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Preliminary communication

Sterically induced opening of a *closo* carbametallaborane: synthesis and characterisation of 1,2-Ph_2-3-(η-C_5Me_5)-3,1,2-*pseudocloso*-$RhC_2B_9H_9$

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Abstract

The structure of the cage in 1,2-Ph_2-3-Cp*-3,1,2-$RhC_2B_9H_9$ is distorted from icosahedral by repulsion between the two phenyl rings, forced to lie nearly coplanar by the presence of the Cp* ligand. Thus the C(1) ··· C(2) distance is 2.51 Å, and B(6) approaches to within 2.92 Å of Rh(3). The nature of the distortion, which engenders the description *pseudocloso* for the RhC_2B_9 polyhedron, is discussed in relation to ^{11}B NMR chemical shifts and to recent controversy over *iso-closo versus hyper-closo* descriptors.

Cluster compounds with bulky exopolyhedral substituents are potentially interesting molecules if the steric requirements of the substituent can be made to act against the normal geometrical requirements of the cluster. The effects can be particularly dramatic in boranes and heteroboranes since, for a particular number of polyhedral vertices and cluster electron count, these compounds generally have relatively few accessible cluster geometries compared to analogous metal clusters. Thus, for example, the sterically demanding alkyne ($SiMe_3$)C≡C($SiMe_3$) does not undergo simple insertion into *arachno*-$B_{10}H_{12}(SMe_2)_2$ to afford a 12-vertex carbaborane, but rather gives rise to an alkenyldecaborane and a monocarbon carbaborane [1]. Equally, (H)(PPh_3)$_2$Rh($C_2B_9H_{11}$) exists primarily in the 3,1,2-*closo*-$Rh^{III}C_2B_9$ form [2] whilst (H)(PPh_3)$_2$Rh($PhMeC_2B_9H_9$) is primarily an *exo*-Rh^I-7,8-*nido*-C_2B_9 complex [3], and, as such, an efficient homogeneous catalyst precursor.

Although diphenylcarbaborane, 1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$, has been known for nearly thirty years [4], no metal complexes of the [7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$]$^{2-}$ ligand (note the change in numbering convention between *closo* and *nido* icosahedral heteroboranes [5]) have, to our knowledge, ever been reported. Given the

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Table 1

^{11}B chemical shifts (ppm) in 3-Cp*-3,1,2-*closo*-$RhC_2B_9H_{11}$, II, 1,2-*closo*-$C_2B_{10}H_{12}$ and 1,2-Ph_2-1-*closo*-$C_2B_{10}H_{10}$

3-Cp*-3,1,2-*closo*-$RhC_2B_9H_{11}$	II	1,2-*closo*-$C_2B_{10}H_{12}$	1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$
+8.6(1B)	+33.1(1B)	−2.3(2B)	−1.7(2B)
−1.8(1B)	+12.9(1B)	−9.1(2B)	−8.5(4B)
−3.5(2B)	−10.3(2B)	−13.6(4B)	−9.72(4B)
−8.3(2B)	−4.0(2B)	−14.7(2B)	
−18.6(2B)	−1.2(2B)		
−23.4(1B)	−18.0(1B)		

likelihood of severe crowding between the cage-bonded phenyl groups and the ligand set exopolyhedral to the metal atom, and the possible consequent adoption of unusual molecular structures and reactivity, we have begun to develop the transition metal chemistry of {$Ph_2C_2B_9H_9$}. Herein we report the synthesis and characterisation of 1,2-Ph_2-3-Cp*-3,1,2-*pseudocloso*-$RhC_2B_9H_9$, II, (Cp* = C_5Me_5) in which a formally *closo* 12 vertex heteroborane suffers a sterically induced diamond → square opening.

1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$ [4,6] can be efficiently converted into the partially degraded salt Tl_2[7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$], I, by a procedure fully analogous to that which affords $Tl_2[C_2B_9H_{11}]$ from $C_2B_{10}H_{12}$ [7]. I is a convenient precursor for complexes of {$Ph_2C_2B_9H_9$}, and reacts with $[Cp^*RhCl_2]_2$ [8] to afford 1,2-Ph_2-3-Cp*-3,1,2-*pseudocloso*-$RhC_2B_9H_9$, II, in 8% yield (not optimised).

