An Unusual Direct Conversion of Metallaboranes to Metallacarbaboranes and the Isolation of a Novel *isoarachno* Twelve-vertex Cluster Compound

Evert J. Ditzel, Xavier L. R. Fontaine, Norman N. Greenwood, John D. Kennedy, Zhu Sisan, Bohumil Štíbr and Mark Thornton-Pett

School of Chemistry, University of Leeds, Leeds LS2 9JT, UK

Reaction of [6-(η^5-C_5Me_5)-*nido*-6-RhB_9H_{13}] with RN≡C (R = Et, Me) in toluene at room temperature quickly gave a high yield of the bis(ligand) adducts [6,9-$(RNC)_2$-6-(η^5-C_5Me_5)-*arachno*-6-RhB_9H_{11}] which, on being heated in boiling toluene, undergo carbon incorporation to yield one- and two-carbon, eleven-vertex *closo*-type metallacarbaborane species rather than a reduction of RN≡C, whereas reaction of the isoelectronic cluster compound [6-(η^6-C_6Me_6)-8-(OMe)-*nido*-6-RuB_9H_{12}] with MeN≡C traps an unprecedented intermediate twelve-vertex *isoarachno*-{$RuCNB_9$} cluster type that has four-, five-, and six-membered open faces.

Reaction between EtN≡C and [6-(η^5-C_5Me_5)-*nido*-6-RhB_9H_{13}] **1** in toluene at room temperature quickly gave a high yield of the bis(ligand) adduct [6,9-$(EtNC)_2$-6-(η^5-C_5Me_5)-*arachno*-6-RhB_9H_{11}] and this, when heated in boiling toluene, followed by chromatographic separation of the products, gave an 18% yield of a red amino-substituted eleven-vertex *closo*-type metallamonocarbaundecaborane product [1-(η^5-C_5Me_5)-2-(NHEt)-7-(CNEt)-*closo*-1,2-$RhCB_9H_9$] **2** [Fig. 1 (top)]. Trace quantities of a yellow species were also formed. Conversely, reaction with MeNC instead of EtNC resulted in similar quantities (*ca.* 15% yield) of a red species (less stable than the ethyl analogue **2**), together with larger quantities (*ca.* 33% yield) of the yellow *C*-methyl substituted *closo*-type eleven-vertex metalladicarbaundecaborane [1-(η^5-C_5Me_5)-2-Me-*closo*-1,2,3-$RhC_2B_8H_9$] **3** [Fig. 1 (bottom)]. This latter compound **3** can also be synthesized independently in 64% yield by the straightforward reaction between [{(η^5-C_5Me_5)$RhCl_2$}$_2$] and the dianion [6-Me-*nido*-

6,9-$C_2B_8H_9]^{2-}$ in dichloromethane solution. Compounds **2** and **3** were characterized by single-crystal X-ray diffraction experiments† and by NMR spectroscopy.‡

As far as we are aware: (*a*) the incorporation of an isocyanide carbon atom to give direct conversion of a metallaborane to a metallacarbaborane (**1** → **2**), and (*b*) the insertion of two isocyanide carbon atoms together with the elimination of a boron vertex to convert a metallaborane to a metalladicarbaborane (**1** → **3**) are both without precedent. Additionally, the reactions have other remarkable characteristics such as the conjoining of carbon atoms and the complete elimination of nitrogen in the formation of the *C*-methyl substituted compound **3**. Furthermore, this behaviour contrasts completely with the reaction of the [6-(η^6-C_6Me_6)-*nido*-6-RuB_9H_{13}] analogue under similar circumstances;[3] this last reaction results in an overall well defined redox process involving the stepwise oxidation of the [6-(η^6-C_6Me_6)-*nido*-6-RuB_9H_{13}] *via* a series of intermediates to give, ultimately, the *isocloso*-cluster compound [1-(η^6-C_6Me_6)-*isocloso*-1-RuB_9H_9] with the concomitant stepwise and essentially quantitative stoichiometric reduction of MeN≡C to Me_2NH.

