*Electronic Supplementary Information (ESI)*

# Reversible Water Activation Driven by Contraction and Expansion of the 12-vertex-*closo*-12-vertex-*nido* Biscarborane Cluster.

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## Experimental.

NMR spectra were recorded using Varian spectrometers at 400 ($^1$H), 100 ($^{13}$C), 162 ($^{31}$P), 128 ($^{11}$B) MHz, reported in $\delta$ (parts per million) and referenced to the residual $^1$H/$^{13}$C signals of the deuterated solvent or an external 85% phosphoric acid ($^{31}$P ($\delta$): 0.0 ppm) and $BF_3(Et_2O)$ ($^{11}$B($\delta$): 0.0 ppm) standards. Midwest Microlab, Indianapolis, Indiana provided the elemental analysis results.

1,1'-bis(*o*-carborane) $(C_2B_{10}H_{11})(C_2B_{10}H_{11})$ (biscarborane) was prepared according to the reported procedure[1]. *Closo*-$(C_2B_{10}H_{10})(P\{N(i\text{-}Pr)_2\}_2)$-*nido*-$(C_2B_{10}H_9)(PH\{N(i\text{-}Pr)_2\}_2)$ cluster **(1)** was prepared according to the reported procedure[2]. $P\{N(i\text{-}Pr)\}_2Cl$, MeLi solution in hexanes, and *o*-carborane were used as received. ACS-grade acetonitrile was used as received, containing ca. 0.5 % water according to the manufacturer's analysis.

1. S. Ren, Z. Xie, *Organometallics* 2008, **27**, 5167–5168.
2. Y. O. Wong, M. D. Smith, D. V. Peryshkov, *Chem.–Eur. J.* 2016, **22**, 6764–6767.

### Synthesis of *closo*-$(C_2B_{10}H_{10})(P\{N(i\text{-}Pr)_2\}_2)$-*nido*-$(CB_9H_{10})(CB(H)(OH)(PH\{N(i\text{-}Pr)_2\}_2)$ (2).

A portion of solution of *closo*-$(C_2B_{10}H_{10})(P\{N(i\text{-}Pr)_2\}_2)$-*nido*-$(C_2B_{10}H_9)(PH\{N(i\text{-}Pr)_2\}_2)$ (**1**) (25 mg, 0.033 mmol) was added to 1 mL of acetonitrile containing ca. 0.5 % wt. of water. The mixture was stirred at room temperature for 2 h. The volatiles were removed under vacuum at room temperature producing a white crystalline solid **2** (25 mg, 0.033 mmol, 97% yield). The compound **2** was found to convert back to **1** upon heating at 50 ºC in $CDCl_3$ solution in the presence of $MgSO_4$.

**$^1$H NMR** ($CDCl_3$): $\delta$ 5.93 (d, 1H, $^1J_{PH}$ = 527 Hz, $PH\{N(i\text{-}Pr)_2\}_2$), 5.62 (d, 1H, $^3J_{HH}$ = 3 Hz, (C)(B)(H)(O*H*)), 4.67 (m, 2H, $P\{N(CH(CH_3)_2)_2\}_2$), 4.44 (m, 2H, $P\{N(CH(CH_3)_2)_2\}_2$), 3.97 (m, 2H, $P\{N(CH(CH_3)_2)_2\}_2$), 3.80 (m, 2H, $P\{N(CH(CH_3)_2)_2\}_2$), 4.00–1.00 (br m, 19H, B*H*), 1.42 to 1.30 (overlapping m, 48H, $P(N\{CH(CH_3)_2)_2\}_2)$, –2.26 (br, 1H, B(*H*)B). **$^{31}$P{$^1$H} NMR** ($CDCl_3$): $\delta$ 86.2 (br, 1P, (C)(B)$P\{N(i\text{-}Pr)_2\}_2$), 56.8 (s, 1P, (C)(H)$P\{N(i\text{-}Pr)_2\}_2$). **$^{11}$B{$^1$H}** NMR ($CDCl_3$): $\delta$ 13.8 (br), 10.0, –0.3, –7 to –15 (overlapping signals), –18.3, –29.7, –31.4, –35.9. **$^{13}$C NMR** ($CDCl_3$): $\delta$ 108.4 ($B_{10}CC$–$CCB_{10}$), 98.5 (d, $^2J_{PC}$ = 20 Hz, $B_{10}CC$–$P\{N(i\text{-}Pr)_2\}_2$), 80.7 (d, $^1J_{PC}$ = 44 Hz, $B_{10}CC$–$P\{N(i\text{-}Pr)_2\}_2$), 53.3 (d, $P\{N(CH(CH_3)_2)_2\}_2$), 50.7 (d, $P\{N(CH(CH_3)_2)_2\}_2$), 48.5 (d, $P\{N(CH(CH_3)_2)_2\}_2$), 46.5 (d, $P\{N(CH(CH_3)_2)_2\}_2$), 27.3 (d, $P\{N(CH(CH_3)_2)_2\}_2$), 26.4 (d, $P\{N(CH(CH_3)_2)_2\}_2$), 25.2 (d, $P\{N(CH(CH_3)_2)_2\}_2$), 24.9 (d, $P\{N(CH(CH_3)_2)_2\}_2$), 23.9 (d, $P\{N(CH(CH_3)_2)_2\}_2$), 23.0 (d, $P\{N(CH(CH_3)_2)_2\}_2$), 22.5 (d, $P\{N(CH(CH_3)_2)_2\}_2$), 12.0 (d, $^1J_{PC}$ = 63 Hz, (OH)(H)B*C*–$P\{N(i\text{-}Pr)_2\}_2$). Calcd. for $C_{28}H_{78}B_{20}N_4OP_2$: C, 43.74; H, 10.22. Found: C, 43.91; H, 9.90.

The mass-spectrum of **2** (EI) contained the molecular ion peak at 748 m/z (corresponding to **1**) indicating dehydration under instrument conditions.

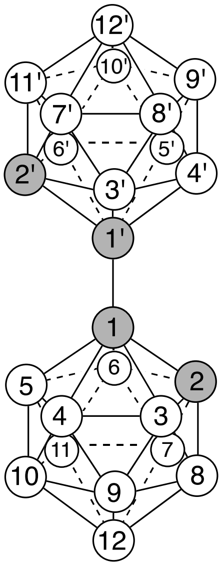


Figure S-1. The numbering scheme for the icosahedral biscarborane cluster. For the 1,1'-bis(*o*-carborane) ($C_2B_{10}H_{11}$)($C_2B_{10}H_{11}$) cluster (biscarborane), carbon atoms are at positions 1, 2, 1', and 2' (shaded circles).

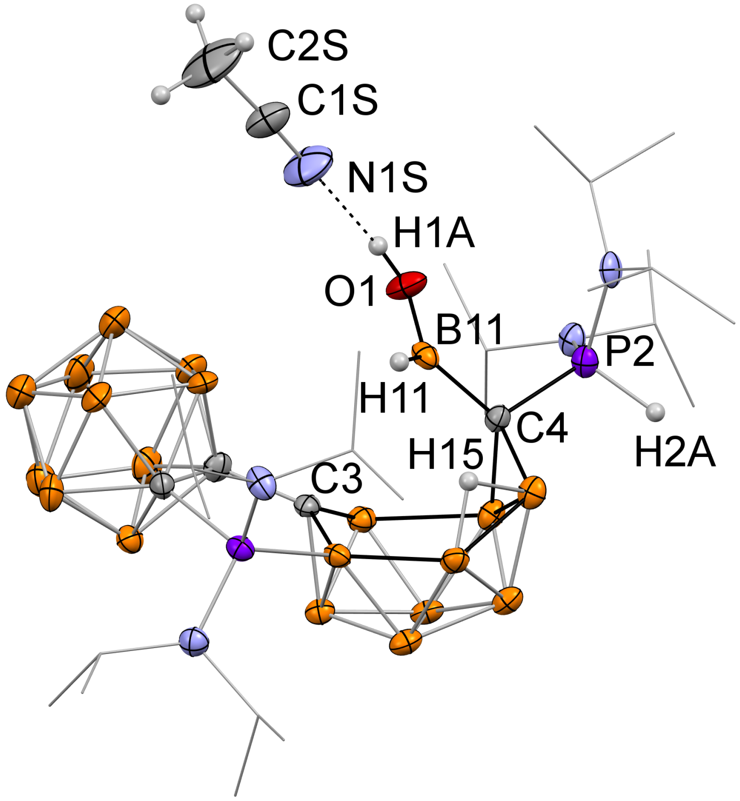
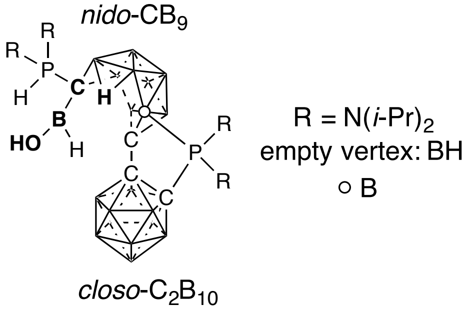