Compound II is formally analogous to 3-Cp*-3,1,2-*closo*-$RhC_2B_9H_{11}$ [9], shown by a crystallographic study to have the expected icosahedral cage (RhC_2B_9) geometry and full η^5-coordination of the Cp* ligand to Rh(3). However, simple model building implied that II could not accommodate a similar regular structure because of steric congestion in the Ph/Ph/Cp* region.

The first experimental indication that II has an unusual cluster geometry was afforded by comparison of its ^{11}B NMR chemical shifts with those of 3-Cp*-3,1,2-*closo*-$RhC_2B_9H_{11}$. As shown in Table 1 there is a clear indication that, on average, the boron nuclei in II are substantially deshielded with respect to those in 3-Cp*-3,1,2-*closo*-$RhC_2B_9H_{11}$ (note that resonances in the latter have been assigned *via* COSY spectroscopy [9]; those in II have not yet been assigned). Also given in Table 1 are ^{11}B chemical shifts in 1,2-*closo*-$C_2B_{10}H_{12}$ and 1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$, comparison of which shows that the extent of deshielding of the boron nuclei that results from the introduction of phenyl substituents at the cage carbon atoms is minimal. This allows the reasonable assertion that II possesses an unusual cluster geometry.

A molecular structure determination confirmed this assertion. Although the precision of this study is not as high as would normally be expected, largely because of disorder problems, the structure of compound II is established beyond doubt. There are two crystallographically independent molecules in the asymmetric fraction of the unit cell, between which there is no significant structural difference. Figure 1 shows a perspective view of molecule A and details some important molecular parameters; the corresponding parameters for molecule B are given in square brackets.

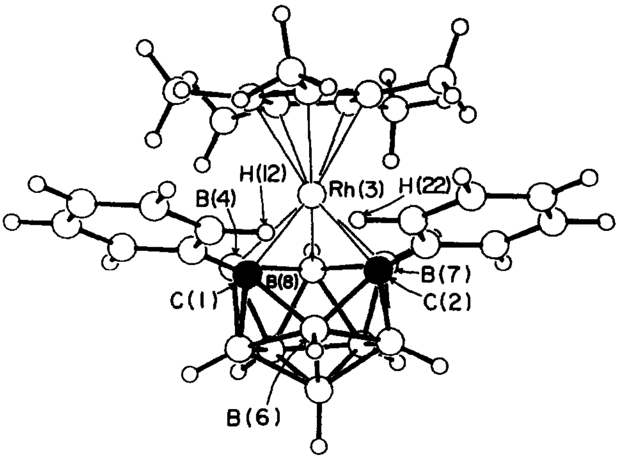

Fig. 1. Crystallographically determined structure of II (molecule A) with atom numbering. Cage carbon atoms are shown in black and hydrogen atoms have an artificial radius of 0.1 Å for clarity. Important molecular parameters (Å) for molecule A [molecule B]: Rh(3)–C(1) 2.185(20) [2.143(18)]; Rh(3)–C(2) 2.167(21) [2.144(18)]; Rh(3)–B(4) 2.18(3) [2.236(25)]; Rh(3)–B(8) 2.236(25) [2.16(3)]; Rh(3)–B(7) 2.05(3) [2.210(22)]; Rh(3)–Cp* 2.189(8)–2.277(8) [2.169(7)–2.327(7)]; Rh(3) ··· B(6) 2.922(24) [2.908(24)]; C(1) ··· C(2) 2.51(3) [2.50(3)].

