$W_2Se_{10}^{2-}$ ions are present in the same cell with occupancies of 0.66 and 0.34, respectively. The $W_2Se_9^{2-}$ ion (Figure 1) has approximate C_s symmetry with square-pyramidal coordination about the W atoms. The analogous sulfide ion $W_2S_9^{2-}$ is unknown. The thermal reaction of WSe_4^{2-} in refluxing acetonitrile in the presence of $[PPh_4]Cl$ (in similar quantities to those described above) and 0.12 g of black selenium afforded two isomers of $[PPh_4]_2[W_2Se_{10}]$[11] in the ratio of 7:3 in 75% yield. The major isomer (Figure 2) is identical with that found in the mixed $[PPh_4]_2[W_2Se_9]/[PPh_4]_2[W_2Se_{10}]$ crystals and its structure closely resembles the analogous sulfide ion $W_2S_{10}^{2-}$.[12] The minor isomer of $W_2Se_{10}^{2-}$ (Figure 3) has no known sulfide analogue. The four-membered MSe_3 rings reported here have no counterparts in the literature; indeed, there appears to be a single example known of an MS_3 ring, that in $TiS_3(Me_5C_5)_2$.[13] The geometries of these rings are similar, although the ring-puckering angles differ ($W_2Se_9^{2-}$, 23°; $W_2Se_{10}^{2-}$, 25 and 35°; $TiS_3(Me_5C_5)_2$, 49°).

The generation of multiple components in solution and subsequent coprecipitation of different species are prevalent here as they are in the sulfides.[14] While electronic spectra have been of some utility in the study of sulfide solutions, selenide solutions of the present red-black materials exhibit no characteristic bands. But, as opposed to the sulfide solutions, NMR spectroscopy provides a convenient probe of these selenide solutions. In Figure 4 we show the ^{77}Se NMR spectrum for the solution from which the two $W_2Se_{10}^{2-}$ ions were isolated as their PPh_4 salts. While there is an extensive literature on ^{77}Se NMR spectra of organoselenium compounds,[15,16] no corresponding data base for inorganic selenides exists. Consequently the assignment in Figure 4 is based on comparisons with other spectra and on shielding arguments; it is not based on intensities as T_1 values have not been obtained. Successive preparations yielded spectra that have slightly differing a:a′, b:b′, b″, etc. ratios and so it was possible to link the four lines, a, b, c, and d, to the symmetrical isomer. The remaining six lines were assigned to the six unique Se sites in the unsymmetrical isomer. The ten lines lie in a range between that of WSe_4^{2-} (δ 1235, not shown) at the low-field end and that of Ph_2Se_2 (δ 460) at the high-field end. The resonance for the W^{VI} ion, WSe_4^{2-} would be expected to lie at the low-field end of resonances from the formally W^V $W_2Se_{10}^{2-}$ ions. Shielding arguments suggest the relative placement of the different types of Se sites.[17] Type "a" ring sites are least shielded, being furthest from W nuclei. Type "b" sites are less shielded than type "d" sites, as the latter are involved in stronger W–Se bonding; type "c" sites are highly shielded, being in close proximity to two W nuclei. Evidence to support this assignment is provided by the ^{77}Se NMR spectrum of $WS(Se_4)_2^{2-}$,[18] which contains WSe_4 five-membered rings and exhibits resonances at δ 824 and 988 from Se atoms in "b"- and "a"-type environments, and by the ^{77}Se NMR spectrum of $Rh_2Se_5(Me_5C_5)_2$,[19] which contains an Se_4 bridge between two Rh sites and has resonances at δ 485 and 783 for sites that are approximately type "c" and type "b". Complete confirmation of the assignment in Figure 4 must await the isolation of pure materials, a process that can now be followed by ^{77}Se NMR techniques. Indeed, we anticipate that ^{77}Se NMR spectroscopy will prove to be as valuable in the chemistry of soluble transition-metal selenides as have ^{17}O NMR techniques in the chemistry of the polyoxoanions.[20] On the basis of the preliminary work reported here the details of the selenide chemistry will be easier to delineate and will differ significantly from those of the sulfide chemistry.

