

Preliminary communication

Reversible on/off switching of CH → Rh interactions
in rhodathiaboranes with “anomalous” electron counts. Synthesis
and molecular structure of $[(\text{Ph}_3\text{P})_2\text{N}][1\text{-dppe-1,2-closo-RhSB}_9\text{H}_9]$

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Abstract

Reconsideration of the “rule-breaking” rhodathiaborane 8,8-(Ph₃P)₂-8,7-*nido*-RhSB₉H₁₀, its 9-OEt and dppe analogues, reveals the existence of agostic CH → Rh (from PPh₃) bonding which accounts for its molecular structure. Deprotonation [H(9, 10) bridging proton] “switches off” this agostic bonding and affords a *closo* cluster. This structural change is fully reversible on reprotonation.

Keywords: CH → Rh interactions; Reversible switching; Synthesis

There is continuing interest in borane [1], heteroborane and related polyhedra whose molecular structures appear to be at variance with those expected by the application of the polyhedral skeletal electron pair (PSEP) theory [2]. One such species is 8,8-(Ph₃P)₂-8,7-*nido*-RhSB₉H₁₀, **1** [3] which has a *nido* 11-vertex (icosahedral) geometry and, seemingly, only 12 skeletal electron pairs, the electron contribution from the rhodium vertex being $v + x - 12 = 9 + 4 - 12 = 1e$. Similar apparently anomalous geometries are also observed in **2**, the 9-OEt analogue of **1** [4] and in 8-dppe-8,7-*nido*-RhSB₉H₁₀, **3** [5].

We have performed root-mean-square misfit calculations [6] on the {B(1-6)H₆} residues of **1–3** against similar fragments taken from well-defined icosahedra and octadecahedra (the geometry of these species anticipated by the PSEP theory). In every case the calculations confirm that the unexpected open structures observed really are better described as *nido* fragments of icosahedra. The confidence in the optimal structural description of these rhodathiaboranes gained from the results of the geometrical calculations has allowed us to recognise that an alternative interpretation of their structures, which does not contravene the PSEP expectation, is possible.

In every crystallographically-characterised case we

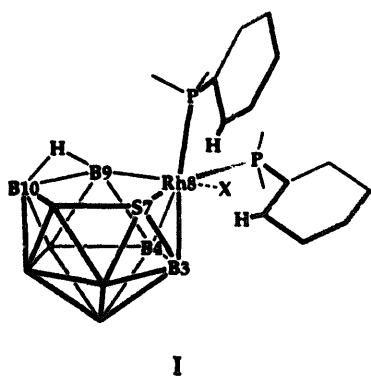
note that the {P₂Rh} fragment is markedly non-orthogonal to the plane through S(7)B(3)B(4)B(9) ¹ and that two *ortho* H atoms, one from each phosphine ligand, are located ca. 3 Å from the rhodium centre, with X, the mid-point of the H ··· H vector, constituting the third site of a pseudo-conical {RhP₂X} fragment which has P–Rh–X angles close to 90°.

We therefore propose the existence of two weak, nominally 1e, CH → Rh agostic interactions which furnish an additional electron pair to the metal centre and hence to the overall cluster electron count ^{2,3}. Thus, the skeletal electron contribution from the Rh vertex is now $v + x - 12 = 9 + 6 - 12 = 3e$, and the observed *nido* structures are fully in accord with expectation. Although agostic CH → M interactions normally involve a for-

¹ P₂Rh/SB₉ dihedral angles in **1** [3], **2** [4] and **3** [5] are 66.6, 68.6 and 55.5° respectively.

² Although two 1e agostic interactions are consistent with the crystallographically-determined structures, the preferred arrangement in solution may involve a single 2e CH → Rh bond, involving either just one phosphine ligand or both in a fluxional process. We thank Prof. K. Wade for this useful suggestion.

³ A notation for 1e agostic interactions is clearly required. We suggest CH → M.



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mally saturated CH function there are precedents for the *ortho* CH units of aryl phosphines acting as the source of an agostic bond [7].

