Supporting information

for

Diverse chemistry of the [*closo*-B$_9$H$_9$]$^{2-}$: Synthesis and reactivity of its monoanionic derivative [*arachno*-B$_9$H$_{12}$-4,8-Cl$_2$]$^-$

Florian Schlüter[a], Eduard Bernhardt[a]*, Konstantin Zhizhin[b].

AUTHOR ADDRESS

[a] Fakultät für Mathematik und Naturwissenschaften, Anorganische Chemie, Bergische

Universität Wuppertal, Gaußstr. 20, 42119 Wuppertal, Germany, Fax: +49 202 439 3503, e-mail:

edbern@uni-wuppertal.de

[b] Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,

Moscow 119991, Russia, e-mail: zhizhin@igic.ras.ru

KEYWORDS: Boron clusters, Protonation, Reactivity, X-ray diffraction.

Materials and Apparatus

All the chemicals were obtained commercially. The commercial solvents were dried by distillation and stored in the flasks equipped with valves with PTFE stems (Young, London) over molecular sieves (4 Å) under argon. $Cs_2[closo\text{-}B_9H_9]$ was prepared as described elsewhere [S1].

The multinuclear NMR experiments were measured from CD_2Cl_2 solutions with a Bruker ARX 400 spectrometer (400.13 MHz for ^1H, 128.38 MHz for ^{11}B and 161.97 MHz for ^{31}P). $SiMe_4$ ($\delta_{^1H} = 0$ ppm), $BF_3 \cdot OEt_2$ ($\delta_{^{11}B} = 0$ ppm) and 85 % H_3PO_4 ($\delta_{^{31}P}$) = 0 ppm) were used as the external standards.

Theoretical Calculations

Quantum chemical calculations were performed to support the experimental results. DFT calculations [S2] were carried out with the B3LYP-Method [S3–S5]. The 6-311++G(d,p) basis set was used as implemented in the Gaussian03 program suite [S6]. The shielding constants (GIAO) [S7–S11] and the coupling constants were calculated as described in literature [S12–S15]. Intrinsic reaction path (IRC) calculations were performed for all transition states [S16 and S17].

Supporting Information References

S1. F. Klanberg and E.L. Muetterties, "Chemistry of Boranes. XXVII. New Polyhedral Borane Anions, $B_9H_9^{2-}$ and $B_{11}H_{11}^{2-}$", Inorg. Chem., 1966, 5(11), 1955-1960

S2. W. Kohn and L.J. Sham, "Self-Consistent Equations Including Exchange and Correlation Effects", Phys. Rev., 1965, 140(4), A1133-A1138

S3. A.D. Becke, "Density-functional exchange-energy approximation with correct asymptotic behavior", Phys Rev. A, 1988, 38(6), 3098-3100

S4. C. Lee, W. Yang, and R.G. Parr, "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density", Phys Rev. B, 1988, 37(2), 785-789.

S5. A.D. Becke, "Density-functional thermochemistry. III. The role of exact exchange", J. Chem. Phys., 1993, 98(7), 5648-5652.

S6. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A.M. Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A.

Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, and J.A. Pople, Gaussian 03, Revision B.05; 2003.

S7. F. London, "Theorie quantique des courants interatomiques dans les combinaisons aromatiques", J. Phys. Radium, 1937, 8(10), 397-409.

S8. R. McWeeny, "Perturbation Theory for the Fock-Dirac Density Matrix", Phys Rev., 1962, 126(3), 1028-1034.

S9. R. Ditchfield, "Self-consistent perturbation theory of diamagnetism I. A gauge-invariant LCAO method for N.M.R. chemical shifts", Mol. Phys., 1974, 27(4), 789-807.

S10. K. Wolinski and A.J. Sadlej, "Self-consistent perturbation theory Open-shell states in perturbation-dependent non-orthogonal basis sets", Mol. Phys., 1980, 41(6), 1419-1430.

S11. K. Wolinski, J.F. Hinton, and P. Pulay, "Efficient Implementation of the Gauge-Independent Atomic Orbital Method for NMR Chemical Shift Calculations", J. Am. Chem. Soc., 1990, 112(23), 8251-8260.

S12. T. Helgaker, M. Watson, and N.C. Handy, "Analytical calculation of nuclear magnetic resonance indirect spin–spin coupling constants at the generalized gradient approximation and hybrid levels of density-functional theory", J. Chem. Phys., 2000, 113(21), 9402-9409.

S13. V. Sychrovsky, J. Gräfenstein, and D. Cremera, "Nuclear magnetic resonance spin–spin coupling constants from coupled perturbed density functional theory", J. Chem. Phys., 2000, 113(9), 3530-3547.

S14. V. Barone, J.E. Peralta, R.H. Contreras, and J.P. Snyder, "DFT Calculation of NMR JFF Spin-Spin Coupling Constants in Fluorinated Pyridines", J. Phys. Chem. A, 2002, 106(23), 5607-5612.

S15. J.C. Rienstra-Kiracofe, G.S. Tschumper, H.F.S. III, S. Nandi, and G.B. Ellison, "Atomic and Molecular Electron Affinities: Photoelectron Experiments and Theoretical Computations", Chem. Rev., 2002, 102(1), 231-282.

S16. C. Gonzalez and H.B. Schlegel, "An improved algorithm for reaction path following", J. Chem. Phys., 1989, 90(4), 2154-2161.

S17. C. Gonzalez and H.B. Schlegel, "Reaction Path Following in Mass-Weighted Internal Coordinates", J. Phys. Chem. A, 1990, 94(14), 5523-5527.