Synthesis and characterization of the nine-atom, rhena- and tungsta-boranes $(Cp^*Re)_2B_7H_7$ and $(Cp^*W)_2B_7H_9$, Cp* = η^5-C_5Me_5. Molecular mimics of hypoelectronic main-group clusters in Zintl phases

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Geometric and molecular orbital analyses of the metallaboranes $(Cp^*Re)_2B_7H_7$ and $(Cp^*W)_2B_7H_9$, which display unusual, but identical, core structures and skeletal electron pair counts of $n - 2$, demonstrate a close connection between these molecular compounds and anionic, hypoelectronic main-group clusters found in the solid state.

The chemistry of metallaborane complexes is dominated by two-valence electron fragments of Group 8 and Group 9 metals[1–3] such as $\{Fe(CO)_3\}$ or {CoCp}, Cp = η^5-C_5H_5, in which the metal fragment replaces a boron vertex in the resulting metallaborane.[4] The fact that transition-metal halides, $[Cp^*MCl_n]_m$, Cp* = η^5-C_5Me_5, react with monoboron reagents to yield metallaboranes[5] permits the synthesis of compounds containing earlier transition metals (M = Ta,[6] Cr,[7] Mo[8] and W[9,10]). We anticipated that the lower number of valence electrons and higher frontier orbital energies of such fragments would lead to unusual behavior. Indeed, in small clusters the metal center introduces unsaturation on the bonding network supported, in part, by the relatively higher energy metal functions.[6–8] Alternatively, when more boron atoms are available, highly capped structures result.[9] Moving to Group 7 transition metals[11,12] we now report the synthesis of the first example of a dirhenaborane, which displays an unprecedented nine-atom molecular structure. For support, the nearly isostructural and isoelectronic tungsten analog is also described.

Addition of BH_3·thf to Cp^*ReCl_4[13] at room temperature and subsequent gentle heating affords the pale yellow rhenaborane $(Cp^*Re)_2B_7H_7$ **1** in good yield after chromatographic work-up.† Its red, isostructural and isoelectronic partner, $(Cp^*W)_2B_7H_9$ **2** is formed as a minor product during the pyrolysis of $Cp^*WH_3B_4H_8$ in toluene.‡[9] Both compounds **1** and **2** have been fully characterized by single-crystal X-ray diffraction, ^{11}B and ^{1}H NMR spectroscopy and high-resolution mass spectrometry. The ^{11}B NMR spectra of **1** and **2** display four signals in the ratio 1 : 2 : 2 : 2, distributed over an unusually large[14] chemical shift range of ≈ 100 ppm. In addition to signals due to Cp* and BH_t groups, the ^{1}H NMR spectrum of **2** displays a broad integral two resonance at δ −8.9 in the region associated with μ or μ_3 B–H–M groups while for **1** the high-field region is featureless.

The solid-state molecular structures of compounds **1** and **2** are shown in Fig. 1.§ Both feature similar structural cores, although the structural motif is not one anticipated for a nine-atom cluster *e.g.* tricapped trigonal prism. Compound **1** has effective C_{2v} symmetry, while the presence of the two μ_3 B–H–W hydrogen atoms affords **2** with approximate C_2 symmetry. The metal–metal distances of 2.7875(6) in **1** and 2.9522(8) Å in **2**, both fall in the range associated with their respective M–M single bonds.[15] The seven skeletal electron pairs (sep) associated with **1** and **2** are three less than expected for a normal nine-vertex *closo* cluster.[16] Hence, we have explored the geometric and electronic factors responsible.

Fenske–Hall calculations[17,18] on the Cp analogs of **1** and **2** show a large HOMO–LUMO gap for both compounds consistent with the observed stability and electron count. The respective HOMOs are metal–metal bonding and their unfilled antibonding partners are found to higher energy. Further confirmation of a metal–metal bond is provided by Mulliken overlap populations of 0.12 and 0.13 for **1** and **2**, respectively. Corbett has described examples of hypoelectronic main-group clusters in Zintl phases[19] with accompanying non-standard deltahedral structures. Distortion of the standard deltahedron for a given *closo* *n*-atom skeleton to that observed leads to a reduced number of low-energy cluster bonding orbitals thereby supporting the low sep count found. In a similar spirit, we note that the observed geometry of **1** (and **2**) may be generated by a 45° rotation of one of the square pyramidal faces of a tricapped trigonal prism around its C_2 axis thereby converting the four

