | 4.034221 | 0.355752 |
| C | -4.330200 | 1.709397 | -2.241943 |
| H | -4.181570 | 0.855652 | -1.560374 |
| C | -5.838051 | 2.030144 | -2.231010 |
| H | -6.076164 | 2.545220 | -1.288521 |
| H | -6.045723 | 2.765106 | -3.029282 |
| C | -6.752436 | 0.821018 | -2.367245 |
| H | -7.811139 | 1.122342 | -2.345279 |
| H | -6.590651 | 0.115808 | -1.537140 |
| H | -6.589678 | 0.274562 | -3.308920 |
| C | -3.838514 | 1.292664 | -3.630210 |
| H | -4.474802 | 0.468097 | -3.988589 |
| H | -4.003724 | 2.114046 | -4.349544 |
| C | -2.381613 | 0.854370 | -3.667062 |
| H | -2.179286 | 0.069870 | -2.921204 |
| H | -1.705651 | 1.690917 | -3.445101 |
| H | -2.105997 | 0.453292 | -4.654431 |
| C | -2.523781 | 4.132647 | 1.854056 |
| H | -2.980703 | 3.240656 | 2.312759 |
| C | -1.028930 | 4.106700 | 2.197491 |
| H | -0.516206 | 4.915268 | 1.651078 |
| H | -0.885041 | 4.324496 | 3.268059 |
| C | -0.373818 | 2.783328 | 1.854651 |
| H | -0.725096 | 1.979421 | 2.527554 |
| H | 0.719035 | 2.822333 | 1.949821 |
| H | -0.577318 | 2.499912 | 0.812092 |
| C | -3.236848 | 5.362763 | 2.439594 |
| H | -2.682915 | 6.274466 | 2.155607 |
| H | -4.226139 | 5.455275 | 1.963413 |
| C | -3.408610 | 5.314075 | 3.951768 |
| H | -3.939077 | 6.204558 | 4.322398 |
| H | -2.442737 | 5.266240 | 4.477819 |
| H | -3.991397 | 4.429018 | 4.255533 |
| Ca | 1.858024 | 0.211799 | -0.766259 |
| N | 3.626952 | -1.304552 | -1.191460 |
| N | 3.659639 | 1.756027 | -0.518868 |
| C | 5.565082 | -1.901844 | -2.558676 |
| H | 6.060030 | -2.562299 | -1.833147 |
| H | 6.335419 | -1.426362 | -3.177964 |
| H | 4.941110 | -2.551778 | -3.188084 |
| C | 4.708658 | -0.880755 | -1.845299 |
| C | 5.158693 | 0.457821 | -1.922768 |
| H | 6.054880 | 0.586374 | -2.531730 |
| C | 4.761806 | 1.635812 | -1.241489 |
| C | 5.695612 | 2.816249 | -1.407189 |
| H | 5.574851 | 3.245546 | -2.414875 |
| H | 6.744697 | 2.504778 | -1.308862 |
| H | 5.485003 | 3.609085 | -0.678407 |
| C | 3.456925 | -2.695111 | -0.978245 |
| C | 4.183579 | -3.330184 | 0.063997 |
| C | 4.003445 | -4.698749 | 0.277525 |
| H | 4.567382 | -5.196841 | 1.068663 |
| C | 3.119808 | -5.441019 | -0.502504 |
| H | 2.997076 | -6.512345 | -0.327325 |
| C | 2.388951 | -4.806667 | -1.499882 |
| H | 1.696388 | -5.391354 | -2.107736 |
| C | 2.531998 | -3.435886 | -1.751439 |
| C | 1.679462 | -2.763772 | -2.811695 |
| H | 2.187476 | -1.816960 | -3.068589 |
| C | 0.283006 | -2.391209 | -2.264631 |
| H | 0.358704 | -1.699559 | -1.404860 |
| H | -0.247815 | -1.821775 | -3.049058 |
| C | -0.589372 | -3.549018 | -1.803845 |
| H | -0.868324 | -4.224982 | -2.626167 |