Figure S-2. Displacement ellipsoid plot (50% probability) of the *closo*-($C_2B_{10}H_{10}$)(P{N(*i*-Pr)$_2$}$_2$)-*nido*-($CB_9H_{10}$)(CB(H)(OH)(PH{N(*i*-Pr)$_2$}$_2$) acetonitrile solvate **2•$CH_3CN$**. Carbon atoms belonging to P(N(*i*-Pr)$_2$)$_2$ groups and all hydrogen atoms, except for the protonated phosphonium cation, the B(H)(OH) group, the endo proton on the *nido* cage, and in the acetonitrile molecule have been omitted for clarity. Selected interatomic distances (Å) and angles (º): N1S···O1 = 2.787(5), N1S···H1A = 1.95(5), B11–O1 = 1.339(5), B11–C4 = 1.547(5), C1–C2 = 1.708(5), C2–C3 = 1.505(5), C3···C4 = 3.235(5), P2–C4 = 1.749(4), N1S···H1A–O1 =172(5), C1S–N1S···O1 =178.0(4), H1A–O1–B11 = 116(4).

The interatomic distances and angles in **2•$CH_3CN$** (above) can be compared to those in **2•$CD_2Cl_2$** (below):
P1–C1 = 1.916(1), P1–B12 = 1.957(1), C1–C2 = 1.712(1), C2–C3 = 1.498(1), C3···C4 = 3.320(1), P2–C4 = 1.770(1), C4–B11 = 1.552(2), C1–C2–C3 = 113.5(1), B12–C3–C2 = 116.6(1), C1–P1–B12 = 96.4(1), B15–C4–B19 = 71.0(1), P2–C4–B11 = 117.9(1).



**2**

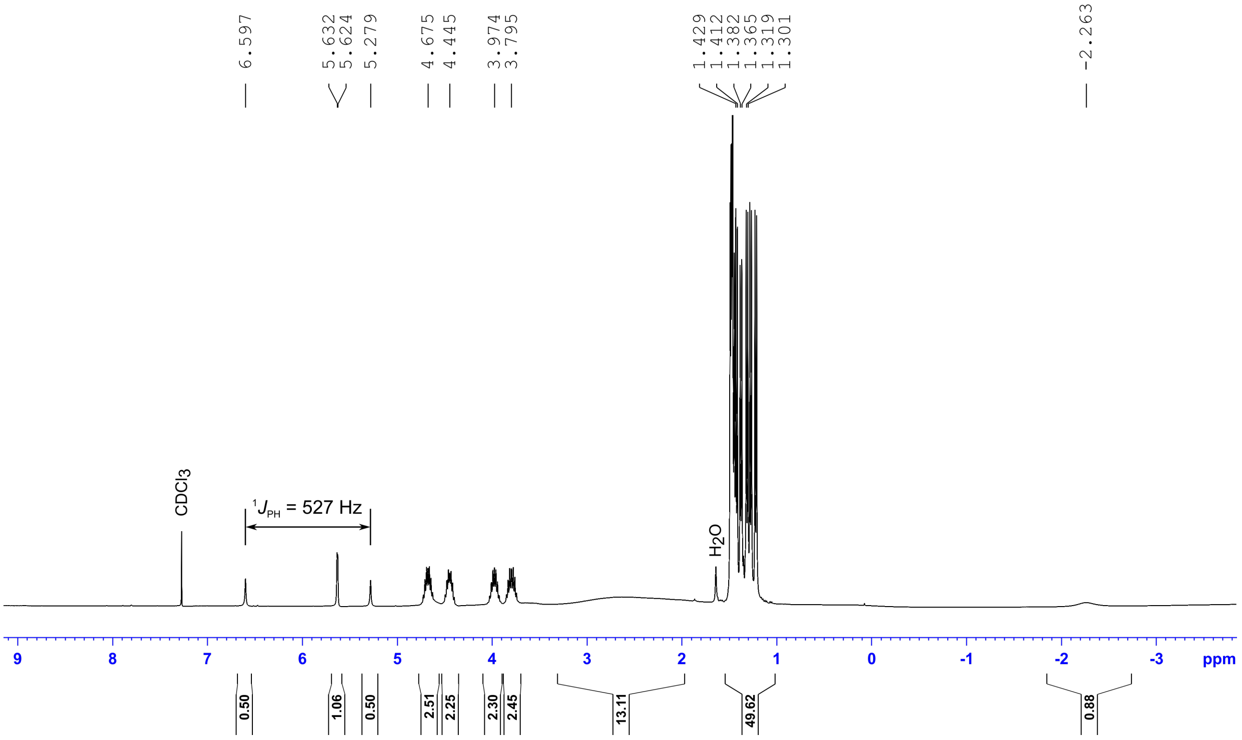
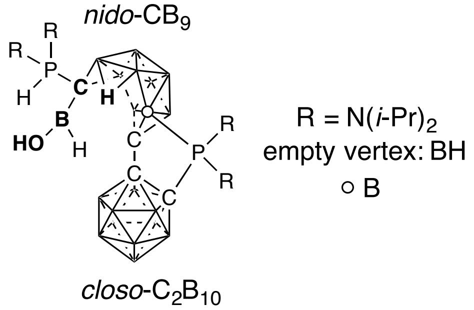


Figure S-3. The $^1H$ NMR spectrum of *closo*-($C_2B_{10}H_{10}$)(P{N(*i*-Pr)$_2$}$_2$)-*nido*-($CB_9H_{10}$)(CB(H)(OH)(PH{N(*i*-Pr)$_2$}$_2$) (**2**) in $CDCl_3$.

$^1H$ NMR ($CDCl_3$): δ 5.93 (d, 1H, $^1J_{PH}$ = 527 Hz, P*H*{N(*i*-Pr)$_2$}$_2$), 5.62 (d, 1H, $^3J_{HH}$ = 3 Hz, (C)(B)(H)(O*H*)), 4.67 (m, 2H, P{N(C*H*($CH_3$)$_2$)$_2$}$_2$), 4.44 (m, 2H, P{N(C*H*($CH_3$)$_2$)$_2$}$_2$), 3.97 (m, 2H, P{N(C*H*($CH_3$)$_2$)$_2$}$_2$), 3.80 (m, 2H, P{N(C*H*($CH_3$)$_2$)$_2$}$_2$), 4.00–1.00 (br m, 19H, B*H*), 1.42 to 1.30 (overlapping m, 48H, P(N{CH(C*H*$_3$)$_2$)$_2$}$_2$), –2.26 (br, 1H, B(*H*)B).