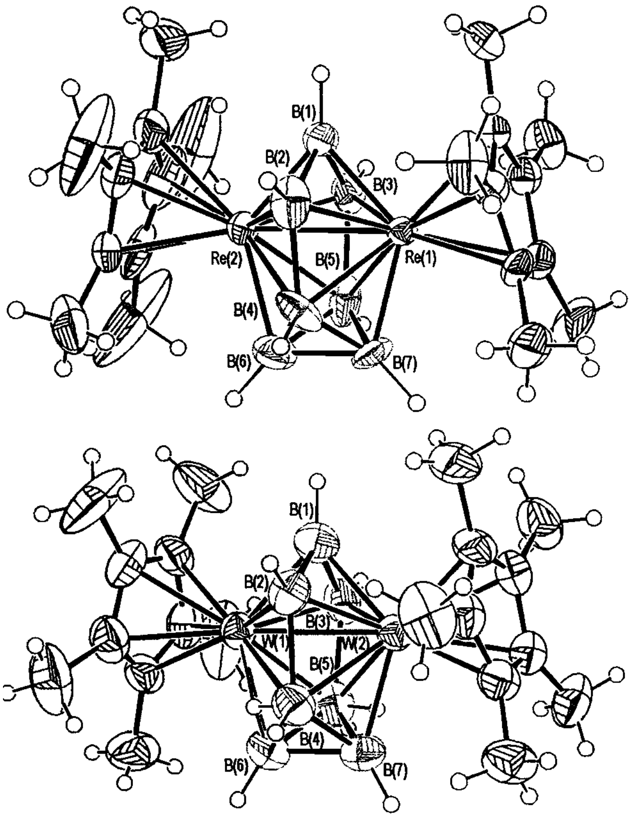
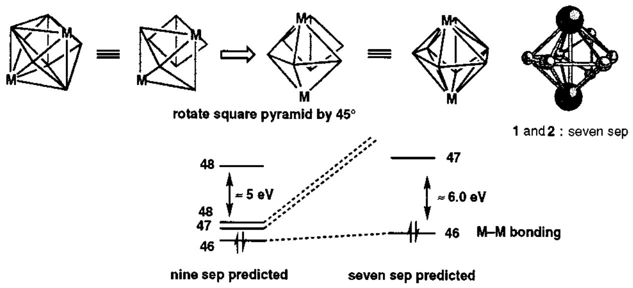


Fig. 1 The molecular structure of $(Cp^*Re)_2B_7H_7$ **1** (top) and $(Cp^*W)_2B_7H_9$ **2** (bottom). Selected bond distances (Å) for **1**: Re(1)–Re(2) 2.7875(6), Re(1)–B(1) 2.053(13), Re(1)–B(2) 2.14(2), Re(1)–B(3) 2.12(2), Re(1)–B(4) 2.231(14), Re(1)–B(5) 2.28(2), Re(1)–B(7) 2.116(14), B(1)–B(2) 1.81(2), B(2)–B(4) 1.80(2), B(3)–B(5) 1.85(3), B(5)–B(6) 1.69(3), B(6)–B(7) 1.70(2). Selected bond distances (Å) for **2**: W(1)–W(2) 2.9522(8), W(1)–B(1) 2.154(14), W(1)–B(3) 2.160(12), W(1)–B(6) 2.209(15), W(1)–B(2) 2.268(14), W(1)–B(5) 2.285(14), W(1)–B(4) 2.441(15), B(1)–B(2) 1.809(19), B(2)–B(4) 1.937(19), B(3)–B(5) 1.89(2), B(5)–B(6) 1.75(2), B(6)–B(7) 1.74(2).



Scheme 1

five-connect vertices of the square base into two four- and two six-connect vertices (Scheme 1). Inclusion of a metal–metal bond generates the observed structure. We have successfully modeled this distortion for **1**. On moving from a hypothetical neutral Re_2B_7 tricapped trigonal prism with a Re–Re bond to the observed structure, two low lying orbitals move to higher energy, thereby accounting for the observed sep count of $n - 2$. Alternatively, the observed structure can be rationalized by inserting a {BH} fragment into a B–B bond of a hypothetical dodecahedral $Cp^*_2Re_2B_6H_6$ cluster. Note that the observed geometry accommodates the electropositive metal centers in high connectivity cluster vertices as well as the propensity for both rhenium and tungsten to form metal–metal bonds.

Compounds **1** and **2** can thus be described as molecular metallaborane counterparts of hypoelectronic main-group cluster Zintl phases. Of course, they possess different properties being neutral (no cations or high cluster charges), molecular (soluble in aliphatic solvents) and modestly air-stable. Full details as well as related chemistry will appear in due course.

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Notes and References

† Reaction of Cp^*ReCl_4 (0.06 g, 0.130 mmol) with BH_3·thf (6 equiv.) for 16 h at 45 °C in toluene, followed by removal of volatiles *in vacuo* and purification by chromatography (toluene–hexane 1 : 2) afforded moderately air-stable, pale yellow, $(Cp^*Re)_2B_7H_7$ **1** (0.036 g, 0.497 mmol, 66% yield based on Re). *Spectroscopic data* for **1**: MS (FAB, NBA matrix), $M^+ = 728$, 2 Re, 7 B, 20 C atoms, calc. *m/z* 728.2662, obs. 728.2676. ^{11}B NMR (C_6D_6, 21 °C) [$J(^{11}B–^{1}H)$ in parentheses]: δ 101.7 [d, 1 B (169 Hz)], 85.6 [d, 2 B (164 Hz)], 82.1 [d, 2 B (164 Hz)], 3.6 [d, 2 B (166 Hz)]. ^1H NMR (C_6D_6, 21 °C): δ 11.21 [partially collapsed quartet (pcq), 2 H (162 Hz)], 10.12 [pcq, 1 H (167 Hz)], 8.63 [pcq, 2 H (173 Hz)], 1.92 (s, 30 H, Cp*), −0.04 [pcq, 2 H (166 Hz)].