| H | -1.519159 | -3.176719 | -1.350418 |
| H | -0.083538 | -4.146620 | -1.034477 |
| C | 1.577950 | -3.562351 | -4.117017 |
| H | 1.061677 | -4.519414 | -3.936277 |
| H | 0.918835 | -3.001985 | -4.802596 |
| C | 2.916456 | -3.823592 | -4.790757 |
| H | 2.792611 | -4.384141 | -5.730139 |
| H | 3.583315 | -4.407555 | -4.137695 |
| H | 3.430382 | -2.879163 | -5.032841 |
| C | 5.054767 | -2.504960 | 0.991738 |
| H | 5.388008 | -1.620604 | 0.428330 |
| C | 6.313314 | -3.213561 | 1.497842 |
| H | 6.804207 | -2.544349 | 2.225663 |
| H | 6.043281 | -4.115683 | 2.070831 |
| C | 7.301686 | -3.584308 | 0.402290 |
| H | 8.188441 | -4.090608 | 0.813846 |
| H | 7.651021 | -2.689113 | -0.136439 |
| H | 6.843693 | -4.261538 | -0.335640 |
| C | 4.198656 | -1.957363 | 2.150391 |
| H | 4.754992 | -1.137721 | 2.626303 |
| H | 3.297790 | -1.497289 | 1.712376 |
| C | 3.790685 | -2.963149 | 3.215821 |
| H | 4.656507 | -3.311823 | 3.799333 |
| H | 3.300906 | -3.844601 | 2.778841 |
| H | 3.079698 | -2.509372 | 3.923120 |
| C | 3.355694 | 2.908167 | 0.236966 |
| C | 3.573390 | 2.873179 | 1.638773 |
| C | 3.159510 | 3.956419 | 2.417385 |
| H | 3.331091 | 3.936922 | 3.495935 |
| C | 2.530150 | 5.058881 | 1.842099 |
| H | 2.203213 | 5.893638 | 2.466358 |

C 2.324594 5.089381 0.466720
H 1.836430 5.956885 0.015086
C 2.736836 4.033898 -0.355823
C 4.330695 1.709089 2.241836
H 4.182041 0.855364 1.560249
C 5.838542 2.029836 2.230821
H 6.076579 2.544910 1.288308
H 6.046264 2.764801 3.029077
C 6.752934 0.820710 2.367010
H 7.811636 1.122033 2.344992
H 6.591109 0.115496 1.536915
H 6.590222 0.274254 3.308695
C 3.839023 1.292318 3.630095
H 4.475300 0.467729 3.988449
H 4.004235 2.113678 4.349453
C 2.382119 0.854028 3.666929
H 2.179821 0.069451 2.921143
H 1.706157 1.690546 3.444861
H 2.106461 0.453038 4.654323
C 2.524171 4.132263 -1.854116
H 2.981022 3.240231 -2.312804
C 1.029307 4.106356 -2.197495
H 0.516625 4.915062 -1.651247
H 0.885423 4.323919 -3.268108
C 0.374148 2.783084 -1.854353
H 0.725384 1.979015 -2.527079
H -0.718708 2.822115 -1.949474
H 0.577651 2.499912 -0.811724
C 3.237306 5.362304 -2.439728
H 2.683554 6.274074 -2.155598
H 4.226687 5.454643 -1.963708
C 3.408833 5.313690 -3.951931
H 3.939714 6.203949 -4.322512
H 2.442876 5.266422 -4.477876
H 3.991134 4.428373 -4.255866

2
$O_2$
O 0.000000 -0.000000 0.599016
O -0.000000 0.000000 -0.599016

2
$N_2$
N -0.000000 -0.000000 0.545367
N 0.000000 0.000000 -0.545367

196
[(BDI*)Ca]$_2$($\mu_2$-O$_2$) THP free
N -3.845878 -1.472318 0.214013
N 3.846074 -1.472219 -0.213955
O -0.000737 -0.001825 0.757085
C -5.152020 -1.271339 0.144461