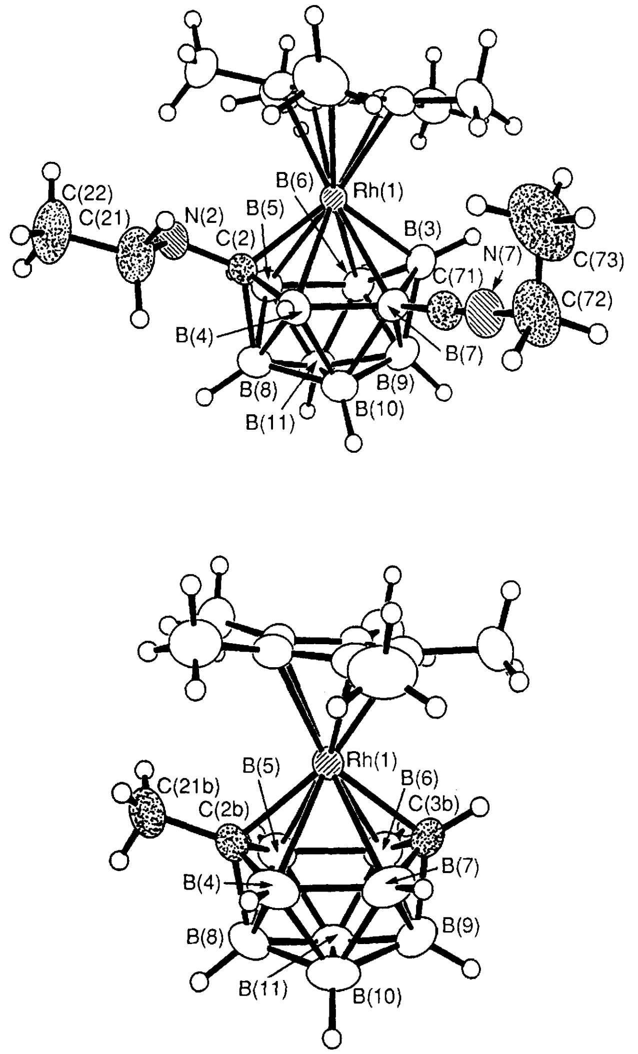

Fig. 1 (top) Drawing of the molecular structure of [1-(η^5-C_5Me_5)-2-(NHEt)-7-(CNEt)-*closo*-1,2-$RhCB_9H_8$] (compound **2**). Salient interatomic dimensions are as follows: Rh(1)–C(2) 216.4(4), Rh(1)–C(cyclopentadienyl) 217.7(4)–228.3(4), Rh(1)–B(3) 212.1(5), Rh(1)–B(4) 246.1(5), Rh(1)–B(5) 238.4(5), Rh(1)–B(6) 235.4(5), Rh(1)–B(7) 236.2(5), C(2)–N(2) 141.6(4), C(21)–N(2) 146.5(4), B(7)–C(71) 153.3(6), C(71)–N(7) 114.4(4), C(72)–N(7) 144.8(5) pm, C(2)–N(2)–C(21) 117.5(3) and C(71)–N(7)–C(72) 177.2(3)°.

(bottom) Drawing of the molecular structure of [1-(η^5-C_5Me_5)-2-Me-*closo*-1,2,3-$RhC_2B_8H_9$] (compound **3**). Salient interatomic dimensions are as follows: Rh(1)–C(2b) 211.5(4), Rh(1)–C(3b) 208.9(4), Rh(1)–C(cyclopentadienyl) 218.5(4)–220.9(4), Rh(1)–B(4) 236.6(5), Rh(1)–B(5) 237.6(5), Rh(1)–B(6) 239.6(5), Rh(1)–B(7) 237.4(5) and C(2b)–C(21b) 152.0(6) pm.

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† *Crystal data for* **2**: $C_{16}H_{34}B_9N_2Rh$, $M = 454.66$, monoclinic, space group $P2_1/n$, (= $P2_1/c$, no. 14), $a = 995.3(1)$, $b = 1682.6(2)$, $c = 1401.4(1)$ pm, $\beta = 94.77(1)°$. $U = 2.3387(4)$ nm^3, $D_c = 1.29$ g cm^{-3}, $Z = 4$, $F(000) = 935.99$, $\mu = 6.55$ cm^{-1}, $4.0 < 2\theta < 50.0°$. $R(R_w) = 0.0280$ (0.0287) for 3957 reflections with $F > 4.0\sigma(F)$.

