

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]¹ 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, CH_{cage}), 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, CH_{cage}), 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⁺).

Synthesis of **4**, **5**, **7**, **8** and **9**: Similarly, 2 mmol of 3-Cp-3,1,2-*closo*-CoC₂B₉H₁₁ was reduced and treated with 6 mmol of NaCp and 8 mmol of CoCl₂ at -78°C. Purification by column then thin layer chromatography (Et₂O:40-60 petrol, 3:2) revealed a complex mixture of compounds **4**, **5**, **7**, **8** and **9**. Compound **4**: Green, R_f 0.71, 0.122 g (16%). ¹H NMR: δ 5.32 (s, 10H, Cp), 2.62 (br s, 2H, CH_{cage}). ¹¹B-{¹H} NMR: δ 25.30 (3B), 8.75 (4B), 2.99 (3B). Mass spectrometry: *m/z* envelope centred on 380 (M⁺). Compound **5**: Green, R_f 0.26, 0.060 g (8%). ¹H NMR: δ 5.25 (s, 5H, Cp), 5.03 (s, 5H, Cp), 2.92 (br s, 1H, CH_{cage}), 2.79 (br s, 1H, CH_{cage}). ¹¹B-{¹H} NMR: δ 16.02 (3B), 12.35 (1B), 6.44 (1B), 1.65 (1B), -2.68 (2B), -10.52 (1B). Mass spectrometry: *m/z* envelope centred on 381 (M⁺). Compound **7**: Orange, R_f 0.35, trace. ¹H NMR: δ 5.38 (s, 10H, Cp), 5.27 (s, br, 2H, CH_{cage}). ¹¹B-{¹H} NMR: δ 19.24 (2B), -1.81 (4B), -8.85 (2B). Mass spectrometry: *m/z* envelope centred on 368 (M⁺). Compound **8**: Blue, R_f 0.30, trace. Mass spectrometry: *m/z* envelope centred on 369 (M⁺). Compound **9**: Orange, R_f 0.18, trace. ¹¹B-{¹H} NMR: δ -6.99 (2B), -8.33 (2B), -9.24 (2B), -11.95 (4B). Mass spectrometry: *m/z* envelope centred on 396 (M⁺).

Synthesis of **6**: **2** (0.36 mmol) was dissolved in oxygen-free tetra(ethyleneglycol)dimethylether (dried by distillation over Na metal) and heated to 150°C for 40 hours. Solvent was removed and the product isolated by crystallisation from DCM:petrol, 1:4. Yield 0.170 g (80%). ¹H NMR: δ 5.60 (m, 4H, cym), 5.35 (m, 4H, cym), 2.75 (septet, 1H, CMe₂H), 2.65 (septet, 1H, CMe₂H), 2.6-2.8 (br, 2H, CH_{cage} overlapped by septets), 2.15 (s, 3H, CH₃), 2.08 (s, 3H, CH₃), 1.22 (d, 6H, CMe₂H), 1.18 (d, 6H, CMe₂H). ¹¹B-{¹H} NMR: δ 6.55 (3B), 0.74 (2B), -6.14 (1B), -12.07 (2B), -16.78 (1B). Mass spectrometry: *m/z* envelope centred on 604 (M⁺).

Computational details: Gaussian 03, Revision C.02² employing the BP86 functional. 6-31G** basis sets were used for B and H atoms.³ *closo*-[B₁₃H₁₃]²⁻ was optimised with no

¹ J. S. Roscoe, S. Kongpricha and S. Papetti, *Inorg. Chem.*, 1970, 9, 1561.

² Gaussian 03, Revision C.02. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, 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.

symmetry constraints and converged on a structure with effective C_{2v} symmetry. This was subsequently confirmed as a local minimum via analytical frequency calculations.

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, Inc., Wallingford CT, 2004.

³ (a) W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257; (b) P. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.