C -6.099594 -2.450974 0.166836
C -3.266332 -2.694214 0.595659
C -3.353660 -3.125220 1.948413
C -2.671390 -4.280543 2.330220
H -2.732914 -4.623746 3.364881
C -1.897678 -4.998610 1.419138
H -1.374025 -5.902953 1.737998
C -1.775484 -4.543604 0.111882
H -1.143439 -5.085884 -0.591739
C -2.443497 -3.391861 -0.319933
C -4.096436 -2.264055 2.950262
H -4.954240 -1.811417 2.431894
C -3.205672 -1.089907 3.406195
H -2.579422 -1.422306 4.251594
H -2.484514 -0.843062 2.609064
C -3.996033 0.154193 3.776736
H -3.338851 0.946405 4.160605
H -4.746594 -0.058582 4.553959
H -4.528748 0.548262 2.896735
C -4.668052 -3.027561 4.146424
H -3.851152 -3.517073 4.704573
H -5.095166 -2.291874 4.848118
C -5.736822 -4.045526 3.773933
H -5.344515 -4.807114 3.082683
H -6.588339 -3.556618 3.274653
H -6.125348 -4.566449 4.662488
C -2.307542 -2.912060 -1.749442
H -2.580896 -1.841320 -1.762453
C -0.869116 -3.020650 -2.271111
H -0.182959 -2.693068 -1.474648
H -0.613986 -4.073353 -2.467962
C -0.599151 -2.191001 -3.515452
H 0.442627 -2.318295 -3.842821
H -0.748908 -1.118948 -3.312076
H -1.247892 -2.473327 -4.359592
C -3.361310 -3.575926 -2.659750
H -4.357191 -3.284673 -2.287948
H -3.278940 -3.138007 -3.667412
C -3.282809 -5.092259 -2.759915
H -2.303941 -5.428478 -3.136568
H -4.047920 -5.475127 -3.452711
H -3.446834 -5.572080 -1.783461
C 5.152203 -1.271167 -0.144384
C 6.099831 -2.450759 -0.166676
C 3.266558 -2.694127 -0.595581
C 3.353880 -3.125137 -1.948334
C 2.671554 -4.280427 -2.330144
H 2.733058 -4.623628 -3.364807
C 1.897801 -4.998453 -1.419062
H 1.374098 -5.902767 -1.737925
C 1.775617 -4.543437 -0.111807
H 1.143526 -5.085674 0.591805
C 2.443684 -3.391723 0.320005
C 4.096673 -2.263979 -2.950179

| | | | |
|---|---|---|---|
| H | 4.954552 | -1.811457 | -2.431834 |
| C | 3.206002 | -1.089700 | -3.405960 |
| H | 2.579700 | -1.421946 | -4.251379 |
| H | 2.484879 | -0.842887 | -2.608784 |
| C | 3.996458 | 0.154381 | -3.776370 |
| H | 4.529241 | 0.548289 | -2.896337 |
| H | 3.339333 | 0.946702 | -4.160115 |
| H | 4.746974 | -0.058362 | -4.553644 |
| C | 4.668136 | -3.027456 | -4.146436 |
| H | 3.851146 | -3.516815 | -4.704586 |
| H | 5.095314 | -2.291766 | -4.848088 |
| C | 5.736788 | -4.045595 | -3.774081 |
| H | 6.588393 | -3.556845 | -3.274799 |
| H | 6.125203 | -4.566493 | -4.662699 |
| H | 5.344408 | -4.807191 | -3.082880 |
| C | 2.307673 | -2.911780 | 1.749464 |
| H | 2.581204 | -1.841082 | 1.762378 |
| C | 0.869177 | -3.020030 | 2.270999 |
| H | 0.183165 | -2.692479 | 1.474399 |
| H | 0.613846 | -4.072652 | 2.468016 |
| C | 0.599206 | -2.190101 | 3.515153 |