The cluster geometry in II is loosely based on that of a 3,1,2-RhC_2B_9 icosahedron, but is substantially distorted in that the C ··· C connectivity is stretched, to 2.51 Å, and concomitantly B(6) is pulled out of the B(5)B(9)B(12)B(11) plane, to within 2.92 Å of Rh(3). This deformation, which creates a square [C(1)Rh(3)C(2) B(6)] from a diamond, apparently results from mutual repulsion between the cage-bonded phenyl rings [10], forced to lie effectively coplanar [11] by the presence of the Cp* ligand which is fully η^5-bonded to Rh(3). It is of note that this sterically induced cluster opening of II could have been at least in part avoided if the Cp* ligand had slipped from η^5- to η^3-bonded, allowing the phenyl rings to adopt orientations more similar to those observed in 1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$ [6,12], but this is presumably unfavourable since it would generate a coordinatively and electronically unsaturated metal centre.

The unusual cluster geometry of II is similar to that previously observed by Stone *et al.* [13] in $[PtW(CO)_2(PEt_3)_2\{\eta^6\text{-}C_2B_9H_8(CH_2C_6H_4Me\text{-}4)Me_2\}]$, although in the latter case the deformation appears to be somewhat greater, with C(1) ··· C(2) 2.88 Å and W ··· B(6) 2.51 Å. The structures of molecules of this sort are of interest in relation to recent discussion of *iso-closo versus hyper-closo* polyhedra. Although neither the carbawolfaborane nor II can properly be defined as *closo*, since the metal–B(6) connectivity is not formally made [14], both appear to lie along the *closo* to *iso / hyper-closo* pathway [completion of this path is a full diamond → square → diamond transformation involving the C(1)MC(2)B(6) fraction of the cluster]. Kennedy and coworkers [15] have suggested that polyhedra isomerised in this way should be termed *iso-closo*, the metal contributing 4 valence orbitals for cluster bonding and the cluster electron count being $(n + 1)$ pairs (n = no. of vertices). In contrast, Baker [16] has argued that a more realistic interpretation of such species is that in which the cluster electron count is only n, *i.e.* the clusters are *hyper-closo*. In this interpretation it is not necessary to increase the formal orbital contribution from the metal atom beyond the usual value of 3. The results of molecular orbital calculations by Johnston and Mingos [17] broadly support the *hyper-closo* view.

The *pseudocloso* carbawolfraborane does not appear to be a particularly crowded molecule, supporting the view that its unusual structure is predominantly determined by electronic factors. In contrast, it seems that steric effects alone are responsible for the *pseudocloso* structure of II, suggesting the potential for the synthesis of a family of progressively opened, related, polyhedra by judicious choice of cage carbon substituents and exopolyhedral ligands. It is possible that detailed analysis of the structures of members of such a family could shed further light on the *iso-closo* / *hyper-closo* controversy. At this early stage we note that the general shift to high frequency of the ^{11}B resonances of II compared to those of 3-Cp*-3,1,2-*closo*-$RhC_2B_9H_{11}$ is not inconsistent with an effective reduction in the number of cluster skeletal electron pairs.

Synthesis and spectroscopy

1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$ (0.91 g, 3.07 mmol) and KOH (1.07 g, 19 mmol) were stirred in EtOH (25 cm^3) for 45 min, and then refluxed for 6 h. After cooling, solvent was removed *in vacuo* and the resultant white solid dissolved in degassed H_2O (15 cm^3) and filtered. To the filtrate was added an aqueous solution of TlOAc (3 g, 12 mmol), causing immediate precipitation of Tl_2[7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$], I, as a bright yellow solid. This was filtered, washed successively with water, ethanol and diethyl ether, and dried *in vacuo*. Yield 64%. Found: C, 24.9; H, 3.13. $C_{14}H_{19}B_9Tl_2$ calc.: C, 24.2; H, 2.80%. To a solid mixture of [Cp*$RhCl_2$]$_2$ (0.40 g, 0.65 mmol) and I (0.90 g, 1.30 mmol) at −196°C, was added CH_2Cl_2 (25 cm^3). The mixture was allowed to warm to room temperature with stirring. After 15 h the mixture was filtered under N_2 and the deep red filtrate concentrated *in vacuo*. Preparative TLC (CH_2Cl_2 : hexane eluant, 2 : 3) afforded one major dark orange band (R_f *ca.* 0.85) which was collected and recrystallised (CH_2Cl_2 : hexane, 1 : 3, −30°C) to afford deep orange crystals of 1,2-Ph_2-3-Cp*-3,1,2-*pseudocloso*-$RhC_2B_9H_9$, II. Yield 8%. Found: C, 54.4; H, 6.47. $C_{24}H_{34}B_9Rh$ calc.: C, 55.2; H, 6.56%. IR ν_{max} at 2570 cm^{-1} (B–H). NMR: ($CDCl_3$) ^{1}H; δ 7.52 [d, ^3J(HH) 4 Hz, 4H, *H*(12,16,21,26) (*ortho*)], 7.30 [d of d, app t, ^3J(HH) 4 Hz, 4H, *H*(13,15,23,25) (*meta*)], 7.21 [t, ^3J(HH) 4 Hz, 2H, *H*(24,24) (*para*)] and 1.29 [s, 15H, $(CH_3)_5C_5$] ppm: ^{11}B-{^{1}H}; δ 33.06 (1B), 12.93 (1B), 10.26 (2B), 4.04 (2B), −1.15 (2B) and −17.97 (1B) ppm.