Although all attempts to measure the agostic bonding in **1** and **3** directly have so far been frustrated, support for its existence derives from the structural and spectroscopic consequences of the deprotonation of these compounds via removal of the H(9, 10) bridging atom. Reaction (thf, -78°C) of **3** with 1 equiv. MeLi followed by addition of 1 equiv. $[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ (PPNCl) affords $\text{P}^-\text{N}[1\text{-dpepe-}1,2\text{-}closo\text{-RhSB}_9\text{H}_9]$, **4**, characterised by multinuclear NMR spectroscopy⁴. Compound **1** is also readily deprotonated by MeLi, and the product similarly characterised⁵ as $[\text{Me}_3\text{NCH}_2\text{Ph}]\{1,1\text{-}(\text{Ph}_3\text{P})_2\text{-}1,2\text{-}closo\text{-RhSB}_9\text{H}_9\}$, **5**. In their ^{11}B NMR spectra, salts **4** and **5** both display chemical shifts typical [8] of a *closo* 11-vertex 1,2-heteroborane cluster, and this geometry is confirmed by a crystallographic study⁶ on 4.0.5MeCN (Fig. 1), obtained as orange needles after recrystallisation from MeCN/Et₂O.

Thus the anionic *closo* rhodathiaboranes of **4** and **5**, derived from **3** and **1** respectively, have molecular structures which accord with the PSEP theory. These

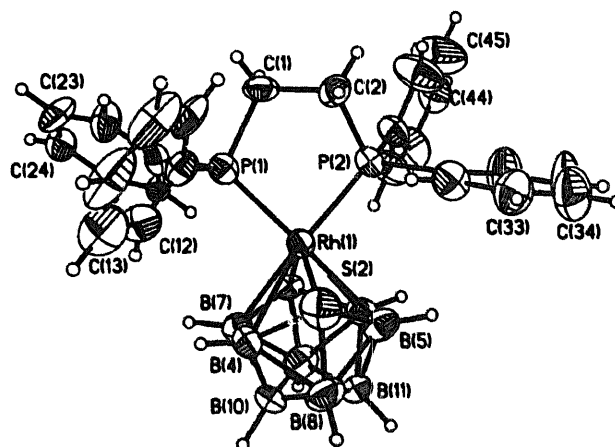
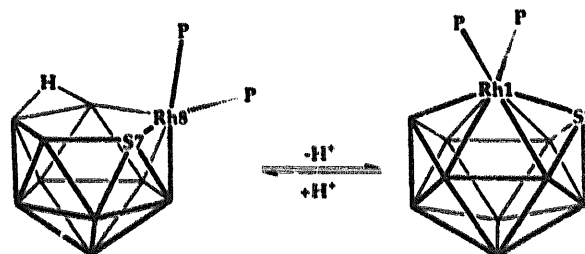


Fig. 1. Perspective view of the anion $[1\text{-dpepe-}1,2\text{-}closo\text{-RhSB}_9\text{H}_9]^-$ in **4**. Important molecular parameters (Ångstroms and degrees): Rh(1)–S(2) 2.379(3); Rh(1)–B(3) 2.168(13); Rh(1)–B(4) 2.460(12); Rh(1)–B(5) 2.405(14); Rh(1)–B(6) 2.35(2); Rh(1)–B(7) 2.400(14); Rh(1)–P(1) 2.260(4); Rh(1)–P(2) 2.243(3); P(1)–Rh(1)–P(2) 85.24(12). In the PPN⁺ cation: N(1)–P(3) 1.558(10); N(1)–P(4) 1.582(9); P(3)–N(1)–P(4) 146.4(7). No Rh...H distances < 3.3 Å.



Scheme 1.

reactions are fully reversible (Scheme 1) since addition of one drop of HBF_4 to a CD_2Cl_2 solution of **4** in an NMR tube immediately regenerates **3**.

Clearly, dramatic structural changes are effected by the removal and subsequent addition of zero-electron sources. We contend that the two 1e agostic interactions^{2,3} in **1–3** which are responsible for their "anomalous" electron counts are "switched off" in the anions of **4** and **5** by virtue of the overall negative charge, the change from 13 to 12 skeletal electron pairs resulting in a structural change from *nido* icosahedral to *closo* octadecahedral. This affords strong additional (albeit indirect) evidence of the existence of the agostic bond(s) in **1–3** which, we conclude, are therefore not examples of rule-breaking heteroboranes after all.