| H | 1.247791 | -2.472385 | 4.359427 |
| H | -0.442637 | -2.317151 | 3.842411 |
| H | 0.749181 | -1.118111 | 3.311598 |
| C | 3.361244 | -3.575716 | 2.659951 |
| H | 4.357209 | -3.284699 | 2.288191 |
| H | 3.278874 | -3.137639 | 3.667545 |
| C | 3.282453 | -5.092020 | 2.760323 |
| H | 4.047424 | -5.474933 | 3.453250 |
| H | 3.446488 | -5.572009 | 1.783952 |
| H | 2.303485 | -5.428007 | 3.136925 |
| Ca | -2.036018 | 0.000163 | -0.001969 |
| Ca | 2.036096 | 0.000114 | 0.001738 |
| N | -3.846721 | 1.472301 | -0.210858 |
| N | 3.846686 | 1.472374 | 0.210856 |
| O | 0.000817 | -0.001869 | -0.757277 |
| C | -5.750623 | -0.000204 | 0.003465 |
| H | -6.841953 | -0.000414 | 0.004670 |
| C | -5.152721 | 1.271063 | -0.138389 |
| C | -6.100156 | 2.450824 | -0.157610 |
| C | -3.268219 | 2.694373 | -0.593359 |
| C | -3.358271 | 3.125488 | -1.945939 |
| C | -2.677033 | 4.281004 | -2.328988 |
| H | -2.740661 | 4.624283 | -3.363497 |
| C | -1.901744 | 4.999204 | -1.419331 |
| H | -1.378940 | 5.903707 | -1.739121 |
| C | -1.776873 | 4.544095 | -0.112364 |
| H | -1.143585 | 5.086482 | 0.590073 |
| C | -2.443670 | 3.392085 | 0.320658 |
| C | -4.103019 | 2.264272 | -2.946311 |
| H | -4.959826 | 1.811717 | -2.426205 |
| C | -3.213372 | 1.089956 | -3.404029 |
| H | -2.589116 | 1.421998 | -4.251045 |
| H | -2.490195 | 0.843408 | -2.608611 |
| C | -4.004659 | -0.154266 | -3.772190 |
| H | -3.348472 | -0.946660 | -4.157381 |
| H | -4.757057 | 0.058343 | -4.547674 |
| H | -4.535332 | -0.547954 | -2.890784 |
| C | -4.676968 | 3.027689 | -4.141414 |
| H | -3.861189 | 3.517287 | -4.701120 |
| H | -5.105335 | 2.291930 | -4.842272 |
| C | -5.745160 | 4.045516 | -3.766896 |
| H | -5.351589 | 4.807243 | -3.076516 |
| H | -6.595609 | 3.556505 | -3.265892 |
| H | -6.135524 | 4.566300 | -4.654727 |
| C | -2.304469 | 2.911948 | 1.749747 |
| H | -2.577434 | 1.841133 | 1.763023 |
| C | -0.864930 | 3.020857 | 2.268289 |
| H | -0.180307 | 2.694747 | 1.469913 |
| H | -0.610012 | 4.073504 | 2.465728 |
| C | -0.591538 | 2.189943 | 3.511020 |
| H | 0.450793 | 2.317947 | 3.836345 |
| H | -0.740694 | 1.118032 | 3.306508 |
| H | -1.238779 | 2.470628 | 4.356858 |
| C | -3.356213 | 3.575417 | 2.662668 |
| H | -4.352898 | 3.283382 | 2.293680 |
| H | -3.270826 | 3.137850 | 3.670228 |
| C | -3.278486 | 5.091834 | 2.762154 |
| H | -2.298756 | 5.428872 | 3.135823 |
| H | -4.041820 | 5.474364 | 3.457096 |
| H | -3.445722 | 5.571256 | 1.786048 |
| C | 5.750712 | 0.000011 | -0.003414 |
| H | 6.842041 | -0.000115 | -0.004592 |
| C | 5.152703 | 1.271233 | 0.138410 |
| C | 6.100051 | 2.451065 | 0.157640 |
