Supplementary material

Synthesis

All steps of the synthesis are executed under exclusion of air and humidity in an atmosphere of protective gas. For the preparation of [Li(NH3)4]2[B6H6]2 NH3, 0.092 g of dried [N(C4H9)4]B6H7 (1.6 mmol) and 0.012 g of distilled lithium (1.6 mmol) were put in a Schlenk vessel, and approximately 20 mL dried ammonia were condensed at -78 °C. This resulted in a deep-blue solution. After 10 days at -38 °C, colourless, air- and temperature sensitive cubic crystals were obtained.

Computational Details

For all calculations the Gaussian03 [ref#1] program system has been used. For calculations of energies and gradients the Møller-Plesset perturbation theory 2nd order (MP2) [ref#2] has been employed and the standard basis set 6-311+G(2d,2p) [ref#3] has been used for all atoms. For calculations of the anion [B6H6]2- and the contact ion pair [(Li(NH3)4)2][B6H2]2- the initial coordinates have been taken from X-ray structure analysis data without symmetry constraints and were fully optimized. Calculations of bond critical points and topological analysis have been performed using the AIM2000 program. [ref#4]

Figure1: Graphical representation of the optimized structure of the contact ion pair [(Li(NH3)4)2][B6H2]2-.