A Novel 9-Vertex Metallocarborane Containing a Monocarbon Carborane Ligand

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Summary The base degradation of orange $(\pi\text{-C}_5\text{H}_5)\text{Co}^{\text{III}}(\pi\text{-B}_{10}\text{C}_2\text{H}_{12})$ has been found to effect a polyhedral contraction reaction to give $[(\pi\text{-C}_5\text{H}_5)\text{Co}^{\text{III}}(\pi\text{-B}_7\text{CH}_8)]^-$; this reaction constitutes the first reported example of a small metallocarborane formed by the removal of a carbon atom and three boron atoms from a larger, parent metallocarborane.

Recent work in this laboratory has resulted in the development of the polyhedral contraction reaction[1] in which a polyhedral metallocarborane is transformed into its next smaller homologue by the formal removal of a B–H unit. Treatment of an ethanol solution of orange $(\pi\text{-C}_5\text{H}_5)\text{Co}^{\text{III}}(\pi\text{-B}_{10}\text{C}_2\text{H}_{12})$[2] with potassium hydroxide gave compound (I), a black, monoanionic complex that was isolated (60%) as either the tetramethylammonium or caesium salt.

The 100 MHz ^{1}H n.m.r. spectrum of the caesium salt of (I) in pyridine showed a sharp singlet of area 5 at τ 5·18 and a broad singlet of area 1 at τ 7·24 but showed no evidence of bridging B–H–B protons up to τ 30. The 80·5 MHz ^{11}B n.m.r. spectrum of (I) consisted of doublets of area ratios 2:2:2:1 at −41·1 p.p.m. (J 138 Hz) +2·2 (157), +17·3 (151), and +25·2 (147) [chemical shifts, p.p.m. relative to $\text{BF}_3\cdot\text{O(C}_2\text{H}_5)_2$].

Orange $(\pi\text{-C}_5\text{H}_5)\text{Co}^{\text{III}}(\pi\text{-B}_{10}\text{C}_2\text{H}_{11}\text{CH}_3)$ was prepared from $1,2\text{-B}_{10}\text{C}_2\text{H}_{11}(\text{CH}_3)$ in exactly the same manner as reported for the orange $(\pi\text{-C}_5\text{H}_5)\text{Co}^{\text{III}}(\pi\text{-B}_{10}\text{C}_2\text{H}_{12})$.[2] The degradation of orange $(\pi\text{-C}_5\text{H}_5)\text{Co}^{\text{III}}(\pi\text{-B}_{10}\text{C}_2\text{H}_{11}\text{CH}_3)$ gave two products. The first was identified as compound (I). The second, compound (II), was a dark green complex isolated as the tetramethylammonium salt.

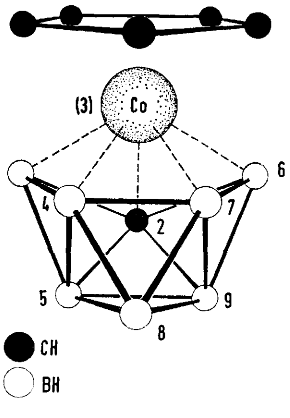

Figure. *The suggested structure of π-cyclopentadienyl-π-octahydro-2-carba-*nido*-octaboratocobaltate*(−1), $[(\pi\text{-C}_5\text{H}_5)\text{Co}^{\text{III}}(\pi\text{-2-B}_7\text{CH}_8)]^-$.

The 60 MHz ^{1}H n.m.r. spectrum of (II) in pyridine consisted of sharp singlets of area 5 at τ 5·21, area 12 at

τ 6·63, and area 3 at τ 7·37 which were assigned to the cyclopentadienyl protons, the tetramethylammonium ion protons and the carborane methyl group protons, respectively. The 80·5 MHz ^{11}B n.m.r. spectrum of (II) gave doublets of area ratios 2 : 2 : 2 : 1 at −41·7 p.p.m. (J 138 Hz), −2·8 (131), +12·7 (134), and +22·0 (128).

These results suggest that compound (I) is $[(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}2\text{-}B_7CH_8)]^-$, and that (II) is its *C*-methyl derivative.† The proposed structure of (I) consistent with the n.m.r. data, is shown in the Figure. The metallocarborane moiety assumes the configuration of a nine-vertex polyhedron isostructural with the known compounds $B_9H_9^{2-}$,[3] $B_7C_2H_9$,[4] $(B_6C_2H_8)Mn(CO)_3^-$,[5] and $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_6C_2H_8)$.[6] An *X*-ray diffraction study is in progress.

The $B_7CH_8^{3-}$ ligand and its *C*-methyl derivative are members of a series of anionic, *nido*-carborane ligands whose general formula is $B_nCH_{n+1}^{3-}$. The only other known member of this series is the $B_{10}CH_{11}^{3-}$ carbollide ion.[7,8] Compounds (I) and (II) are novel in that they are formed by what is only the second example of the removal of a carbon atom from a polyhedral environment[9] and the first such example involving a metallocarborane. Furthermore, a degradation reaction in which one carbon atom and three boron atoms are removed from the parent polyhedral metallocarborane to give, in high yield, a smaller metallocarborane is unprecedented. This reaction and its applicability to other metallocarboranes are now under study.

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† Satisfactory elemental analyses have been received for $[(CH_3)_4N][(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_7CH_8)]$, $Cs[(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_7CH_8)]$, and $[(CH_3)_4N][(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_7CH_7CH_3)]$.

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