| C | 3.268118 | 2.694421 | 0.593341 |
| C | 3.358138 | 3.125533 | 1.945919 |
| C | 2.676881 | 4.281045 | 2.328952 |
| H | 2.740472 | 4.624322 | 3.363464 |
| C | 1.901598 | 4.999229 | 1.419277 |
| H | 1.378768 | 5.903721 | 1.739056 |
| C | 1.776738 | 4.544102 | 0.112315 |
| H | 1.143429 | 5.086458 | -0.590126 |
| C | 2.443559 | 3.392096 | -0.320689 |
| C | 4.102853 | 2.264284 | 2.946290 |
| H | 4.959624 | 1.811679 | 2.426167 |
| C | 3.213135 | 1.090019 | 3.404006 |
| H | 2.588993 | 1.422057 | 4.251106 |
| H | 2.489874 | 0.843607 | 2.608627 |
| C | 4.004316 | -0.154330 | 3.771977 |
| H | 4.534844 | -0.548004 | 2.890477 |
| H | 3.348076 | -0.946683 | 4.157165 |
| H | 4.756823 | 0.058116 | 4.547400 |
| C | 4.676869 | 3.027666 | 4.141383 |
| H | 3.861136 | 3.517360 | 4.701074 |
| H | 5.105152 | 2.291878 | 4.842260 |

| | | | |
|---|---|---|---|
| C | 5.745181 | 4.045367 | 3.766861 |
| H | 6.595580 | 3.556247 | 3.265878 |
| H | 6.135594 | 4.566121 | 4.654687 |
| H | 5.351710 | 4.807126 | 3.076460 |
| C | 2.304310 | 2.911874 | -1.749746 |
| H | 2.577232 | 1.841047 | -1.762948 |
| C | 0.864757 | 3.020776 | -2.268254 |
| H | 0.180152 | 2.694798 | -1.469810 |
| H | 0.609875 | 4.073406 | -2.465821 |
| C | 0.591282 | 2.189710 | -3.510868 |
| H | 1.238501 | 2.470257 | -4.356766 |
| H | -0.451057 | 2.317711 | -3.836176 |
| H | 0.740403 | 1.117821 | -3.306221 |
| C | 3.356061 | 3.575215 | -2.662756 |
| H | 4.352742 | 3.283229 | -2.293724 |
| H | 3.270677 | 3.137502 | -3.670254 |
| C | 3.278344 | 5.091618 | -2.762465 |
| H | 4.041681 | 5.474041 | -3.457464 |
| H | 3.445584 | 5.571182 | -1.786430 |
| H | 2.298617 | 5.428609 | -3.136185 |
| H | 7.013167 | -2.221586 | -0.732903 |
| H | 6.404584 | -2.684238 | 0.866723 |
| H | 5.631427 | -3.349456 | -0.586841 |
| H | 7.019020 | 2.219540 | 0.713616 |
| H | 6.394194 | 2.690307 | -0.877543 |
| H | 5.635325 | 3.347454 | 0.586764 |
| H | -7.019084 | 2.219254 | -0.713637 |
| H | -6.394366 | 2.689996 | 0.877571 |
| H | -5.635478 | 3.347264 | -0.586679 |
| H | -7.012751 | -2.221935 | 0.733407 |
| H | -6.404691 | -2.684263 | -0.866503 |
| H | -5.631024 | -3.349731 | 0.586692 |

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$[(BDI^*)Ca]_2(N_2)$

| | | | |
|---|---|---|---|
| N | -3.980432 | -1.471573 | 0.187846 |
| N | 3.977515 | -1.475581 | -0.187673 |
| N | -0.004230 | -0.001547 | 0.626642 |
| C | -5.286696 | -1.270697 | 0.143005 |
| C | -6.229812 | -2.453369 | 0.167335 |
| C | -3.373353 | -2.675219 | 0.575867 |
| C | -3.452187 | -3.104364 | 1.930896 |
| C | -2.731565 | -4.232691 | 2.322455 |