‡ Pyrolysis of $Cp^*WH_3B_4H_8$ in toluene at 110 °C for 20 min afforded $(Cp^*W)_2B_7H_9$ **2** in low yield (5%) after preparative thin-layer chromatography as an inseparable mixture with $(Cp^*W)_3(\mu\text{-}H)B_8H_8$. *Spectroscopic data* for **2**: MS (FAB), $M^+ = 723$, 2 W, 7 B, 20 C atoms, calc. *m/z* 723.2785, obs. 723.2773. ^{11}B NMR (C_6D_6, 21 °C): δ 99.0 [d, 1 B (147 Hz)], 83.5 [d, 2 B (153 Hz)], 46.6 [d, 2 B (158 Hz)], 17.6 [d, 2 B (136 Hz)]. ^1H NMR (C_6D_6, 21 °C): δ 10.40 [pcq, 2 H (146 Hz)], 10.15 [pcq, 1 H (143 Hz)], 5.98 [pcq, 2 H (156 Hz)], 2.23 [pcq, 2 H (136 Hz)], 2.04 (s, 30 H, Cp*), −8.88 (2 H, μ_3-H).

§ *Crystallographic data* for **1**, $C_{20}H_{37}B_7Re_2$, $M = 725.57$, tetragonal, $P4_2bc$, $a = 23.750(3)$, $b = 23.750(3)$, $c = 9.0035(7)$ Å, $U = 5078.7(10)$ Å^3, $Z = 8$, $\mu = 9.530$ mm^{-1}. 5079 independent reflections collected (293 K) and 3870 were observed [$I > 2\sigma(I)$]. $R_1 = 0.0388$, (wR_2 0.0855).

For **2**: $C_{20}H_{39}B_7W_2$, $M = 722.88$, monoclinic, $P2_1/n$, $a = 8.8158(17)$, $b = 18.068(5)$, $c = 16.623(4)$ Å, $\beta = 101.34(3)°$, $U = 2596.0(11)$ Å^3, $Z = 4$, $\mu = 8.860$ mm^{-1}. 4525 independent reflections collected (293 K) and 3835 were observed [$I > 2\sigma(I)$]. $R_1 = 0.0492$, (wR_2 0.1337). CCDC 182/941.

1 L. Barton and D. K. Srivastava in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, ch. 8.
2 J. D. Kennedy, *Prog. Inorg. Chem.*, 1984, **32**, 519.
3 J. D. Kennedy, *Prog. Inorg. Chem.*, 1986, **34**, 211.
4 T. P. Fehlner, *Struct. Bonding* (*Berlin*), 1997, **87**, 111.
5 Y. Nishihara, K. J. Deck, M. Shang and T. P. Fehlner, *J. Am. Chem. Soc.*, 1993, **115**, 12 224.
6 S. Aldridge, H. Hashimoto, M. Shang and T. P. Fehlner, *Chem. Commun.*, 1998, 207.
7 S. Aldridge, H. Hashimoto, K. Kawamura, M. Shang and T. P. Fehlner, *Inorg. Chem.*, 1998, **37**, 928.
8 S. Aldridge, M. Shang and T. P. Fehlner, *J. Am. Chem. Soc.*, 1998, **120**, 2586.
9 A. S. Weller, M. Shang and T. P. Fehlner, *J. Am. Chem. Soc.*, in press.
10 H. J.Bullick, P. D. Grebenik, M. L. H. Green, A. K. Hughes, J. B. Leach and P. C. McGowan, *J. Chem. Soc., Dalton Trans.*, 1995, 67.
11 S. J. Hildebrandt, D. F. Gaines and J. C. Calabrese, *Inorg. Chem.*, 1978, **17**, 790; D. F. Gaines and S. J. Hildebrandt, *Inorg. Chem.*, 1978, **17**, 794.
12 P. Kaur, S. D. Perera, T. Jelinek, B. Stibr, J. D. Kennedy, W. Clegg and M. Thornton-Pett, *Chem. Commun.*, 1997, 217; M. A. Beckett, M. Bown, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1988, 1969; M. A. Beckett, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1985, 1119.
13 W. A. Herrmann, E. Herdtweck, M. Flöel, J. Kulpe, U. Küsthardt and J. Okuda, *Polyhedron*, 1987, **6**, 1165.
14 C. E. Housecroft, *Adv. Organomet. Chem.*, 1991, **33**, 1.
15 See, for example, R. Poli, G. Wilkinson, M. Motevalli and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1985, 931; A. L. Rheingold and J. R. Harper, *Acta Crystallogr., Sect. C*, 1991, **47**, 184.
16 K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.
17 R. F. Fenske, *Pure Appl. Chem.*, 1988, **27**, 61.
18 M. B. Hall and R. F. Fenske, *Inorg. Chem.*, 1972, **11**, 768.
19 J. D. Corbett, *Struct. Bonding* (*Berlin*), 1997, **87**, 157.

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