Crystal data for **3**: $C_{13}H_{27}B_8Rh$, $M = 372.75$, monoclinic, space group $P2_1/c$, $a = 878.7(2)$, $b = 1500.3(3)$, $c = 1366.1(3)$ pm, $\beta = 91.85(2)°$, $U = 1.7999(6)$ nm^3, $D_c = 1.38$ g cm^{-3}, $Z = 4$, $F(000) = 759.99$, $\mu = 8.40$ cm^{-1}, $4.0 < 2\theta < 50.0°$. $R(R_w) = 0.0232$ (0.0247) for 2789 reflections with $F > 3.0\sigma(F)$.

Crystal data for **4**: $C_{16}H_{36}B_9NORu \cdot CH_2Cl_2$, $M = 529.76$ (includes solvate), orthorhombic, space group $Fdd2$, $a = 3046.0(9)$, $b = 3804.3(10)$, $c = 887.9(3)$ pm, $U = 10.289(5)$ nm^3, $D_c = 1.37$ g cm^{-3}, $Z = 16$, $F(000) = 4351.95$, $\mu = 7.43$ cm^{-1}, $4.0 < 2\theta < 50.0°$. $R(R_w) = 0.0354$ (0.0361) for 2070 reflections with $F > 3.0\sigma(F)$.

Intensity data for all three compounds were collected on a Nicolet P3/F diffractometer using $\omega/2\theta$ (for **2** and **3**) and ω (for **4**) scan modes and graphite-monochromated Mo-Kα radiation. All three data sets were corrected for absorption empirically.[1] All three structures were solved using Patterson and Fourier methods and were refined by full-matrix least-squares analysis.[2] In all three cases non-hydrogen atoms, including those of the solvate molecule in **4**, were refined anisotropically. For **2** and **3** ligand-associated hydrogen atoms were included in calculated positions and refined with an overall isotropic thermal parameter, while borane hydrogen atoms were located in Fourier difference syntheses and were refined with individual isotropic thermal parameters. For **4** the methyl hydrogen atoms were placed in calculated positions and, together with the remaining hydrogen atoms which were readily located in a Fourier difference synthesis, were assigned to an overall isotropic thermal parameter. Owing to the restricted amount of data available, however, none of the parameters associated with the hydrogen atoms were refined. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ *NMR Spectroscopic data* for [1-(η^5-C_5Me_5)-2-(NHEt)-7-(CNEt)-*closo*-1,2-$RhCB_9H_9$] **2** (as yet unassigned); $CDCl_3$ solution, 294–297 K; ordered as $\delta(^{11}B)$ [$\delta(^1H)$ of directly bound H atom in square brackets]: +35.9 [+5.58], +4.7 [+2.88], −3.1 [+2.83], −5.1 [+1.86], −9.9 [+0.80], −14.9 [+1.65], −28.5 [−0.06], −30.7 [−0.19], and −36.5 [CNEt]; additional $\delta(^1H)$ data: NCH_2CH_3 at +3.77, +3.78, and at +3.04, +3.09; NCH_2CH_3 at +1.23, +1.47; C_5Me_5 at +1.80. $\delta(^{11}B)$ in ppm to low field (high frequency) of $BF_3 \cdot OEt_2$. In addition, *m/z* (max): found 456, $^{12}C_{16}{}^1H_{34}{}^{11}B_9{}^{14}N_2{}^{103}Rh$ requires 456.

For [1-(η^5-C_5Me_5)-2-Me-*closo*-1,2,3-$RhC_2B_8H_9$] **3**, $CDCl_3$ solution; 294–297 K; ordered as assignment $\delta(^{11}B)$ [$\delta(^1H)$]: BH(8) +13.3 [+3.33], BH(9) +4.4 [+2.96], BH(6,7) −6.5 [+1.64], BH(4,5) −6.5[+1.51], BH(10,11) −22.4 [+0.51], CH(3) — [+4.83]; CMe at $\delta(^1H)$ +2.63, C_5Me_5 at $\delta(^1H)$ +1.94. Assignments by {^1H-^1H}-COSY-{^{11}B} experiments as described in X. L. R. Fontaine and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.*, 1986, 779.