**2**

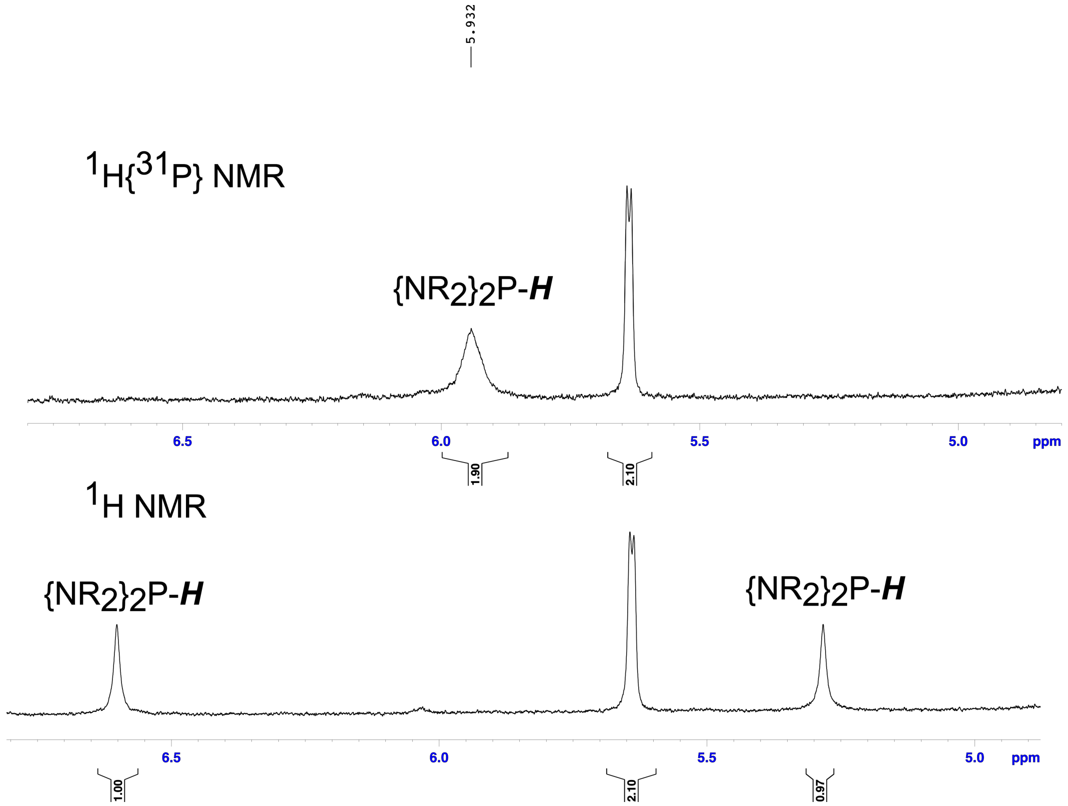
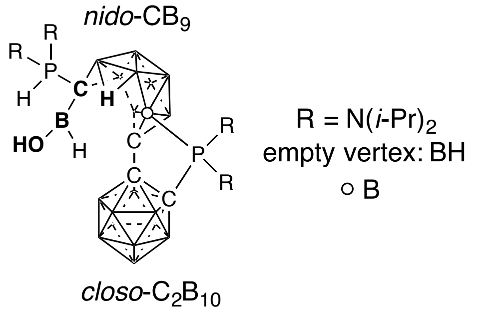


Figure S-4. Portions of $^1$H and $^1$H{$^{31}$P} NMR spectra of *closo*-($C_2B_{10}H_{10}$)(P{N(*i*-Pr)$_2$}$_2$)-*nido*-($CB_9H_{10}$)(CB(H)(OH)(PH{N(*i*-Pr)$_2$}$_2$) (**2**) in $CDCl_3$. The signal from the P*H*{N(*i*-Pr)$_2$}$_2$ group (doublet in $^1$H NMR spectrum, $^1J_{PH}$ = 527 Hz) is converted to the singlet in the $^1$H{$^{31}$P} spectrum.



**2**

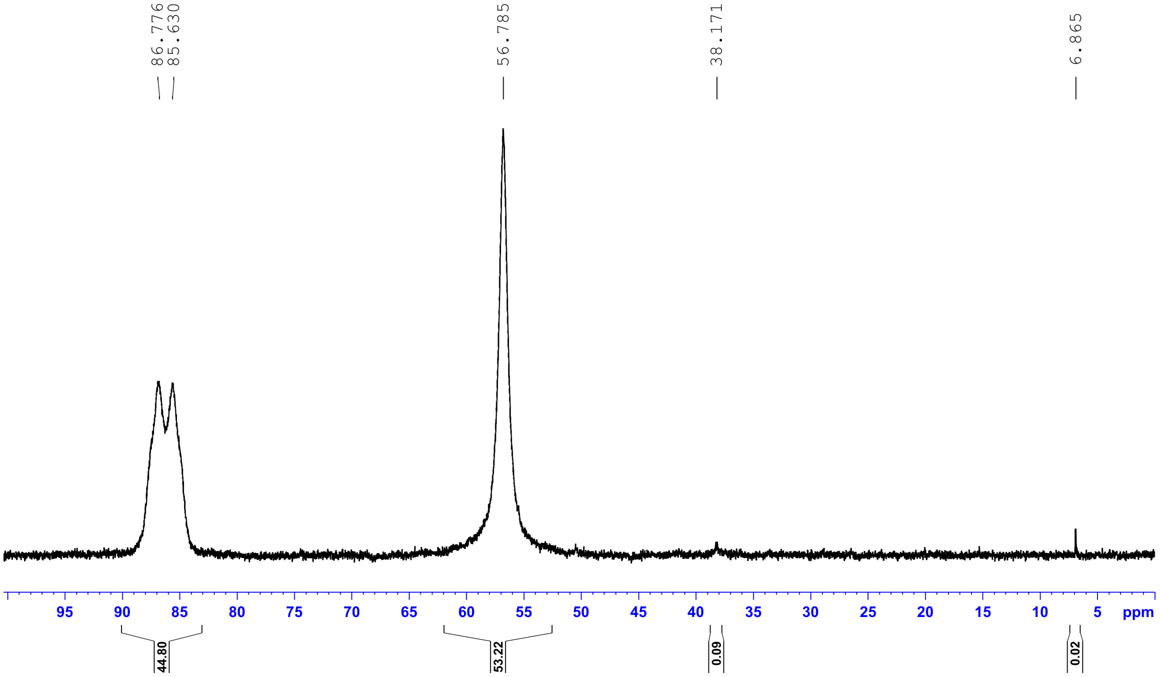
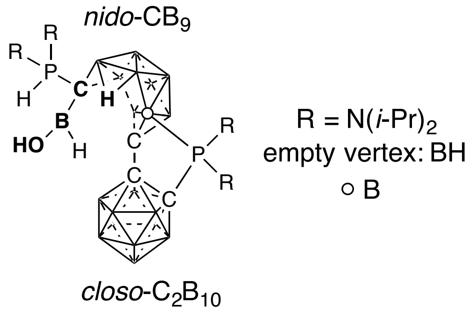


Figure S-5. The $^{31}P\{^{1}H\}$ NMR spectrum of *closo*-($C_2B_{10}H_{10}$)(P{N(*i*-Pr)$_2$}$_2$)-*nido*-($CB_9H_{10}$)(CB(H)(OH)(PH{N(*i*-Pr)$_2$}$_2$) (**2**) in $CDCl_3$.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 86.2 (br, 1P, (C)(B)P{N(*i*-Pr)$_2$}$_2$), 56.8 (s, 1P, (C)(H)P{N(*i*-Pr)$_2$}$_2$). The signal at 6.9 ppm corresponds to an unidentified impurity. The signal at 38.2 ppm corresponds to a trace of starting material **1**.

The signal at 86.2 ppm corresponds to the boronated phosphorus atom in **2** (signal shape due to $^{31}P$-$^{11}B$ coupling) and the signal at 56.8 ppm corresponds to the protonated phosphorus atom.



