Symmetric and asymmetric 13-vertex bimetallacarboranes by polyhedral expansion

Maria Elena Lopez, Michael J. Edie, David Ellis, Anke Horneber, Stuart A. Macgregor, Georgina M. Rosair and Alan J. Welch

Electronic Supplementary Information

† Experimental procedures: synthesis of 1: A THF solution of 0.5 mmol of [Ru(p-cymene)Cl₂]₂ was added to a THF solution of 1 mmol of Li₂[7,8-C₂B₉H₁₁] at −78°C. The reaction was allowed to warm to RT and stirred overnight. The crude mixture was filtered and purified by silica gel column chromatography, isolating one major yellow compound, 1. Yield 0.270 g (73%). ¹H NMR (200 MHz, CDCl₃, throughout): δ 5.90-5.70 (m, 4H, C₆H₄), 3.70 (br s, 2H, CHcage), 2.75 (septet, 1H, CMe₂H), 2.24 (s, 3H, CH₃), 1.20 (d, 6H, CMe₂H). ¹¹B-{¹H} NMR (128 MHz, CDCl₃, throughout): δ 1.87 (1B), 0.34 (1B), -7.68 (2B), -9.17 (2B), -19.54 (2B), -24.23 (1B). Mass spectrometry: m/z envelope centred on 367 (M⁺).

Satisfactory microanalytical data were obtained for all compounds reported.

Synthesis of 2: A THF solution of 0.73 mmol of 1 was reduced with 5 equivalents of sodium over 18 hours then metallated with 0.37 mmol of [Ru(p-cymene)Cl₂]₂ at -78°C. The crude mixture was allowed to warm, stirred overnight, filtered and purified by silica gel column chromatography, to isolate one major orange compound, 2. Yield 0.220 g (50%). ¹H NMR: 5.60-5.50 (m, 8H, cym), 3.70 (br s, 2H, CHcage), 2.75 (septet, 2H, CMe₂H), 2.12 (s, 6H, CH₃), 1.18 (d, 12H, CMe₂H). ¹¹B-{¹H} NMR: δ 12.54 (2B), -2.00 (4B), -5.26 (3B). Mass spectrometry: m/z envelope centred on 605 (M⁺).

Computational details: Gaussian 03, Revision C.02 employing the BP86 functional. 6-31G** basis sets were used for B and H atoms. The closo-[B₁₃H₁₃]⁻ was optimised with no

---

symmetry constraints and converged on a structure with effective $C_2\nu$ symmetry. This was subsequently confirmed as a local minimum via analytical frequency calculations.