For [5-(η^6-C_6Me_6)-7-(OMe)-*arachno*-5-RuN(Me)C(H)B_9H_{11}] **4** (as yet unassigned); $CDCl_3$ solution, 294–297 K; ordered as $\delta(^{11}B)$ [$\delta(^1H)$]: +24.2 [OMe at +3.79], +12.8 [+3.56], +12.1 [+3.75], −6.5 [+1.94], −9.9 [+1.86], −17.5 [+1.57], −21.1 [+0.79], −29.0 [+0.80], −31.2 [+0.98]; additional $\delta(^1H)$ data: H_μ(RuB) −6.46, H_μ(BB) −2.81, H_μ(CHB) −2.54 (doublet splitting 16.4 Hz), CH +0.08 (doublet of doublets, splittings 16.4 and 8.8 Hz), NMe +2.24, and C_6Me_6 +2.09. In addition, *m/z* (max): found 449, $^{12}C_{15}{}^1H_{36}{}^{11}B_9{}^{14}N^{16}O^{101}Ru$ requires 449; elemental analyses (C,H,N) were satisfactory.

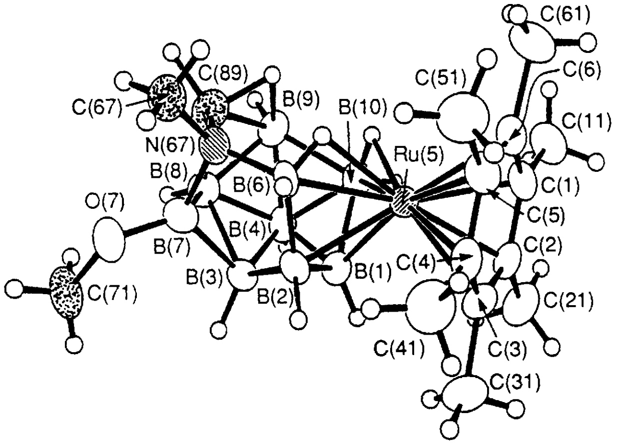

Fig. 2 Drawing of the molecular structure of compound **4**. Salient interatomic dimensions are as follows: Ru(5)–C 218.3(6)–225.9(6), Ru(5)–B(1) 222.1(11), Ru(5)–B(2) 225.2(11), Ru(5)–B(6) 233.6(9), Ru(5)–B(10) 235.2(9), B(6)–N(67) 148.8(10), B(7)–N(67) 152.8(12), B(7)–O(7) 139.8(12), B(7)–C(89) 200.9(15), B(8)–C(89) 178.4(14), B(9)–C(89) 185.5(14), B(9)–H(89a) 150.2(11), C(89)–H(89a) 133.0(11), C(89)–N(67) 157.0(12), C(67)–N(67) 148.4(10) pm, B(6)–N(67)–B(7) 104.4(7), B(8)–C(89)–B(9) 59.0(6), and C(89)–N(67)–C(67) 113.3(7)°.

It is of particular interest to ascertain which factors govern the differences in behaviour observed between the ostensibly very similar starting substrates [6-(η^5-C_5Me_5)-*nido*-6-RhB_9H_{13}] and [6-(η^6-C_6Me_6)-*nido*-6-RuB_9H_{13}] and to assess at which point during the reaction decisions are made by the reaction intermediates either (*a*) to reduce and eliminate the RNC elements or (*b*) to fuse and incorporate these elements into the cluster. Some insight derives from a novel product [5-(η^6-C_6Me_6)-7-(OMe)-*arachno*-5-RuN(Me)C(H)B_9H_{11}] **4**, which exhibits features that must be near this divergence on the reaction coordinates. Compound **4** is best isolated (16% yield) from the products of reaction between MeNC and the methoxy-substituted ruthenadecaborane [6-(η^6-C_6Me_6)-8-(OMe)-*nido*-6-RuB_9H_{12}], and has been characterized by single-crystal X-ray diffraction analysis (Fig. 2)† and NMR spectroscopy.‡ It is found to exhibit a most unusual (unique) twelve-vertex {RuNCB_9} cluster structure that has four-membered (BBCN), five-membered (BBBCN) and six-membered (RuBBBCN) open faces. Formally the compound has a twelve-vertex *arachno* electron count. The four- and five-membered open faces have no bridging H atoms but the six-membered open face has two RuHB bridges and an unprecedented CHB bridge the dimensions of which [C–H_μ 130.0(11), B–H_μ 150.2(11) pm] suggest considerable C–H *endo* character and somewhat weaker B$\cdots$H interaction.

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