**2**

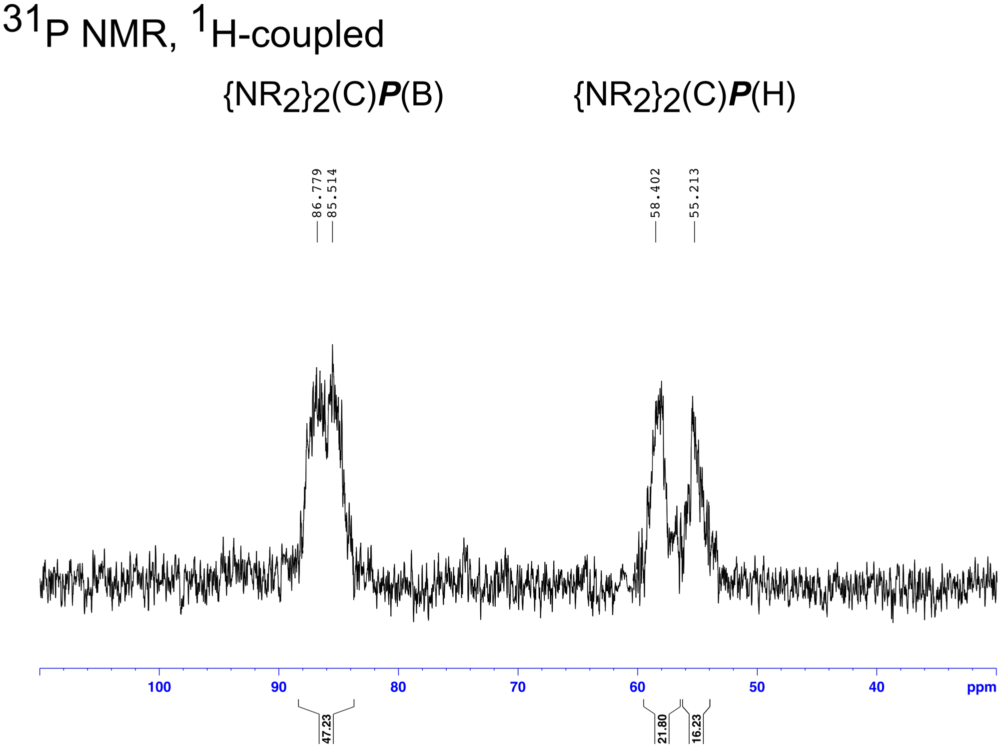
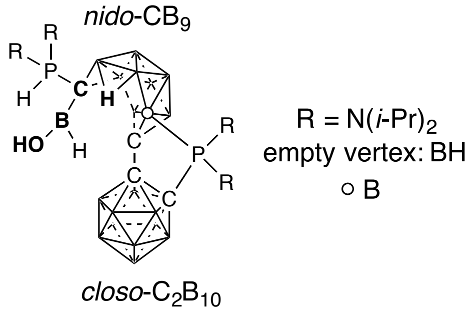


Figure S-6. The $^{31}$P NMR spectrum of *closo*-($C_2B_{10}H_{10}$)(P{N(*i*-Pr)$_2$}$_2$)-*nido*-($CB_9H_{10}$)(CB(H)(OH)(PH{N(*i*-Pr)$_2$}$_2$) (**2**) in $CDCl_3$.

$^{31}$P NMR ($CDCl_3$): δ 86.2 (br, 1P, (C)(B)P{N(*i*-Pr)$_2$}$_2$), 56.8 (d, $^1J_{PH}$ = 516 Hz 1P, (C)(H)P{N(*i*-Pr)$_2$}$_2$).



**2**

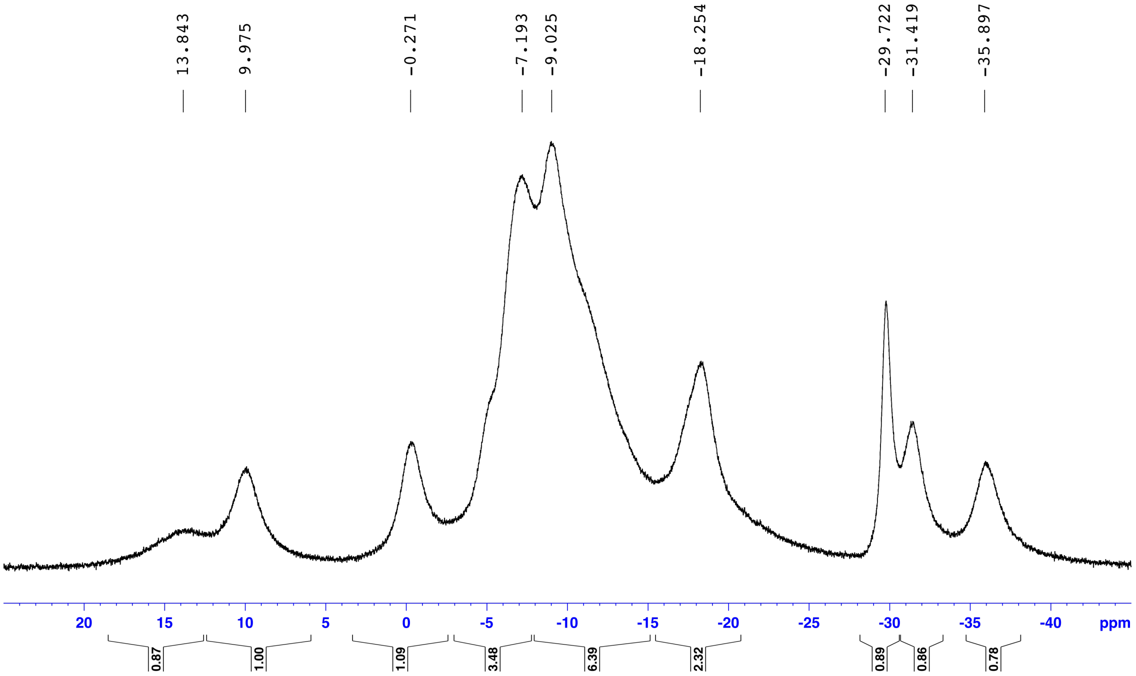
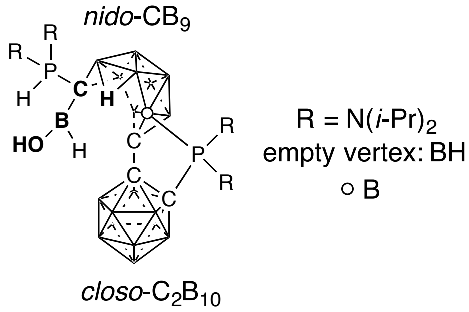


Figure S-7. The $^{11}B\{^1H\}$ NMR spectrum of *closo*-$(C_2B_{10}H_{10})(P\{N(i\text{-}Pr)_2\}_2)$-*nido*-$(CB_9H_{10})(CB(H)(OH)(PH\{N(i\text{-}Pr)_2\}_2)$ (**2**) in $CDCl_3$.

$^{11}B\{^1H\}$ NMR ($CDCl_3$):
δ 13.8 (br), 10.0, –0.3, –7 to –15 (overlapping signals), –18.3, –29.7, –31.4, –35.9.



