Synthesis and Molecular Structures of *nido*-[9-(η-C_5H_5)-7,8,9-$C_2NiB_8H_{11}$], *nido*-[9-(η-C_5H_5)-$\mu_{10,11}$-(Ph_3PAu)-7,8,9-$C_2NiB_8H_{10}$], and *closo*-[1,3-(η-C_5H_5)$_2$-1,2,3,4-$CrCCrCB_8H_{10}$]; Evidence for a Multiple Metal–Metal Bond in a Dimetallacarbaborane

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From *nido*-5,6-$C_2B_8H_{12}$, the compounds *nido*-[9-(η-C_5H_5)-7,8,9-$C_2NiB_8H_{11}$], *nido*-[9-(η-C_5H_5)-$\mu_{10,11}$-(Ph_3PAu)-7,8,9-$C_2NiB_8H_{10}$], and *closo*-[1,3-(η-C_5H_5)$_2$-1,2,3,4-$CrCCrCB_8H_{10}$] have been synthesised, and their structural identities established by *X*-ray crystallography.

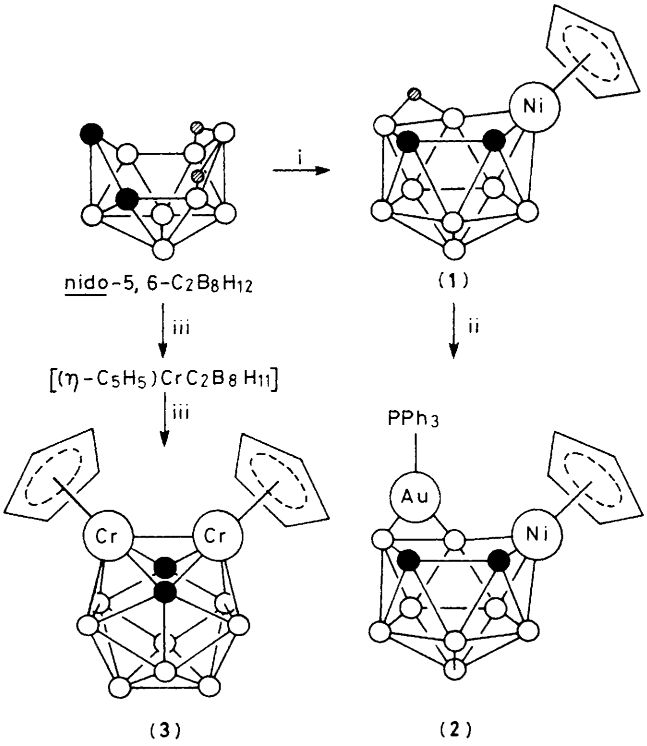
We have previously shown[1] that the μ-B–H–B bonds in *nido*-5,6-$C_2B_8H_{12}$ are sufficiently electrophilic to react with [Pt_2(μ-cod)(PEt_3)$_4$] to give [9-H-9,9-(Et_3P)$_2$-$\mu_{10,11}$-H-7,8,9-$C_2PtB_8H_{10}$] (cod = cyclo-octa-1,5-diene). This suggested that the μ-B–H–B groups in the *nido*-carbaborane might cleave metal–carbon bonds (formally a protolysis) allowing stepwise introduction of metal–ligand fragments into the carbaborane cage. Some years ago the compound $MeGaC_2B_4H_6$ was obtained from the reaction between $GaMe_3$ and *nido*-$C_2B_4H_8$,[2] and it has long been known that certain main group metal alkyls react with boranes with release of alkane and formation of a metallaborane.[3]

Treatment (60 °C, light petroleum) of *nido*-5,6-$C_2B_8H_{12}$ with [Ni(η-C_5H_5)$_2$] afforded (Scheme 1) wine-red crystals of (**1**) (85%).† Having 26 skeletal electrons, (**1**) should adopt a *nido*-icosahedral geometry. In order to establish unambiguously the nature of its open face an *X*-ray diffraction study was carried out.‡

The analysis confirms that the cage structure of (**1**) (Figure 1) is that of a *nido*-icosahedron with an open $\overline{\text{Ni·C·C·B·B}}$ pentagonal face. The crystal structure suffers from two unrelated rotational disorders, one involving the cyclopentadienyl ring and the other the C_2B_8 unit. The latter has not allowed location of the H atom that bridges the B(10) · · · B(11) connectivity, although all terminal hydrogen atoms have been positionally refined. Formation of (**1**) corresponds to protonation of one of the η-C_5H_5 ligands of nickelocene, followed by loss of C_5H_6, and incorporation of an Ni(η-C_5H_5) fragment into the cage.