Acknowledgements

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⁴ ^1H NMR (200 MHz, CD_3CN): 7.90 (m br, 4H, Ph), 7.68–7.25 (m, 44H, Ph), 2.40 (m, 4H, CH_2). ^{11}B - ^1H NMR (128 MHz, CD_3CN): 58.6 (1B), 28.3 (1B), 4.6 (br, 2B), -9.88 (1B), -24.4 (2B), -29.5 (2B). ^{31}P - ^1H NMR (162 MHz, CD_3CN): 69.4 [d, $J(\text{RhP})$ 155 Hz].

⁵ ^1H NMR (400 MHz, CD_2Cl_2): 7.71–6.93 (m, 35H, Ph), 4.38 (s, 2H, NCH_2), 3.01 (s, 9H, NMe_3). ^{11}B - ^1H NMR (128 MHz, CD_2Cl_2): 54.5 (1B), 22.8 (1B), 1.7 (br, 3B), -25.1 (2B), -31.7 (2B). ^{31}P - ^1H NMR (162 MHz, CD_2Cl_2): 44.9 [d, $J(\text{RhP})$ 154 Hz].

⁶ Crystal data. $[\text{C}_{36}\text{H}_{30}\text{P}_2\text{N}][\text{C}_{26}\text{H}_{33}\text{B}_9\text{P}_2\text{RhS}] \cdot 0.5\text{C}_2\text{H}_5\text{N}$, $a = 10.865(2)$, $b = 24.924(3)$, $c = 22.750(2)$ Å; $\beta = 92.797(9)^\circ$; $V = 6153.6(13)$ Å³, $P2_1/n$, $Z = 4$ ion pairs. 10650 independent reflections were measured from a decomposing crystal (ca. 50%) to $\theta_{\text{max}} 25^\circ$ on a Siemens P4 diffractometer at 290K. The structure has been refined (using all data) to $R = 0.0839$ [4110 observed data, $F \geq 4\sigma(F)$] using SHELXTL. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

gift of B₁₀H₁₄, and Dr G.M. Rosair for crystallographic support.

References

- [1] For example, C.S. Jun, T.P. Fehlner and A.L. Rheingold, *J. Am. Chem. Soc.*, **115** (1993) 4393.
- [2] K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18** (1976) 1.
- [3] G. Ferguson, M.C. Jennings, A.J. Lough, S. Coughlan, T.R. Spalding, J.D. Kennedy, X.L.R. Fontaine and B. Stibr, *J. Chem. Soc., Chem. Commun.*, (1990) 891.
- [4] M. Murphy, T.R. Spalding, G. Ferguson and J.F. Gallagher, *Acta Crystallogr.*, **C48** (1992) 638.
- [5] K.J. Adams, T.D. McGrath and A.J. Welch, *Acta Crystallogr.*, **C51** (1995) 401.
- [6] For method see S.A. Macgregor, A.J. Wynd, N. Moulden, R.O. Gould, P. Taylor, L.J. Yellowlees and A.J. Welch, *J. Chem. Soc., Dalton Trans.*, (1991) 3317.
- [7] S.J. LaPlaca and J.A. Ibers, *Inorg. Chem.*, **1965**, **4**, 778; A.C. Skapski and P.G.H. Troughton, *J. Chem. Soc., Chem. Commun.*, (1968) 1230; R.-M. Catalá, D. Cruz-Garriz, P. Sosa, P. Terreros, H. Torrens, A. Hills, D.L. Hughes and R.L. Richards, *J. Organomet. Chem.*, **359** (1989) 219; S.D. Chappell, L.M. Engelhardt, A.H. White and C.L. Raston, *J. Organomet. Chem.*, **462** (1993) 295; S.D. Perera and B.L. Shaw, *J. Chem. Soc., Dalton Trans.*, (1995) 3861.
- [8] See for example, Table 1 of S. Coughlan, T.R. Spalding, G. Ferguson, J.F. Gallagher, A.J. Lough, X.L.R. Fontaine, J.D. Kennedy and B. Stibr, *J. Chem. Soc., Dalton Trans.*, (1992) 2865 for a recent compilation.