**2**

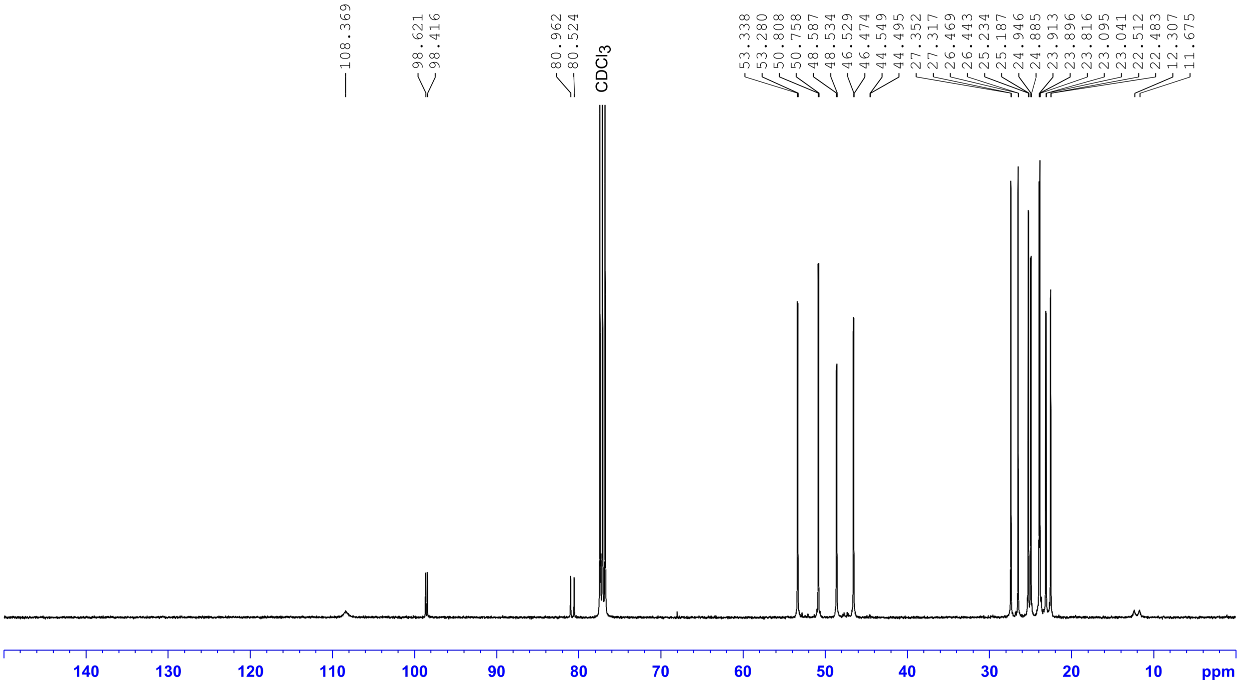


Figure S-8. The $^{13}$C NMR spectrum of *closo*-($C_2B_{10}H_{10}$)(P{N(*i*-Pr)$_2$}$_2$)-*nido*-($CB_9H_{10}$)(CB(H)(OH)(PH{N(*i*-Pr)$_2$}$_2$) (**2**) in $CDCl_3$.

$^{13}$C NMR ($CDCl_3$): δ 108.4 ($B_{10}C$*C*–$CCB_{10}$), 98.5 (d, $^2J_{PC}$ = 20 Hz, $B_{10}$*C*C–P{N(*i*-Pr)$_2$}$_2$), 80.7 (d, $^1J_{PC}$ = 44 Hz, $B_{10}C$*C*–P{N(*i*-Pr)$_2$}$_2$), 53.3 (d, P{N(*C*H(CH$_3$)$_2$)$_2$}$_2$), 50.7 (d, P{N(*C*H(CH$_3$)$_2$)$_2$}$_2$), 48.5 (d, P{N(*C*H(CH$_3$)$_2$)$_2$}$_2$), 46.5 (d, P{N(*C*H(CH$_3$)$_2$)$_2$}$_2$), 27.3 (d, P{N(CH(*C*H$_3$)$_2$)$_2$}$_2$), 26.4 (d, P{N(CH(*C*H$_3$)$_2$)$_2$}$_2$), 25.2 (d,`` P{N(CH(*C*H$_3$)$_2$)$_2$}$_2$), 24.9 (d, P{N(CH(*C*H$_3$)$_2$)$_2$}$_2$), 23.9 (d, P{N(CH(*C*H$_3$)$_2$)$_2$}$_2$), 23.0 (d, P{N(CH(*C*H$_3$)$_2$)$_2$}$_2$), 22.5 (d, P{N(CH(*C*H$_3$)$_2$)$_2$}$_2$), 12.0 (d, $^1J_{PC}$ = 63 Hz, (OH)(H)B*C*–P{N(*i*-Pr)$_2$}$_2$).

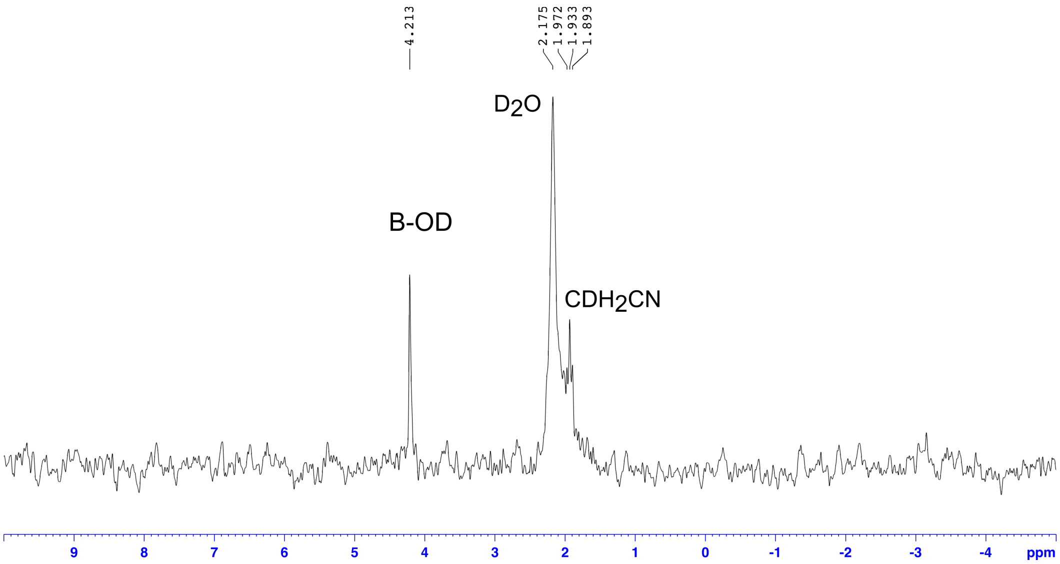


Figure S-9. The $^2$H NMR spectrum of *closo*-($C_2B_{10}H_{10}$)(P{N(*i*-Pr)$_2$}$_2$)-*nido*-($CB_9H_9D$)(CB(H)(OD)(PH{N(*i*-Pr)$_2$}$_2$) (**2-*d***) in $CH_3CN$. The sample of **2-*d*** was prepared by addition of an excess $D_2O$ and $CD_3CN$ to a sample of **1** at room temperature. Note the appearance of the signal corresponding to the B-OD group. The signal from the B–D–B group on the boron cage is not observed, possibly because of broadening due to coupling to $^{11}$B nuclei.