The remaining μ-B–H–B hydrogen in (**1**) is also reactive, and in refluxing tetrahydrofuran (8 h) with [AuMe(PPh$_3$)] affords (Scheme 1) a green crystalline complex (**2**) (45%).† A single-crystal *X*-ray diffraction study‡ showed (Figure 2) that in (**2**) the $\mu_{10,11}$-H of (**1**) had been replaced by the isolobal AuPPh$_3$ fragment without any major change in cluster geometry.[4–7]

Formation of (**1**) followed by (**2**) illustrates successive replacement of μ-B–H–B hydrogens by metal fragments. Evidently with more reactive precursors a 'double' metal insertion occurs. Thus $C_2B_8H_{12}$ with [Cr(η-C_5H_5)$_2$] (tetrahydrofuran, 25 °C, 20 h) gives (Scheme 1) a dark olive-green compound (**3**) (70%),† structurally identified by *X*-ray crystallography (Figure 3).‡ The molecule bestrides a crystallographic mirror plane perpendicular to the Cr(1)–Cr(1′) connectivity. There is rotational disorder of the η-C_5H_5 groups about the η-C_5H_5–Cr axis (two discrete rings, site occupancy factors 59:41). The polyhedron of (**3**) is a *closo*-icosahedron with a 1,2,3,4-Cr·C·Cr·C heteroatom pattern.



Scheme 1. i, [Ni(η-C_5H_5)$_2$]; ii, [AuMe(PPh$_3$)]; iii, [Cr(η-C_5H_5)$_2$]. Filled circle = CH, empty circle = BH, hatched circle = H.

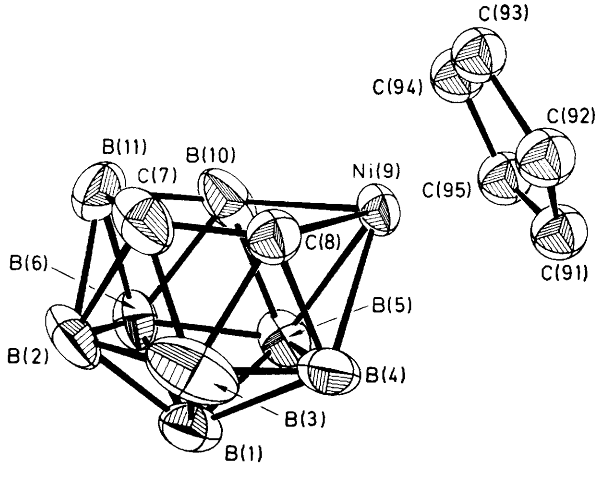


Figure 1. Molecular structure of *nido*-[9-(η-C_5H_5)-7,8,9-$C_2NiB_8H_{11}$], (**1**), showing only the major components of the disordered structure. Important interatomic separations include Ni–B(4) 2.053(10), Ni–B(5) 2.056(8), Ni–C(8) 2.011(13), Ni–B(10) 2.049(10), B(10)–B(11) 1.754(17), B(11)–C(7) 1.682(15), C(7)–C(8) 1.390(15), Ni–C(η-C_5H_5) 2.100(15) (mean) Å.