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(10) Crystal data for $[PPh_4]_2[W_2Se_9]/[PPh_4]_2[W_2Se_{10}]$ (ratio 0.66/0.34). $C_{48}H_{40}P_2Se_{9.34}W_2$, triclinc, C_i^1-$P\bar{1}$, $Z = 2$, $a = 10.556$ (5) Å, $b = 11.480$ (6) Å, $c = 22.324$ (11) Å, $\alpha = 76.90$ (2) °, $\beta = 86.58$ (2)°, $\gamma = 79.28$ (2)°. $V = 2588$ Å^3 at −150 °C, 8941 reflections measured out to 2θ(Mo Kα_1) = 46°, $R = 0.068$ on 4700 reflections having $F_o^2 > 3\sigma(F_o^2)$. ν(Se–Se) = 330 cm^{-1}; ν(W–Se) = 288, 273 cm^{-1}.

(11) Crystal data for $[PPh_4]_2[W_2Se_{10}]$ (two isomers, ratio 0.70/0.30). $C_{48}H_{40}P_2Se_{10}W_2$, triclinic, C_i^1-$P\bar{1}$, $Z = 2$, $a = 10.678$ (2) Å, $b = 11.492$ (3) Å, $c = 22.392$ (5) Å, $\alpha = 77.20$ (2)°, $\beta = 86.94$ (2)°, $\gamma = 79.81$ (2)°. $V = 2637$ Å^3 at −150 °C, 10376 reflections measured out to 2θ(Mo Kα_1) = 46°, $R = 0.075$ on 5132 reflections having $F_o^2 > 3\sigma(F_o^2)$. ν(Se–Se) = 330 cm^{-1}; ν(W–Se) = 286, 270 cm^{-1}.

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Borane–THF as a Dual Reagent. Preparation and Characterization of the Metal-Rich Cobaltaborane $(\mu_3\text{-}H)_2[(\eta^5\text{-}C_5H_5)Co]_4B_2H_2$

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The range of metallaboranes synthesized continues to increase as does the number of synthetic methods.[1-3] The great majority of metallaboranes have low metal to boron ratios and only a few metal-rich systems (M/B ratio >1, unbridged M–B interactions) are known. The latter systems present an unusual environment to the borane fragment as well as offering useful comparisons to metal-rich, transition-metal hydrocarbyl clusters.[4,5] Here we present a new route to a metal-rich metallaborane based on well-known, but not fully appreciated, properties of $BH_3 \cdot THF$. Borane coordinates Lewis bases just like a transition metal,[6] and, hence, BH_3 can be used to remove ligands from a transition-metal complex.[7,8] With excess BH_3 present further reaction with the transition-metal fragments is possible.[9] We show below that when BH_3 can be induced to remove two ligands from $CpCoL_2$, the highly unsaturated CpCo fragments condense with themselves and borane to produce the metal-rich cluster $(CpCo)_4B_2H_4$ in useful (16% based on cobalt) yield. This strategry constitutes an alternative to using complexes with weakly coordinating ligands, e.g., $CpCo(C_2H_4)_4$.[10]

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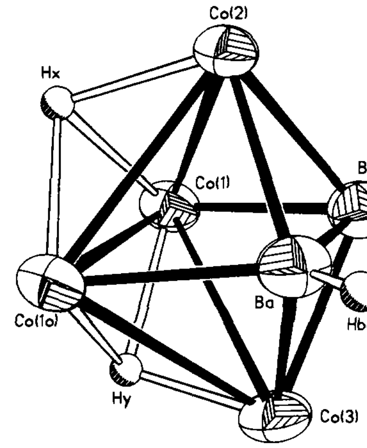
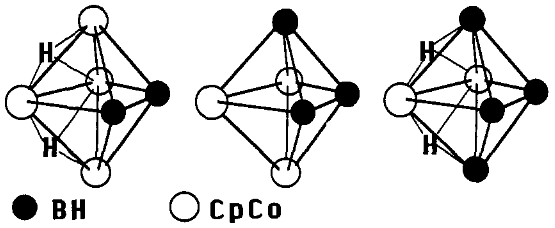


Figure 1. $Co_4(BH)_2(\mu_3\text{-}H)_2$ core of I. Co(1)–Co(2), 2.456 (1); Co(1)–Co(3), 2.461 (2); Co(1)–Co(1a), 2.501 (2); Co(1)–B, 2.070 (8); Co(2)–B, 2.009 (8); Co(3)–B, 2.019 (8), B–B(a), 1.80 (2) Å.