| H | -2.787222 | -4.571348 | 3.359036 |
| C | -1.922774 | -4.925207 | 1.422104 |
| H | -1.368825 | -5.808289 | 1.749098 |
| C | -1.804154 | -4.468306 | 0.115245 |
| H | -1.144003 | -4.987144 | -0.580352 |
| C | -2.511257 | -3.344324 | -0.327524 |
| C | -4.204897 | -2.253820 | 2.934060 |
| H | -5.060466 | -1.796192 | 2.416966 |
| C | -3.311123 | -1.086116 | 3.400712 |
| H | -2.673607 | -1.434097 | 4.231582 |
| H | -2.598838 | -0.822454 | 2.600028 |
| C | -4.096497 | 0.150996 | 3.803356 |
| H | -3.433068 | 0.936766 | 4.189851 |
| H | -4.835575 | -0.073625 | 4.588175 |
| H | -4.641225 | 0.559656 | 2.937521 |
| C | -4.779156 | -3.028414 | 4.121928 |
| H | -3.962044 | -3.511539 | 4.685283 |
| H | -5.220685 | -2.300708 | 4.822901 |
| C | -5.832223 | -4.057362 | 3.735495 |
| H | -5.423807 | -4.811111 | 3.044860 |
| H | -6.685341 | -3.577110 | 3.230715 |
| H | -6.222110 | -4.586928 | 4.618328 |
| C | -2.367239 | -2.862256 | -1.755912 |
| H | -2.666359 | -1.798165 | -1.777527 |
| C | -0.919714 | -2.938287 | -2.262304 |
| H | -0.242256 | -2.639113 | -1.446780 |
| H | -0.651968 | -3.981076 | -2.494075 |
| C | -0.643718 | -2.057688 | -3.469855 |
| H | 0.402647 | -2.161525 | -3.791415 |
| H | -0.805080 | -0.997268 | -3.220514 |
| H | -1.282190 | -2.312141 | -4.330507 |
| C | -3.391875 | -3.551903 | -2.680579 |
| H | -4.399548 | -3.271088 | -2.333071 |
| H | -3.293432 | -3.124217 | -3.691331 |
| C | -3.288666 | -5.067958 | -2.760158 |
| H | -2.296993 | -5.394335 | -3.111092 |
| H | -4.032532 | -5.470489 | -3.464803 |
| H | -3.466893 | -5.538065 | -1.781487 |
| C | 5.284201 | -1.277330 | -0.142546 |
| C | 6.225019 | -2.461866 | -0.166701 |
| C | 3.368475 | -2.678267 | -0.575749 |
| C | 3.446903 | -3.107673 | -1.930697 |
| C | 2.724806 | -4.235059 | -2.322248 |
| H | 2.780183 | -4.573962 | -3.358762 |
| C | 1.914954 | -4.926374 | -1.421932 |
| H | 1.359893 | -5.808765 | -1.748909 |
| C | 1.796745 | -4.469137 | -0.115158 |
| H | 1.135831 | -4.986997 | 0.580441 |
| C | 2.505309 | -3.346065 | 0.327559 |
| C | 4.201078 | -2.258364 | -2.933814 |
| H | 5.057175 | -1.801886 | -2.416559 |
| C | 3.309094 | -1.089469 | -3.400815 |
| H | 2.671075 | -1.436697 | -4.231615 |
| H | 2.597196 | -0.824504 | -2.600224 |
| C | 4.096327 | 0.146388 | -3.803809 |
| H | 4.641823 | 0.554311 | -2.938108 |
| H | 3.434056 | 0.933131 | -4.190311 |
| H | 4.834959 | -0.079431 | -4.588707 |
| C | 4.774541 | -3.033949 | -4.121402 |
| H | 3.956897 | -3.516007 | -4.684904 |
| H | 5.217262 | -2.306978 | -4.822391 |
| C | 5.826050 | -4.064336 | -3.734553 |