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† Selected spectroscopic data [i.r. measured in Nujol, ^{11}B-{^{1}H} and ^{11}B n.m.r. in CDCl$_3$ with δ (p.p.m.) to high frequency of BF$_3$·OEt$_2$ and coupling constants in Hz]: compound (**1**), ν_{BH} (max) at 2 546s and 2 542(sh) cm^{-1}, ^{11}B-{^{1}H} n.m.r., δ 19.5, 13.7, 3.4, −2.7, −7.9, −17.7, −19.5, and −22.2, ^{11}B n.m.r., δ 19.3 [d, 1 B, *J*(BH) 142], 13.7 [d, 1 B, *J*(BH) 156], 3.4 [d, 1 B, *J*(BH) 156], −2.7 [d(br.), 1 B, *J*(BH) 151], −7.9 [d of d, 1 B, *J*(BH) 149, *J*(BHB) 46], −17.5 [d(br.), 1 B, *J*(BH) 117], −19.7 [d(br.), 1 B, *J*(BH) 161], and −22.2 [d(br.), 1 B, *J*(BH) 156]. Compound (**2**), ν_{BH} (max) at 2 601m, 2 530(sh), and 2 438w cm^{-1}, ^{11}B-{^{1}H} n.m.r., δ 13.2 (1 B), 7.0 (1 B), 3.0 (1 B), 1.1 (1 B), −13.3 (1 B), −16.4 (1 B), and −20.8 (2 B). Compound (**3**), ν_{BH} (max) at 2 583m, 2 561m, 2 529s, 2 490w(sh), and 2 457w cm^{-1}.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Crystal data for (**1**): $C_7H_{16}B_8Ni$, $M = 245.3$, monoclinic, space group $P2_1/c$, $a = 11.534\,3(14)$, $b = 6.546\,4(9)$, $c = 16.393(2)$ Å, $\beta = 99.306(10)°$, $U = 1\,221.5$ Å^3, $D_c = 1.334$ g cm^{-3}, $Z = 4$, $F(000) = 504$ electrons, μ(Mo-$K_{\bar{\alpha}}$) = 14.79 cm^{-1}. Of 3 713 symmetry-independent intensities measured on an Enraf–Nonius CAD4 diffractometer to $\theta_{max} = 27.5°$ (Mo-K_α *X*-radiation, $\bar{\lambda} = 0.710\,69$ Å) at 291 K, 1 490 significant [$F_o \geqslant 2.0\sigma(F_o)$] observations were used to solve (Patterson) and refine (full matrix least squares) the structure to a current *R* of 0.071 4.

Crystal data for (**2**): $C_{25}H_{30}B_8NiAuP$, $M = 703.7$, monoclinic, space group $P2_1/c$, $a = 11.804\,5(8)$, $b = 12.208\,0(8)$, $c = 19.533(2)$ Å, $\beta = 93.976(6)°$, $U = 2\,808.2$ Å^3, $D_c = 1.664$ g cm^{-3}, $Z = 4$, $F(000) = 1\,368$ electrons, μ(Mo-$K_{\bar{\alpha}}$) = 57.25 cm^{-1}. Intensity data were collected as for (**1**) to $\theta_{max} = 26°$ supplying 5 440 unique structure factor amplitudes corrected for absorption. Structural solution (Patterson) and refinement (full matrix least squares) using 3 886 data [$F_o \geqslant 2.0\sigma(F_o)$] gave the final converged residual *R* of 0.038 8.

Crystal data for (**3**): $C_{12}H_{20}B_8Cr_2$, $M = 354.76$, orthorhombic, space group *Pnam*, $a = 11.714(3)$, $b = 9.483\,0(17)$, $c = 14.256(3)$ Å, $U = 1\,583.6$ Å^3, $D_c = 1.488$ g cm^{-3}, $Z = 4$, $F(000) = 720$ electrons, μ(Mo-$K_{\bar{\alpha}}$) = 12.86 cm^{-1}. Using 1 661 data [$F_o \geqslant 2.0\sigma(F_o)$] collected to $\theta_{max} = 30°$ (Mo-K_α *X*-radiation) at 293 K, the structure has been solved and refined, as for (**1**) and (**2**), to $R = 0.099\,7$.