Crystallographic study

All measurements were carried out using an Enraf–Nonius CAD4 diffractometer operating with graphite-monochromated Mo-K_αX-radiation (λ_{bar} = 0.71069 Å) and equipped with a ULT-1 low temperature device. Crystal data: Compound II, $C_{24}H_{34}B_9Rh$, $M = 522.74$, monoclinic, space group $P2_1/a$, $a = 17.622(10)$, $b = 18.266(3)$, $c = 18.039(6)$ Å, $\beta = 118.41(4)°$, $V = 5107.2$ Å^3, from least-squares refinement of 25 centred reflections ($10 < \theta < 12°$), $T = 185 \pm 1$ K, $Z = 8$, $D_{calc} = 1.359$ g cm^{-3}, μ(Mo-K_α) = 6.69 cm^{-1}, $F(000) = 2144$. Data ($+h+k\pm l$) were collected for $1 \leqslant \theta \leqslant 22°$ by ω–2θ scans (ω scan width $0.8 + 0.34 \tan \theta$) with no crystal movement or decay. Of 4852 independent reflections measured, 4823 [$F \geqslant 2.0\sigma(F)$] were retained. Metal atom positions were found from a Patterson synthesis, and the structure developed by iterative full-matrix least-squares refinement (SHELX76 [18]). Two ghost rhodium atoms, Rh(3X) and Rh(3Y) were included with refined occupancies of 10 and 5% respectively, their identities confirmed by their chemically non-sensible positions close to Rh(3A) and Rh(3B) respectively, and by the fact that their positions are *pseudo* symmetry related to Rh(3B) and Rh(3A) respectively (x, $0.5 - y$, z). Complementary occupancies were assigned to Rh(3A) and Rh(3B). Carbon atoms in 5- and 6-membered rings were idealised. After isotropic convergence an empirical absorption correction [19] was applied. Phenyl H atoms were set in idealised positions, and cage and methyl H atoms were refined with bond distance constraints. Non-H atoms were refined with a mixture of isotropic and anisotropic thermal parameters, and all H atoms with a common isotropic one, 0.129(6) Å^2 at convergence. In the final stages data were weighted according to $w^{-1} = [\sigma^2(F) + 0.001621F^2]$, and independent molecules were refined in alternate cycles. $R = 0.1236$, $R_w = 0.1499$, $S = 1.394$, the relatively high residuals attributed mainly to the disorder which is only modelled at the rhodium atoms. Maximum and minimum residues in final ΔF synthesis were 0.78 and -0.86 e Å^{-3} respectively. Atomic scattering factors for B, C and H were those inlaid in SHELX76, with those for Rh being taken from *International Tables* [20]. Programs used in addition to those referenced above were CALC [21] and EASYORTEP [22]. A table of atom coordinates and a complete list of bond lengths and angles will be deposited with the Cambridge Crystallographic Data Centre.

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12 $\theta = 6°$ and C(1)–C(2) = 1.727 Å (average of two crystallographically independent molecules).
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