Figure 1S. Graphical inter-comparison of the experimental \(^{11}\)B NMR chemical shifts (given as \(\delta^{(11)}B/^{1}J_{BH}\) in Hz, where possible) (Et\(_3\)NH\(^+\) salts in CD\(_3\)CN) and relative intensities in individual cage positions for the more stable tautomers of structure 2\(^-\) (for numbering see Scheme 1).
Experimental Section

Materials and Methods. All synthetic procedures were performed under Ar atmosphere. CH$_3$CN (CD$_3$CN) and Et$_3$N were distilled over CaH$_2$ and Na, respectively. The starting carboranes of structures 1 have been prepared according to literature.$^1$ NMR spectroscopy was performed at 400 and 600 MHz (for $^1$H), inclusive of standard $^{11}$BB$_{11}$B-COSY$^2$ NMR experiments leading to complete assignments of all resonances to individual cage BH units. The assignment of the proton resonances has been done by using $^1$H($^{11}$Bselective) and 2D $[^1$H-$^{11}$B]-HMOC (150 and 25 Hz for σ–bonded and bridged hydrogen atoms, respectively) puls sequences. Chemical shifts are given in ppm to high-frequency (low field) of $\Xi = 32.083971$ MHz (nominally BF$_3 \times$Et$_2$O in CDCl$_3$) for $^{11}$B (quoted ± 0.5 ppm), $\Xi = 25.144$ MHz for $^{13}$C (quoted ± 0.5 ppm), and $\Xi = 100$ MHz for $^1$H (quoted ± 0.05 ppm), $\Xi$ is defined as in reference$^3$ and the solvent resonances were used as internal secondary standards.

2a: $^1$H NMR (600 MHz, CD$_3$CN, 297K), δ = -4.31 (µ-H$^{8,9}$), 0.23 (H4), 0.86 (H2), 1.30 (H3), 1.74 (H10), 2.69 (H1), 2.73 (H8), 3.19 (H7), 3.48 (CH5), 3.57 (H9), 4.59 (CH6).

2b: $^1$H NMR (600 MHz, CD$_3$CN, 297K), δ = -4.22 (µ-H$^{8,9}$), 0.01 (H4), 0.71 (H2), 1.38 (H3), 1.67 (Me), 1.82 (Me), 2.64 (H8), 2.88 (H1), 2.90 (H7), 3.25 (H9).

2c: $^1$H NMR (600 MHz, CD$_3$CN, 297K), δ = -3.64 (µ-H$^{8,9}$), 0.43 (H4), 1.76 (H2), 1.84 (H10), 1.93 (H3), 2.03 (H1), 3.00 (H8), 3.18 (H7), 3.82 (H9), 7.15 (t, 1H, Ph, $^3J(^1$H, $^1$H) = 7.6 Hz), 7.23 (m, 2H, Ph), 7.41 (d, 2H, Ph, $^3J(^1$H, $^1$H) = 7.8 Hz). $^{13}$CNMR (150.9 MHz, CD$_3$CN, 297K), δ = 144.7-126.8 (6 C, Ph), 80.4 (C5), 121.3 (C6).

Theoretical calculations. The geometries of 2a, 2b and 3a, 3b were optimized using Gaussian09$^4$ with the combination of the method and basis set mentioned, the character of each stationary point being verified by frequency calculations. Their magnetic shieldings were calculated by running GIAO jobs with a TZP basis set II by Huzinaga$^5$ which is well designed for these purposes. The hydrogen migration was also examined with Gaussian09, using the B3LYP/6-31+G* model. Note that DFT computational protocols employed for the mechanistic purpose provide almost identical results with those using the MP2 approach.$^6$
**X-ray Crystallography.** The X-ray data for tautomeric dicarbaborane anions 2d\(^-\) and 3b\(^-\) were obtained at 150K using Oxford Cryostream low-temperature device and a Nonius KappaCCD diffractometer with MoK\(_\alpha\) radiation (\(\lambda = 0.71073\) Å), a graphite monochromator, and the \(\phi\) and \(\chi\) scan mode. Data reductions were performed with DENZO-SMN.\(^7\) The absorption was corrected by integration methods.\(^8\) Structures were solved by direct methods (SIR92)\(^9\) and refined by full matrix least-squares based on \(F^2\) (SHELXL97).\(^10\) Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors \(H_{iso}(\text{pivot atom}) = 1.2U_{eq}\) or of 1.5\(U_{eq}\) (methyl). H atoms in methyl, methylene and hydrogen atoms in aromatic rings were placed with CBH distances of 0.96, 0.97 and 0.93Å, and 1.1Å for B-H and C-H bonds in the carborane cage.

Crystallographic data for 2d\(^-\): \(\text{C}_8\text{H}_{15}\text{B}_8\cdot\text{C}_4\text{H}_{12}\)N\(^+\), \(M = 271.82\), orthorhombic, \(P2_12_12_1\), \(a = 9.3751(5)\)Å, \(b = 11.7200(8)\)Å, \(c = 15.5900(8)\)Å, \(\beta = 90^\circ\), \(Z = 4\), \(V = 1712.96(17)\)Å\(^3\), \(D_\text{c} = 1.054\) g.cm\(^{-3}\), \(\mu = 0.053\) mm\(^{-1}\), \(\text{R}_{\text{int}} = 0.0856\), \(25625\) reflections measured (\(\theta_{\text{max}} = 26.996^\circ\)), \(3702\) independent (\(R_{\text{int}} = 0.0856\)), \(2828\) with \(I > 2\sigma(I)\), \(190\) parameters, \(S = 1.056\), \(R_1(\text{obs. data}) = 0.0590\), \(wR_2(\text{all data}) = 0.1264\); max., min. residual electron density = 0.230, \(B_{0.241}\) eÅ\(^{-3}\). Crystallographic data for 3b\(^-\): \(\text{C}_4\text{H}_{15}\text{B}_8\cdot\text{NC}_6\text{H}_{16}\)\(^+\), \(M = 251.84\), triclinic, \(P\overline{1}\), \(a = 7.4490(8)\)Å, \(b = 7.8910(11)\)Å, \(c = 14.8260(17)\)Å, \(\alpha = 88.895(12)^\circ\), \(\beta = 82.014(10)^\circ\), \(\gamma = 75.824(9)^\circ\), \(Z = 2\), \(V = 836.64(18)\)Å\(^3\), \(D_\text{c} = 1.000\) g.cm\(^{-3}\), \(\mu = 0.049\) mm\(^{-1}\), \(\text{R}_{\text{int}} = 0.1047\), \(15715\) reflections measured (\(\theta_{\text{max}} = 27.499^\circ\)), \(3804\) independent (\(R_{\text{int}} = 0.1047\)), \(2573\) with \(I > 2\sigma(I)\), \(180\) parameters, \(S = 1.070\), \(R_1(\text{obs. data}) = 0.0777\), \(wR_2(\text{all data}) = 0.1662\); max., min. residual electron density = 0.468, \(B_{0.492}\) eÅ\(^{-3}\). Crystallographic data for structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC deposition no. 1489175 for 2d\(^-\) and no 1452184 for 3b\(^-\). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

**References to SI**