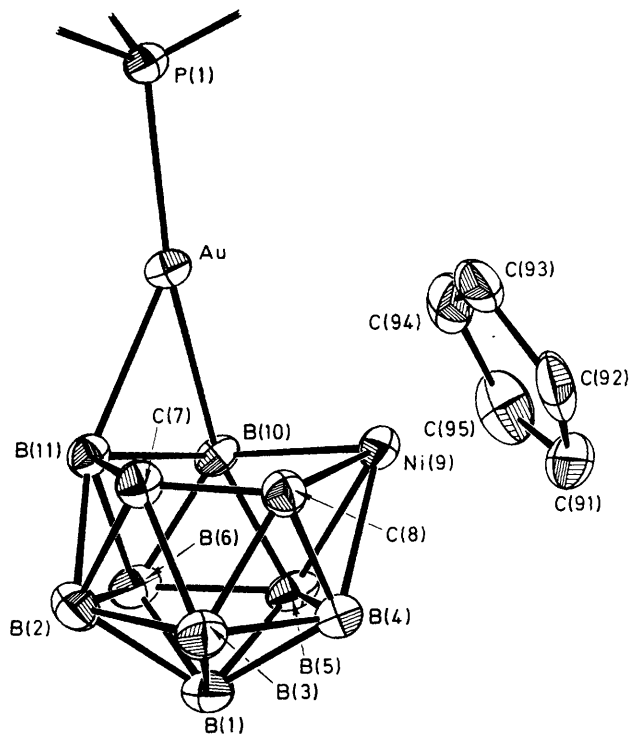

Figure 2. Perspective view of *nido*-[9-(η-C_5H_5)-$\mu_{10,11}$-(Ph_3PAu)-7,8,9-$C_2NiB_8H_{10}$], (**2**). Important molecular parameters Ni–B(4) 2.047(9), Ni–B(5) 2.082(8), Ni–C(8) 1.971(7), Ni–B(10) 2.144(8), B(10)–B(11) 1.787(11), B(11)–C(7) 1.712(10), C(7)–C(8) 1.499(9), Ni–C(η-C_5H_5) (mean) 2.118(28), Au–B(10) 2.308(7), Au–B(11) 2.256(8), Au–P(1) 2.278(2) Å; P(1)–Au–B(10) 167.0(2), P(1)–Au–B(11) 146.5(2)°.

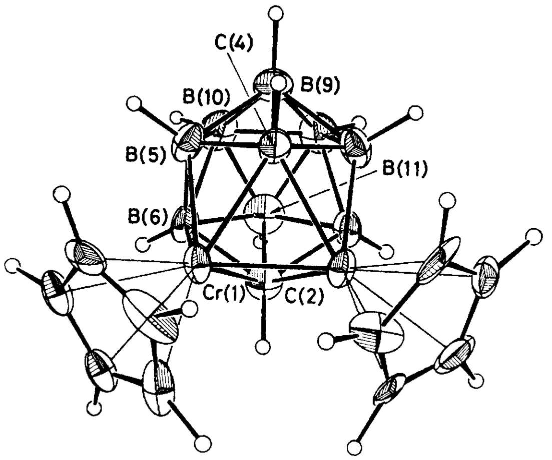

Figure 3. Molecular structure of *closo*-[1,3-(η-C_5H_5)$_2$-1,2,3,4-$CrCCrCB_8H_{10}$], (**3**). For clarity, only one (different) component of the disordered η-C_5H_5 ligand is shown bound to each metal atom. Important molecular parameters Cr(1)–Cr(1′) 2.272(2), Cr(1)–C(2) 2.175(9), Cr(1)–C(4) 2.236(8), Cr(1)–B(5) 2.203(8), and Cr(1)–B(6) 2.146(7) Å.

The Cr–Cr distance [2.272(2) Å] is the shortest¶ (by 0.08 Å) inter-metal distance yet recorded in a heteroborane. In the dicobalt analogue of (**3**) the Co–Co distance is 2.387(2) Å.[8]

Extended Hückel MO calculations on idealised models of [1,3-(η-C_5H_5)$_2$-1,2,3,4-$MCMCB_8H_{10}$] (M = Sc—Cu) species suggest that the M–M connectivity will be strongest when M = Cr, since for this the five lowest unfilled orbitals are all antibonding, and the three highest lying occupied orbitals are bonding, with respect to the M–M interaction.[9]

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¶ The previous shortest M–M distance in a heteroborane is 2.354(1) Å in [(η-C_5H_5)$_4Ni_4B_4H_4$]: J. R. Bowser, A. Bonny, J. R. Pipal, and R. N. Grimes, *J. Am. Chem. Soc.*, 1979, **101**, 6229.