| H | 6.679798 | -3.585216 | -3.229771 |

| | | | |
|---|---|---|---|
| H | 6.215278 | -4.594694 | -4.617203 |
| H | 5.416411 | -4.817296 | -3.043786 |
| C | 2.361904 | -2.863812 | 1.755941 |
| H | 2.662138 | -1.800036 | 1.777503 |
| C | 0.914341 | -2.938121 | 2.262467 |
| H | 0.237200 | -2.638218 | 1.446947 |
| H | 0.645346 | -3.980550 | 2.494431 |
| C | 0.639622 | -2.056979 | 3.469914 |
| H | 1.278044 | -2.311972 | 4.330443 |
| H | -0.406756 | -2.159601 | 3.791816 |
| H | 0.802140 | -0.996800 | 3.220308 |
| C | 3.385783 | -3.554714 | 2.680472 |
| H | 4.393764 | -3.274901 | 2.333059 |
| H | 3.287792 | -3.127178 | 3.691330 |
| C | 3.280926 | -5.070683 | 2.759616 |
| H | 4.024089 | -5.474246 | 3.464407 |
| H | 3.458952 | -5.540683 | 1.780856 |
| H | 2.288769 | -5.396090 | 3.110086 |
| Ca | -2.178112 | -0.000087 | -0.013580 |
| Ca | 2.178003 | -0.000205 | 0.013220 |
| N | -3.980717 | 1.475289 | -0.171574 |
| N | 3.983851 | 1.470929 | 0.171463 |
| N | 0.004136 | -0.002111 | -0.627407 |
| C | -5.885833 | 0.003330 | 0.021137 |
| H | -6.977117 | 0.004069 | 0.028758 |
| C | -5.286547 | 1.276542 | -0.107722 |
| C | -6.227390 | 2.461163 | -0.116576 |
| C | -3.377662 | 2.679353 | -0.564826 |
| C | -3.471666 | 3.109349 | -1.918611 |
| C | -2.756079 | 4.238323 | -2.317464 |
| H | -2.823410 | 4.577798 | -3.353085 |
| C | -1.938109 | 4.930776 | -1.425372 |
| H | -1.388381 | 5.814487 | -1.757723 |
| C | -1.804745 | 4.472902 | -0.120258 |
| H | -1.137362 | 4.991819 | 0.568429 |
| C | -2.505614 | 3.347725 | 0.329430 |
| C | -4.236415 | 2.259282 | -2.913094 |
| H | -5.086369 | 1.802680 | -2.385880 |
| C | -3.349888 | 1.090228 | -3.390370 |
| H | -2.724978 | 1.435474 | -4.231882 |
| H | -2.624622 | 0.829254 | -2.600450 |
| C | -4.141485 | -0.148090 | -3.777000 |
| H | -3.484602 | -0.935062 | -4.172139 |
| H | -4.892900 | 0.074944 | -4.550452 |
| H | -4.672694 | -0.554122 | -2.901570 |
| C | -4.823716 | 3.033917 | -4.094516 |
| H | -4.012915 | 3.517156 | -4.666806 |
| H | -5.272930 | 2.306194 | -4.790615 |
| C | -5.872540 | 4.062665 | -3.696227 |
| H | -5.456416 | 4.816589 | -3.010411 |
| H | -6.719735 | 3.582238 | -3.181709 |
| H | -6.272554 | 4.592035 | -4.574628 |
| C | -2.344529 | 2.863459 | 1.755215 |
| H | -2.639223 | 1.798295 | 1.777452 |
| C | -0.891741 | 2.942971 | 2.245566 |
| H | -0.222726 | 2.648949 | 1.421287 |
| H | -0.624707 | 3.985841 | 2.477879 |
| C | -0.598671 | 2.058841 | 3.446472 |
| H | 0.450564 | 2.166844 | 3.757301 |
| H | -0.758062 | 0.998997 | 3.193814 |
| H | -1.229010 | 2.306978 | 4.314944 |
| C | -3.360205 | 3.549291 | 2.692388 |
