The Chemistry of an 11-Atom Polyhedral Metallocarborane Prepared by Polyhedral Contraction

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Summary The base degradation of $[LCo(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})]^z$ followed by oxidation has been found to effect a polyhedral contraction to give $[LCo(\pi\text{-}B_8C_2H_{10})]^z$ where $L = \pi\text{-}C_5H_5^-$ and $z = 0$ or $L = \pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}{}^{2-}$ and $z = -1$; these new compounds react with pyridine to afford the adducts $[LCo(\pi\text{-}B_8C_2H_{10}\cdot C_5H_5N)]^z$ which constitute the first reported examples of a *nido*-metallocarborane.

PREVIOUS work has established the feasibility of the polyhedral expansion reaction in which a polyhedral carborane $B_nC_2H_{n+2}$, $n = 6, 8, 10$,[1-3] formally undergoes two-electron reduction followed by insertion of $[(\pi\text{-}C_5H_5)Co]^{2+}$ to afford a neutral metallocarborane $[(\pi\text{-}C_5H_5)Co(B_nC_2H_{n+2})]$. We now report the first example of a polyhedral contraction reaction in which a polyhedral metallocarborane is transformed to its next lowest homologue by formal removal of $[BH]^{2+}$ followed by two-electron oxidation.

Degradation of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})]$[4] and $[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})_2Co]^-$ with hydroxide ion, followed by oxidation using hydrogen peroxide, afforded the complexes (I) and (II) in 63% and 86% yield respectively. The

100 MHz ^{1}H n.m.r. spectrum of (I) exhibited resonances attributable to the $C_5H_5^-$ ligand and to two inequivalent carborane CH groups while that of (II) contained signals due to the $(CH_3)_4N^+$ ion and four inequivalent carborane CH groups. The mass spectrum of (I) was consistent with the formula $C_7H_{15}B_8Co$ and the 80·5 MHz ^{11}B n.m.r. spectrum indicated an asymmetric structure for the metallocarborane polyhedron. The ^{11}B n.m.r. spectrum of (II) was complicated by the extensive overlap of resonances but could be qualitatively reconstructed by overlapping the spectra of (I) and $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})]$. On the basis of these data and the known[5] structure of a pyridine adduct of (II) (*vide infra*) we formulate† (I) and (II) as $[(C_5H_5)Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]$ and $[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]^-$ respectively. In each case we suggest a *closo*-geometry for the $\{(B_8C_2H_{10})Co\}$ moiety analogous to that proposed[2] for $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(1)\text{-}2,3\text{-}B_8C_2H_{10})]$.

Both (I) and (II) reacted with pyridine to give the red adducts (III) and (IV) respectively. The structure of (IV) has been established[5] by *X*-ray diffraction methods and, on the basis of ^{1}H n.m.r., ^{11}B n.m.r. and mass spectral measurements, we suggest an analogous structure for (III). These compounds constitute the first reported examples of a *nido*-metallocarborane polyhedron. Although the *X*-ray study[5] did not provide evidence for the presence of a bridging hydrogen atom, the 100 MHz ^{1}H n.m.r. spectra of (III) and (IV) both contained a resonance to the high field side of Me_4Si attributable[6] to a bridging hydrogen atom. Since C–H–B and C–H–C bridge hydrogen atoms are unprecedented[7] we assign the non-terminal hydrogen atom to a location between the two boron atoms in the open face of the *nido*-metallocarborane fragment.

Oxidation of (III) and (IV) with $FeCl_3$ afforded the complexes (V) and (VI) whose ^{1}H n.m.r. spectra indicated the presence of the pyridine ligand and the absence of a bridging hydrogen atom. On the basis of these and other spectral data we formulate (V) and (VI) as $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_9{\cdot}C_5H_5N)]^+$ and $[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_9{\cdot}C_5H_5N)]$ respectively. These complexes are thought to be structurally analogous to (I) and (II) except that, formally, a terminal H^- substituent has been replaced by C_5H_5N.

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† Satisfactory elemental analyses have been obtained.

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