Synthesis of a Mixed-metal Bimetallic Monocarbon Metallocarborane by Polyhedral Expansion

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Summary Addition of $Na^+C_5H_5^-$ and $NiBr_2,2C_2H_4(OMe)_2$ to $[Me_4N][(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}CB_7H_8)]$ previously reduced with sodium naphthalide formed a new bimetallic mixed metal monocarbon metallocarborane $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}CB_7H_8)Ni^{IV}(\pi C_5H_5)$, isolated in at least four isomeric forms, representing an extension of the polyhedral expansion reaction to monocarbon metallocarboranes.

The polyhedral expansion reaction has been used to prepare metallocarboranes from *closo*-carboranes[1,2] as well as bimetallic metallocarboranes from monometallocarboranes.[3] Bimetallic carboranes formed in this way have previously consisted of two-carbon systems containing identical metals. We now report the synthesis of a novel mixed-metal, neutral metallocarborane formulated as $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}CB_7H_8)Ni^{IV}(\pi\text{-}C_5H_5)$, constituting the first example of a bimetallic monocarbon metallocarborane and containing the new ligand $CB_7H_8^{5-}$. This is the first in a series of ligands of general formula $CB_nH_{n+1}^{5-}$.

Reduction of $[Me_4N][(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}CB_7H_8)]$[4] in tetrahydrofuran at 25° with sodium naphthalide (3 mol. equiv.) followed by addition of a threefold excess of $Na^+C_5H_5^-$ and excess of $NiBr_2,2C_2H_4(OMe)_2$ afforded a mixture of products. Two major isomers of $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}CB_7H_8)Ni^{IV}(\pi\text{-}C_5H_5)$, (I) and (II), were separated by column chromatography and isolated in 25 and 6% yields, respectively; m.p.s. 171 and 199° (in evacuated capillaries).

The 80·5 MHz ^{11}B n.m.r. spectrum of (I), measured in $(CD_3)_2CO$, contained doublets of relative area 1:2:2:2 at −41·9 (140), −36·3 (150), −17·5 (150), and +2·6 (160) [chemical shift, p.p.m. relative to F_3B,OEt_2 (coupling constant, Hz)]. The 100 MHz ^1H n.m.r. spectrum of (I) consisted of sharp singlets at τ 4·91 and 3·93 and a broad resonance at τ 1·62 of relative areas 5:5:1. The 80·5 MHz ^{11}B n.m.r. spectrum of (II), measured in $(CD_3)_2CO$, consisted of doublets of relative area 1:2:2:2 at −115·8 (160), −3·6 (155), +1·0 (150), and +6·2 (140). The 100 MHz ^1H n.m.r. spectrum of (II) consisted of sharp singlets at τ 5·10 and 4·70 and a broad resonance at τ 5·65 of relative areas 5:5:1. The sharp singlets were assigned to cyclopentadienyl protons and the broad singlets to carborane C–H. Elemental analyses for both isomers were consistent with the formula $B_7C_{11}H_{18}CoNi$, and both isomers exhibited mass spectra with cut-offs at *m/e* 346 corresponding to the $^{11}B_7{}^{12}C_{11}{}^1H_{18}{}^{59}Co^{60}Ni^+$ ion.

When the reaction was performed at reflux temperature, (I) and (II) were isolated in 8 and 17% yields, respectively. Isomer (I) rearranged slowly in heptane at reflux to isomer (II). At least two other isomers of $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}CB_7H_8)Ni^{IV}(\pi\text{-}C_5H_5)$ have been isolated from these reactions in very low yield and studies are in progress to determine the structures and rearrangement properties of these additional isomers.

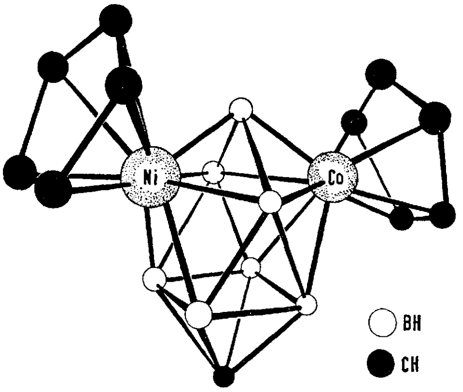

FIGURE. *Proposed structure of* $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_7CH_8)Ni^{IV}(\pi\text{-}C_5H_5)$, *isomer* (II).

Based on the above data, the structure proposed for (II) is shown in the Figure and has the gross geometry of a bicapped Archimedian antiprism. We tentatively assign the very low field (−115·8 p.p.m.) unique boron resonance to the boron in the apical position adjacent to the two metals.[5] We propose for (I) a similar geometry with nickel and carbon at apices and the cobalt atom adjacent to carbon. Other possible structures for (I) and (II) cannot be excluded at this time, however.

This compound may well be the first in a series of $[\pi\text{-}C_5H_5)\text{-}M^1(\pi\text{-}CB_nH_{n+1})M^2(\pi\text{-}C_5H_5)(M^1,M^2 = Co,\ Ni$, for example] mixed-metal monocarbon metallocarborane systems, and affords us an excellent opportunity to study mixed-valence metal–metal interactions in bimetallic metallocarboranes. In addition, further isomers of $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}CB_7H_8)Ni^{IV}\text{-}(\pi\text{-}C_5H_5)$ may possibly contain metal–metal bonds, analogous to the metal–metal bond in the isostructural and isoelectronic $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}C_2B_6H_8)Co^{III}(\pi\text{-}C_5H_5)$ complex[6] and the metal–metal bond in $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}C_2B_8H_{10})Co^{III}\text{-}(\pi\text{-}C_5H_5)$[7].

We thank Dr. D. F. Dustin, W. J. Evans, and Dr. C. J. Jones for helpful discussion and Professor F. A. L. Anet for the use of his high resolution n.m.r. spectrometer. This research was supported by the Office of Naval Research.

(*Received, 4th June* 1973; *Com.* 804.)

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