| H | -4.371119 | 3.264828 | 2.357591 |
| H | -3.247666 | 3.121968 | 3.701789 |
| C | -3.261545 | 5.065726 | 2.770775 |
| H | -2.266573 | 5.395684 | 3.108805 |
| H | -3.997622 | 5.465603 | 3.485055 |
| H | -3.454087 | 5.535291 | 1.794540 |
| C | 5.886027 | -0.004571 | -0.020614 |
| H | 6.977316 | -0.006089 | -0.028039 |
| C | 5.289295 | 1.269840 | 0.107961 |
| C | 6.232312 | 2.452702 | 0.117010 |
| C | 3.382502 | 2.675826 | 0.564586 |
| C | 3.477058 | 3.105801 | 1.918369 |
| C | 2.762876 | 4.235659 | 2.317192 |
| H | 2.830651 | 4.575070 | 3.352805 |
| C | 1.945711 | 4.929078 | 1.425089 |
| H | 1.397042 | 5.813459 | 1.757401 |
| C | 1.811765 | 4.471312 | 0.120006 |
| H | 1.144975 | 4.991009 | -0.568663 |
| C | 2.511269 | 3.345264 | -0.329677 |
| C | 4.240541 | 2.254711 | 2.912956 |
| H | 5.089923 | 1.796928 | 2.385862 |
| C | 3.352308 | 1.086903 | 3.390129 |
| H | 2.727669 | 1.433094 | 4.231459 |
| H | 2.626872 | 0.826795 | 2.600077 |
| C | 4.142124 | -0.152446 | 3.777080 |
| H | 4.673018 | -0.559254 | 2.901820 |
| H | 3.484072 | -0.938507 | 4.172082 |
| H | 4.893616 | 0.069648 | 4.550727 |
| C | 4.828743 | 3.028552 | 4.094438 |
| H | 4.018524 | 3.512777 | 4.666717 |
| H | 5.277017 | 2.300235 | 4.790527 |
| C | 5.878851 | 4.056021 | 3.696236 |
| H | 6.725435 | 3.574582 | 3.181661 |
| H | 6.279531 | 4.584808 | 4.574683 |
| H | 5.463658 | 4.810526 | 3.010493 |
| C | 2.349564 | 2.861198 | -1.755454 |
| H | 2.643284 | 1.795750 | -1.777867 |
| C | 0.896803 | 2.942295 | -2.245722 |
| H | 0.227435 | 2.649512 | -1.421285 |
| H | 0.631124 | 3.985422 | -2.478399 |
| C | 0.602483 | 2.058058 | -3.446245 |
| H | 1.233706 | 2.304449 | -4.314573 |
| H | -0.446397 | 2.168017 | -3.757594 |
| H | 0.759594 | 0.998046 | -3.192862 |

| | | | |
|---|---|---|---|
| C | 3.365888 | 3.545990 | -2.692728 |
| H | 4.376517 | 3.260235 | -2.358156 |
| H | 3.252597 | 3.118960 | -3.702170 |
| C | 3.269126 | 5.062559 | -2.770834 |
| H | 4.005393 | 5.461554 | -3.485412 |
| H | 3.462758 | 5.531737 | -1.794630 |
| H | 2.274437 | 5.393878 | -3.108357 |
| H | 7.146288 | -2.235213 | -0.720752 |
| H | 6.515061 | -2.708247 | 0.868105 |
| H | 5.753383 | -3.352770 | -0.600005 |
| H | 7.167529 | 2.220480 | 0.644624 |
| H | 6.494784 | 2.707755 | -0.923082 |
| H | 5.773430 | 3.340765 | 0.569520 |
| H | -7.163509 | 2.230379 | -0.643208 |
| H | -6.488405 | 2.717305 | 0.923616 |
| H | -5.767306 | 3.348153 | -0.569958 |
| H | -7.151337 | -2.224406 | 0.719986 |
| H | -6.518957 | -2.700381 | -0.867580 |
| H | -5.760352 | -3.344707 | 0.602120 |

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