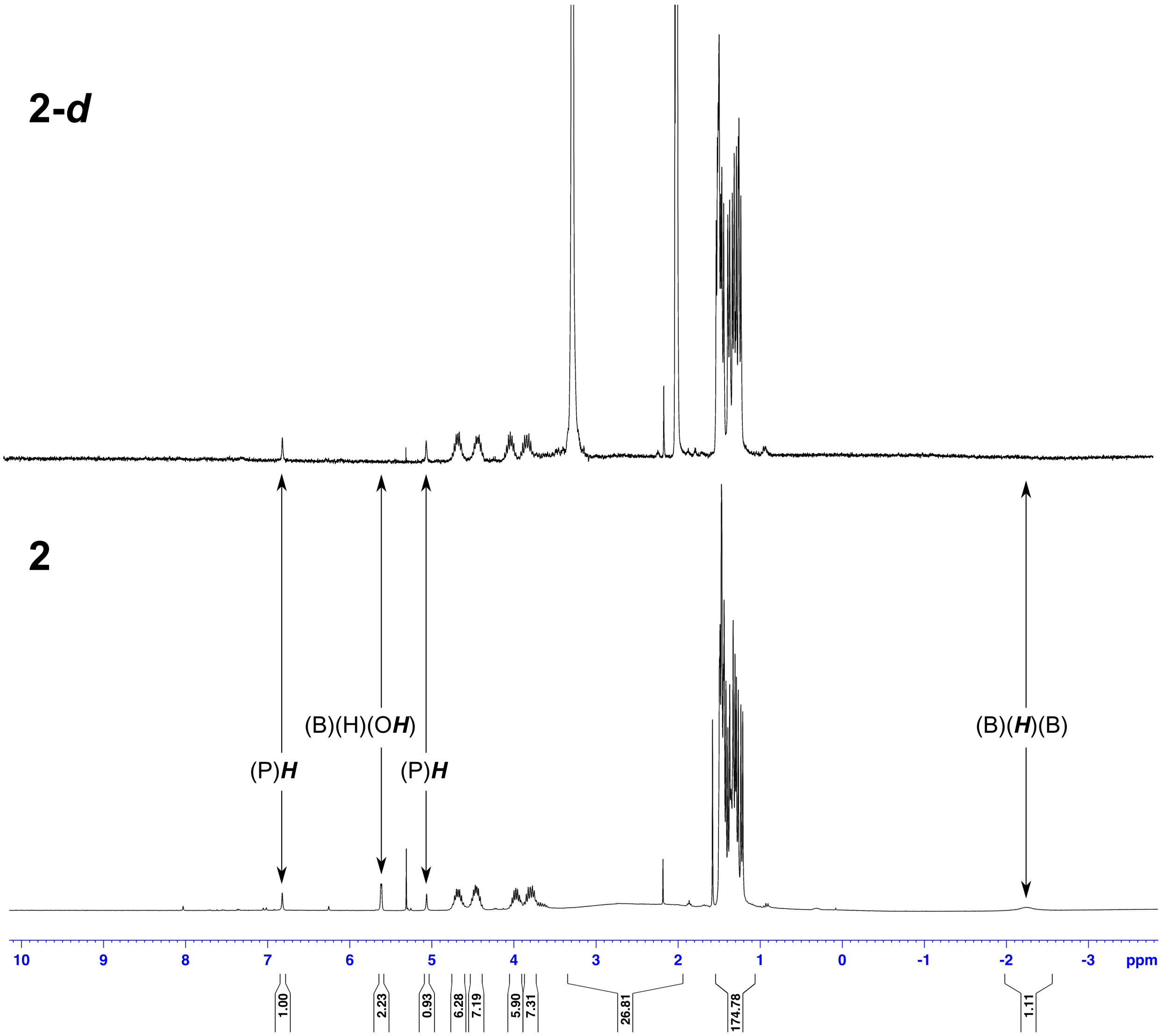


Figure S-10. Comparison of the $^1$H NMR spectra of samples of *closo*-($C_2B_{10}H_{10}$)(P{N(*i*-Pr)$_2$}$_2$)-*nido*-($CB_9H_{10}$)(CB(H)(OH)(PH{N(*i*-Pr)$_2$}$_2$) (**2**, bottom) and *closo*-($C_2B_{10}H_{10}$)(P{N(*i*-Pr)$_2$}$_2$)-*nido*-($CB_9H_9D$)(CB(H)(OD)(PH{N(*i*-Pr)$_2$}$_2$) (**2-*d***, top). The sample of **2-*d*** was prepared by addition of an excess $D_2O$ and $CD_3CN$ to a sample of **1** at room temperature. Note the absence of signals from (B)(***H***)(OH) and (B)(***H***)(B) protons in the spectrum of **2-*d***.

## X-Ray Structure Determination, *closo*-$(C_2B_{10}H_{10})(P\{N(i\text{-}Pr)_2\}_2)$-*nido*-$(CB_9H_{10})(CB(H)(OH)(PH\{N(i\text{-}Pr)_2\}_2)\bullet CH_2Cl_2$ ($2\bullet CH_2Cl_2$)

X-ray intensity data from a colorless block crystal were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an Incoatec microfocus source (Mo Kα radiation, $\lambda = 0.71073$ Å).[1] The raw area detector data frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs.[1] Final unit cell parameters were determined by least-squares refinement of 9778 reflections taken from the data set. The structure was solved by direct methods with SHELXT.[2] Subsequent difference Fourier calculations and full-matrix least-squares refinement against $F^2$ were performed with SHELXL-2014[2] using OLEX2.[3]

The compound crystallizes in the triclinic system. The space group *P*-1 (No. 2) was confirmed by structure solution. The asymmetric unit consists of one $C_{28}H_{78}B_{20}N_4OP_2$ molecule and one dichloromethane molecule. The dichloromethane is disordered over two positions with populations A/B = 0.890(7)/0.110(7). All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystal and data quality were sufficient to permit unambiguous location and unconstrained refinement of all hydrogen atoms of both the closed and open carborane cages, as well as the hydroxyl hydrogen H1A and the bis(di-isopropylamino)phosphine hydrogen H2A. In particular, well-localized, strong electron density peaks corresponding to the bridging hydrogen H15A and the BH group hydrogen H11 were observed. Free refinement of these hydrogen atoms resulted in physically reasonable bonding geometries and displacement parameters. Hydrogen atoms bonded to carbon were also located in difference maps, but were placed in idealized positions and included as riding atoms with C-H = 1.00 Å and $U$(iso,H) = 1.2$U$(eq,C) for CH hydrogens, and C-H = 0.98 Å and U(iso,H) = 1.5$U$(eq,C) for methyl hydrogens. The largest residual electron density peak in the final difference map is 0.45 $e^-/Å^3$, located 0.23 Å from H21A.

(1) APEX2 Version 2014.9-0, SAINT Version 8.34A and SADABS Version 2014/4. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2014.

(2) (a) **SHELXT**: Sheldrick, G.M. *Acta Cryst*. **2015**, *A71*, 3-8. (b) **SHELXL:** Sheldrick, G.M. *Acta Cryst*. **2008**, A64, 112-122.

(3) Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard J. A. K. and Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.

Table S-1 Crystal data and structure refinement for *closo*-($C_2B_{10}H_{10}$)(P{N(*i*-Pr)$_2$}$_2$)-*nido*-($CB_9H_{10}$)(CB(H)(OH)(PH{N(*i*-Pr)$_2$}$_2$)•$CH_2Cl_2$ (**2•$CH_2Cl_2$**).

| | |
|---|---|
| Identification code | C1NPAmino |
| Empirical formula | $C_{29}H_{80}B_{20}Cl_2N_4OP_2$ |
| Formula weight | 850.01 |
| Temperature/K | 100(2) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 11.8867(4) |
| b/Å | 12.3732(4) |
| c/Å | 16.8070(6) |
| α/° | 92.3050(10) |
| β/° | 91.8090(10) |
| γ/° | 98.8840(10) |
| Volume/Å$^3$ | 2438.50(14) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.158 |
| μ/mm$^{-1}$ | 0.230 |
| F(000) | 908.0 |
| Crystal size/mm$^3$ | 0.36 × 0.3 × 0.25 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.31 to 60.154 |
| Index ranges | $-16 \le h \le 16$, $-17 \le k \le 17$, $-23 \le l \le 23$ |
| Reflections collected | 126383 |
| Independent reflections | 14334 [$R_{int}$ = 0.0391, $R_{sigma}$ = 0.0249] |
| Data/restraints/parameters | 14334/3/632 |
| Goodness-of-fit on F$^2$ | 1.036 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0351, $wR_2$ = 0.0800 |
| Final R indexes [all data] | $R_1$ = 0.0461, $wR_2$ = 0.0846 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.45/-0.35 |

## X-Ray Structure Determination, *closo*-$(C_2B_{10}H_{10})(P\{N(i\text{-}Pr)_2\}_2)$-*nido*-$(CB_9H_{10})(CB(H)(OH)(PH\{N(i\text{-}Pr)_2\}_2)\cdot CD_3CN$ $(2\cdot CD_3CN)$

X-ray intensity data from a colorless needle crystal were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector and an Incoatec microfocus source (Mo K$\alpha$ radiation, $\lambda$ = 0.71073 Å).[1] The raw area detector data frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs.[1] Final unit cell parameters were determined by least-squares refinement of 9714 reflections taken from the data set. The structure was solved by direct methods with SHELXT.[2] Subsequent difference Fourier calculations and full-matrix least-squares refinement against $F^2$ were performed with SHELXL-2014[2] using OLEX2.[3]