The reaction of 2 mmol of $CpCo(PPh_3)(C_2Et_2)$[11] in toluene with 4 mmol of $BH_3{\cdot}THF$ at 60 °C for 6 h followed by chromatography on silica gel (hexane/toluene) resulted in the isolation of a deep red material.[12] Recrystallization from toluene yielded 40 mg of ruby red, air-stable, crystals. The mass spectrum (p^+ 522 and isotopic pattern) is consistent with the molecular formula $Cp_4Co_4B_2H_4$. The single ^{11}B NMR resonance of this material indicates a plane of symmetry and the chemical shift suggests terminal BH units in a metallic environment (δ 114, J_{BH} = 170 Hz). The IR spectrum confirms the presence of BH (ν = 2420 cm^{-1}). The ^1H NMR shows the presence of two types of Cp ligands (δ 4.68, 4.46) in a ratio 1:1 again indicating at least one plane of symmetry. A metal hydride resonance is observed at δ −15.6 (fwhm 39 Hz) consistent with an all-cobalt environment. Wade's rules predict a closo octahedral structure (seven skeletal pairs, six atoms) for a single cluster.[13] Two geometrical isomers are possible, one with the boron atoms adjacent and one with the boron atoms at opposite vertices of an octahedron. In a nonfluxional structure, the two endo hydrogens must be symmetrically disposed with respect to the borons and the two types of cobalt atoms and could bridge either cobalt edges or faces.

The results of a single-crystal X-ray diffraction study[14] establish the solid-state structure (Figure 1) as a distorted octahedral Co_4B_2 cluster with boron atoms, each with a terminal hydrogen, occupying adjacent vertices and with cobalt atoms, each coordinated to a η^5-cyclopentadienyl ring, occupying the remaining four vertices. The complex possesses crystallographic mirror-plane symmetry; the plane bisects the B–B and Co(1)–Co(1a) bonds and contains Co(2) and Co(3). Hence, the predicted closo geometry is observed and the isomer with adjacent boron atoms is the one isolated in the solid state. The structural analysis also provides firm evidence for endo hydrogens triply bridging the two equivalent Co_3 faces of the Co_4B_2 core. Cobalt clusters with μ_3-hydrogens on Co_3 faces have been structurally characterized previously[15,16] and the average CoH distance found here (1.72 (12) Å) is comparable to that observed earlier in X-ray studies (1.67 (7) and 1.63 (15) Å). The BH hydrogens, also located, are found 1.16 (8) Å from boron as is typically observed for terminal hydrogens.[17]

Chart I



Besides demonstrating the potential of the synthetic approach, the new cluster is significant in its own right. It is a member of the closo cluster series $(CpCo)_nB_{6-n}H_{8-n}$ (Chart I), two members of which (n =2, III; 3, II) have been characterized in the elegant studies of Grimes and co-workers.[18-20] After taking into account intrinsic differences in cobalt and boron radii, a structural comparison shows the cluster geometry to be independent of metal/boron ratio. This point is further emphasized by the placement of the endo hydrogens which are known to be sensitive to cluster composition.[21] For n = 2 and 4 the two endo hydrogens bridge analogous faces on the octahedron (Chart I).[22] It is interesting that in I the endo hydrogens associate with the metal whereas in related systems they are preferentially found in MHB interactions.[23]

Metallaboranes are analogues of organometallic clusters and intercomparisons reveal information on structure and bonding not gained by observing a single structure.[24] Cobaltaborane I is the borane analogue of the M_4C_2 octahedral clusters[25] and a comparison of R_2C_2 and $H_2B_2^{2-}$ ligands bound to the tetrametal "butterfly" frameworks reveals an interesting point. Note that the borane fragment is not hydrogen bridged. We have previously argued that for borane ligands, binding to a single metal atom, the BHB bridges are crucial in orienting the boron atoms' donor orbitals toward the metal center thereby compensating for unusable π^* orbitals that lie at high energy relative to those of the carbon analogues.[24] Clearly, when four metal atoms are involved, as in I, no such special orientation is required for effective binding. Indeed, the BB distance is longer[26] than one would expect and in the range observed for BHB bonds.[17]

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Supplementary Material Available: Tables of atom coordinates, bond distances and angles, anisotropic temperature factors, and hydrogen atom coordinates (4 pages); tables of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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(11) The reaction of $CpCo(PPh_3)_2$ with $BH_3{\cdot}THF$ yields the same product.

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