The compound crystallizes in the orthorhombic system. The pattern of systematic absences in the intensity data was consistent with the space groups $Pna2_1$ and $Pnma$; intensity statistics suggested an acentric structure. $Pna2_1$ was eventually confirmed by obtaining a stable and reasonable structure, and was confirmed by checking for missed symmetry elements with the ADDSYM program in PLATON.[4] The asymmetric unit consists of two crystallographically independent but chemically similar $C_{28}H_{78}B_{20}N_4OP_2$ molecules and two acetonitrile molecules of crystallization. The $C_{28}H_{78}B_{20}N_4OP_2$ molecules were numbered similarly except for label suffixes A(C) or B(D). Disorder of four -N($^i$Pr)$_2$ substituents (two per independent molecule) was modeled with two components each. Minor disorder component atoms of molecule A were given label suffix C; likewise D for molecule B. Major disorder fractions refined within the range 0.60 – 0.76. 1,2- and 1,3- distances of the disordered groups were restrained to be similar to those of ordered -N(*i*Pr)$_2$ groups by means of SHELX SAME instructions. In total, 346 restraints were used in disorder modeling. All non-hydrogen atoms were refined with anisotropic displacement parameters (ADPs). Displacement parameters of nearly superimposed, fractionally populated atoms were held equal during refinement. An enhanced rigid-bond restraint (RIGU) was applied to the ADPs of the disordered atoms. Hydrogen atoms bonded to carbon were placed in geometrically idealized positions included as riding atoms with $d$(C-H) = 1.00 Å and $U$iso(H) = 1.2$U$eq(C) for methine hydrogen atoms and $d$(C-H) = 0.98 Å and $U$iso(H) = 1.5$U$eq(C) for methyl hydrogens. The methyl hydrogens were allowed to rotate as a rigid group to the orientation of maximum observed electron density. Hydrogen atoms bonded to oxygen and phosphorus were located in difference maps and refined isotropically. O-H distances were restrained to 0.85(2) Å. Hydrogen atoms attached to boron atoms having five neighbors were placed in idealized positions and included as riding atoms with $d$(B-H) = 1.120 Å and $U$iso(H) = 1.2$U$eq(B). Those attached to boron atoms with fewer than five neighbors were located in difference maps and their coordinates refined. The largest residual electron density peak in the final difference map is 0.28 $e^-/Å^3$, located 0.89 Å from C4A. The absolute structure (Flack) parameter near convergence was 0.22(3), indicating the crystal is an inversion twin. The final refinement cycles included an inversion matrix, with the Flack parameter as the minor twin volume fraction.

(1) APEX2 Version 2014.9-0, SAINT+ Version 8.34A and SADABS Version 2014/4. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2014.

(2) (a) **SHELXT**: Sheldrick, G.M. *Acta Cryst*. **2015**, *A71*, 3-8. (b) **SHELXL:** Sheldrick, G.M. *Acta Cryst*. **2008**, A64, 112-122.

(3) Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard J. A. K. and Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.

(4) (a) LePage, Y. *J. Appl. Crystallogr.* **1987**, *20*, 264-269. (b) Spek, A. L. *J. Appl. Crystallogr.*, **1988**, *21*, 578-579. (c) Spek, A. L. *Acta Crystallogr., Sect A* **1990**, *46*, C34. (d) PLATON: Spek, A.L. *Acta Cryst.,* **2009**, *D65*, 148-155.

Table S-2. Crystal data and structure refinement for *closo*-$(C_2B_{10}H_{10})(P\{N(i\text{-}Pr)_2\}_2)$-*nido*-$(CB_9H_{10})(CB(H)(OH)(PH\{N(i\text{-}Pr)_2\}_2)$•$CD_3CN$ **(2•CD₃CN)**

| | |
|---|---|
| Identification code | pna21 |
| Empirical formula | $C_{30}H_{81}B_{20}N_5OP_2$ |
| Formula weight | 806.13 |
| Temperature/K | 100(2) |
| Crystal system | orthorhombic |
| Space group | $Pna2_1$ |
| a/Å | 44.006(2) |
| b/Å | 9.8902(6) |
| c/Å | 22.5051(13) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 9794.9(10) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.093 |
| μ/mm$^{-1}$ | 0.121 |
| F(000) | 3472.0 |
| Crystal size/mm$^3$ | 0.52 × 0.12 × 0.08 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.12 to 52.836 |
| Index ranges | $-55 \le h \le 55$, $-12 \le k \le 12$, $-28 \le l \le 28$ |
| Reflections collected | 286896 |
| Independent reflections | 20096 [$R_{int}$ = 0.1432, $R_{sigma}$ = 0.0745] |
| Data/restraints/parameters | 20096/346/1246 |
| Goodness-of-fit on F$^2$ | 1.026 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0506, $wR_2$ = 0.0984 |
| Final R indexes [all data] | $R_1$ = 0.0842, $wR_2$ = 0.1096 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.28/-0.40 |
| Flack parameter | 0.22(8) |

Details of Computational Study of **1**.

The partial atomic charges in the *closo*-($C_2B_{10}H_{10}$)(P{N(*i*-Pr)$_2$}$_2$)-*nido*-($C_2B_{10}H_9$)(PH{N(*i*-Pr)$_2$}$_2$) biscarborane cluster **1** were calculated using DFT computational methods (BLYP/DZ) in the Amsterdam Density Functional (ADF) program suite.

Table S-3. The Mulliken charges at the selected atoms in *closo*-($C_2B_{10}H_{10}$)(P{N(*i*-Pr)$_2$}$_2$)-*nido*-($C_2B_{10}H_9$)(PH{N(*i*-Pr)$_2$}$_2$) biscarborane cluster **1**.

| Atom | Orthogonal Atomic Coordinates | | | Mulliken Charge |
|---|---|---|---|---|
| P1 | 0.6330 | -1.8937 | 1.7997 | +0.588 |
| P2 | -0.8259 | 2.2029 | -2.4036 | +0.809 |
| **B11** | 0.5243 | -0.1170 | -1.1599 | **+0.255** |
| B12 | -0.2108 | -1.6703 | -0.0478 | -0.081 |
| **B14** | -2.5044 | -0.8180 | -0.9483 | **+0.215** |
| B15 | 0.3060 | -0.5968 | -2.9157 | +0.138 |
| B16 | 0.7094 | -1.7922 | -1.6297 | +0.092 |
| B19 | -1.5475 | -0.5668 | -2.7151 | +0.157 |
| C1 | -0.5730 | -0.6820 | 2.7100 | -0.261 |
| C2 | -1.7961 | -0.3330 | 1.5894 | -0.073 |
| C3 | -1.5751 | -0.9046 | 0.2448 | -0.141 |
| C4 | -0.5152 | 0.5204 | -2.0931 | -0.341 |
| N2 | 0.4838 | -3.4276 | 2.4711 | -0.424 |

The orthogonal atomic coordinates of the optimized model of **1** are listed below:

| | | | |
|---|---|---|---|
| P | 0.63299927 | -1.89371106 | 1.79972149 |
| P | -0.82596937 | 2.20292183 | -2.40357893 |
| H | -0.73293630 | -1.47611718 | 5.08340073 |
| N | 2.18814946 | -1.28125297 | 1.97291649 |
| N | 0.48375067 | -3.42757050 | 2.47106791 |
| N | 0.47991475 | 3.19697459 | -2.12359624 |
| N | -1.60598667 | 2.54059934 | -3.84520166 |
| C | -0.57297480 | -0.68203429 | 2.71003327 |
| C | -1.79607797 | -0.33299988 | 1.58936732 |
| C | -1.57513365 | -0.90461423 | 0.24479206 |
| C | -0.51523798 | 0.52041371 | -2.09313546 |
| C | 2.67254107 | -0.57501338 | 3.19767075 |
| H | 1.83582461 | -0.60402783 | 3.88822883 |
| C | 2.99386512 | 0.90870869 | 2.96126755 |
| H | 3.95131478 | 1.04425755 | 2.46423881 |
| H | 3.04797746 | 1.41819585 | 3.92534998 |
| H | 2.22210993 | 1.39367292 | 2.36879063 |
| C | 3.84471384 | -1.24769495 | 3.92565906 |
| H | 3.66605274 | -2.30287357 | 4.11822889 |
| H | 3.98037451 | -0.74786599 | 4.88668744 |
| H | 4.78001909 | -1.14849751 | 3.37730269 |
| C | 3.14605319 | -1.70796812 | 0.89656745 |
| H | 2.50712146 | -1.98811939 | 0.06434744 |
| C | 4.03858938 | -0.57896792 | 0.37446166 |
| H | 3.47011124 | 0.32104530 | 0.16332088 |
| H | 4.49792613 | -0.91357553 | -0.55747842 |
| H | 4.84619201 | -0.33939739 | 1.06601940 |
| C | 4.00466356 | -2.94148196 | 1.21193557 |
| H | 4.79714286 | -2.73362952 | 1.92744126 |
| H | 4.47861806 | -3.27268142 | 0.28539127 |
| H | 3.40603400 | -3.76655622 | 1.58359358 |
| C | 0.90718956 | -3.64852268 | 3.89095670 |
| H | 1.25498472 | -2.67271762 | 4.22905081 |
| C | -0.22072520 | -4.06527692 | 4.85587920 |
| H | -1.16213275 | -3.57510042 | 4.63332938 |
| H | 0.07021165 | -3.78634162 | 5.87057510 |
| H | -0.38058702 | -5.14072260 | 4.84766861 |
| C | 2.07949968 | -4.62294521 | 4.06285242 |
| H | 1.78316219 | -5.64516455 | 3.83238618 |
| H | 2.39657309 | -4.60668632 | 5.10772653 |
| H | 2.93450152 | -4.36383187 | 3.44507962 |
| C | 0.02614713 | -4.56673789 | 1.60221306 |

| | | | |
|---|---|---|---|
| H | -0.51536792 | -4.09475958 | 0.79570921 |
| C | 1.16960944 | -5.34678031 | 0.94339905 |
| H | 1.80679801 | -4.68998847 | 0.35373057 |
| H | 0.74060282 | -6.07814337 | 0.25598585 |
| H | 1.78661526 | -5.88544344 | 1.66081780 |
| C | -0.97690105 | -5.51817758 | 2.25907754 |
| H | -0.51603626 | -6.18369580 | 2.98852085 |
| H | -1.40160645 | -6.14351838 | 1.47225735 |
| H | -1.79683465 | -4.98452422 | 2.73482434 |
| C | 0.28452152 | 4.55451222 | -1.52241078 |
| H | 1.25736752 | 5.03498880 | -1.61812084 |
| C | -0.71128960 | 5.44476333 | -2.27055262 |
| H | -0.45437002 | 5.53663230 | -3.32392613 |
| H | -0.69970065 | 6.44185003 | -1.82682100 |
| H | -1.73165726 | 5.06855827 | -2.20198468 |
| C | -0.04793197 | 4.48878402 | -0.02742579 |
| H | -1.03152036 | 4.05336950 | 0.15254335 |
| H | -0.05454046 | 5.49559905 | 0.39505711 |
| H | 0.68527954 | 3.89614205 | 0.51564931 |
| C | 1.88405827 | 2.79973245 | -2.42821533 |
| H | 1.83965926 | 1.74920347 | -2.71030841 |
| C | 2.48721114 | 3.57954989 | -3.60334651 |
| H | 1.92494096 | 3.43027883 | -4.52136603 |
| H | 3.51076838 | 3.24266941 | -3.77668567 |
| H | 2.52757855 | 4.65129400 | -3.39808274 |
| C | 2.79983151 | 2.90757710 | -1.20358809 |
| H | 2.98881392 | 3.94545307 | -0.92401459 |
| H | 3.76462536 | 2.45469635 | -1.43705419 |
| H | 2.37769997 | 2.38760345 | -0.34739969 |
| C | -0.77047631 | 2.32385216 | -5.07256012 |
| H | 0.17096146 | 1.90572483 | -4.70758115 |
| C | -0.41998831 | 3.62591676 | -5.80825369 |
| H | -1.26876967 | 4.02967480 | -6.35605327 |
| H | 0.37172750 | 3.42813770 | -6.53415199 |
| H | -0.06623411 | 4.39019895 | -5.12033239 |
| C | -1.33390435 | 1.28554106 | -6.04789026 |
| H | -1.54285543 | 0.34055024 | -5.55245564 |
| H | -0.59249144 | 1.10317372 | -6.82705077 |
| H | -2.24160356 | 1.63662346 | -6.54013803 |
| C | -3.09480028 | 2.55727429 | -4.00210561 |
| H | -3.36375148 | 1.65136491 | -4.54963554 |
| C | -3.87313389 | 2.50268315 | -2.68540179 |
| H | -3.63650906 | 1.62365055 | -2.08946567 |
| H | -4.93434717 | 2.44639714 | -2.92935636 |

| | | | |
|---|---|---|---|
| H | -3.72937904 | 3.39957895 | -2.07971302 |
| C | -3.57098228 | 3.76900352 | -4.81341206 |
| H | -3.26418382 | 4.70282263 | -4.33968022 |
| H | -4.66081790 | 3.75627457 | -4.87039915 |
| H | -3.19419862 | 3.76245113 | -5.83273852 |
| B | -2.11718109 | -1.41621259 | 2.91398636 |
| H | -2.21813409 | -2.55703779 | 2.67276184 |
| B | -1.23016390 | -0.75686175 | 4.30025805 |
| H | -1.74421001 | 2.66281709 | -1.46832460 |
| B | -0.36837327 | 0.68931234 | 3.77172403 |
| H | 0.68521928 | 0.95615363 | 4.20699076 |
| B | -0.68741118 | 0.91340064 | 2.04753395 |
| H | 0.11556992 | 1.24143384 | 1.25975619 |
| B | -3.30500312 | -0.21684593 | 2.37657859 |
| H | -4.25027543 | -0.60086600 | 1.79032454 |
| B | -2.97407991 | -0.46164889 | 4.11041729 |
| H | -3.76409436 | -0.98374837 | 4.81665244 |
| B | -1.89540027 | 0.85181524 | 4.64257226 |
| H | -1.89866884 | 1.26294284 | 5.75085014 |
| B | -1.54525203 | 1.89140479 | 3.23810076 |
| H | -1.30291733 | 3.04552518 | 3.32342036 |
| B | -2.42135409 | 1.23015046 | 1.84719620 |
| H | -2.77250542 | 1.82936336 | 0.89577619 |
| B | -3.17292900 | 1.18855045 | 3.45177411 |
| H | -4.11604287 | 1.85605494 | 3.70006372 |
| B | 0.52433127 | -0.11701455 | -1.15988906 |
| H | 1.39797430 | 0.46734755 | -0.62160084 |
| B | -0.21082160 | -1.67033658 | -0.04780487 |
| B | -1.92543747 | -2.40143618 | -0.25461921 |
| H | -2.47805478 | -3.22838885 | 0.38993906 |
| B | -2.50442076 | -0.81797387 | -0.94831332 |
| H | -3.58784081 | -0.33391268 | -0.90574697 |
| B | 0.30597605 | -0.59677203 | -2.91572644 |
| H | 1.00763053 | -0.38955253 | -3.85395419 |
| B | 0.70944340 | -1.79216497 | -1.62965683 |
| H | 1.77500517 | -2.31768827 | -1.63455882 |
| B | -0.63265876 | -2.92836278 | -1.33894038 |
| H | -0.40171176 | -4.09033052 | -1.32270569 |
| B | -2.11461984 | -2.14896386 | -2.00945580 |
| H | -2.97665410 | -2.71771017 | -2.59558903 |
| B | -1.54750402 | -0.56678445 | -2.71505950 |
| H | -2.23132095 | -0.23310092 | -3.62377028 |
| B | -0.56387635 | -2.11897092 | -2.86908863 |
| H | -0.40998382 | -2.79634880 | -3.83003611 |