Isomeric $(\eta^5-C_5H_5)NiB_9H_9^-$ Metalloborane Anions from $B_9H_{12}^-$ and Nickelocene

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Summary Reaction of $B_9H_{12}^-$ and $Ni(C_5H_5)_2$ with Na amalgam gives the metalloborane $[(\eta^5-C_5H_5)-2-Ni(\eta^5-B_9H_9)]^-$ which is quantitatively converted to a second isomer $[(\eta^5-C_5H_5)-1-Ni(\eta^4-B_9H_9)]^-$ by thermal isomerization.

We have recently prepared the icosahedral nickeloboranes $[(\eta^5\text{-}C_5H_5)Ni(\eta^5\text{-}B_{11}H_{11})]^-$ and $[(\eta^5\text{-}C_5H_5)Ni]_2B_{10}H_{10}$.[1] We now report the synthesis of the two isomeric *closo*-metalloboranes, $[(\eta^5\text{-}C_5H_5)\text{-}2\text{-}Ni(\eta^5\text{-}B_9H_9)]^-$ and $[(\eta^5\text{-}C_5H_5)\text{-}1\text{-}Ni\text{-}(\eta^4\text{-}B_9H_9)]^-$ from a nido-borane anion, $B_9H_{12}^-$, and nickelocene in the presence of a reducing agent. The method is similar to that used to form $[(\eta^5\text{-}C_5H_5)Ni(\eta^5\text{-}B_{11}H_{11})]^-$ from $B_{11}H_{13}^{2-}$.[1]

Treatment of a solution of $Me_4NB_9H_{12}$[2] and nickelocene in acetonitrile at room temperature with one equiv. of Na amalgam produced a rapid colour change from dark green to dark red with noticeable evolution of gas. Red and yellow anionic complexes, (I) and (II), were isolated as the Me_4N^+ salt by chromatography on alumina in 18% and 7% yields, respectively (based on $B_9H_{12}^-$). The yield of (II) was increased at the expense of (I) if care was not taken to minimize even mild heating on work up. Elemental analyses for (I) and (II) were in agreement with the formula $Me_4NB_9H_9NiC_5H_5$. The 80·5 MHz ^{11}B n.m.r. spectrum of (I) in CD_3CN contained doublets of relative area 1 : 1 : 3 : 2 : 2 at −59·0(160), −12·6(150), −6·9(130), + 14·7(150), and +21·8(140) and the spectrum of (II) contained doublets of relative area 1 : 4 : 4 at −73·6(150), −29·0(140) and +1·3-(130) [chemical shift in p.p.m. relative to $BF_3\cdot OEt_2$ (coupling constant, Hz)]. The 60 MHz ^1H n.m.r. spectra consisted of two singlets of relative area 5 : 12 at τ 4·9 and 6·9 for (I) and τ 4·3 and 6·9 for (II) which were due to the cyclopentadienyl and tetramethylammonium resonances, respectively.

The 1 : 1 : 3 : 2 : 2 pattern of doublets observed for compound (I) is consistent with a bicapped Archimedean antiprism geometry with the $(\eta^5\text{-}C_5H_5)Ni$ grouping in an equatorial position if there is coincidental overlap of a doublet of area one with a doublet of area two. The 1 : 4 : 4 pattern of doublets for compound (II) is consistent with a structure with the nickel atom in an apical position.

Compound (I) can be quantitatively converted to (II) thermally and with slight decomposition photochemically. Compound (I) in CD_3CN was heated in a sealed n.m.r. tube until the red colour completely disappeared (several minutes at 150°). The ^{11}B n.m.r. spectrum showed quantitative conversion to compound (II). Irradiation of a sample of (I) in CD_3CN with a u.v. source (through pyrex) for several hours produced (II) and a very small amount of white precipitate. Irradiation of (II) under the same conditions produced no change.

In compound (I) the nickel atom is co-ordinated to five boron atoms, whereas in compound (II) the nickel atom is co-ordinated to four boron atoms. This is the first example of a polyhedral metalloborane rearrangement which results in the metal atom moving to a lower co-ordinate position. The apical position for the cyclopentadienyl nickel grouping is apparently favoured thermodynamically over the equatorial position. This can perhaps be explained by analogy to $B_{10}H_{10}^{2-}$ in which the apical boron atoms are relatively electron rich. In the case of (II) the formal Ni^{IV} oxidation state may obtain more stabilization by electron donation to the apical position. Compound (II) is another example of a boron analogue of a co-ordinated cyclobutadiene dianion.[3] In this case the set of four boron atoms in the bonding face provides a total of 6 electrons to a formal Ni^{IV} vertex and is thus isoelectronic with a cyclobutadiene dianion.

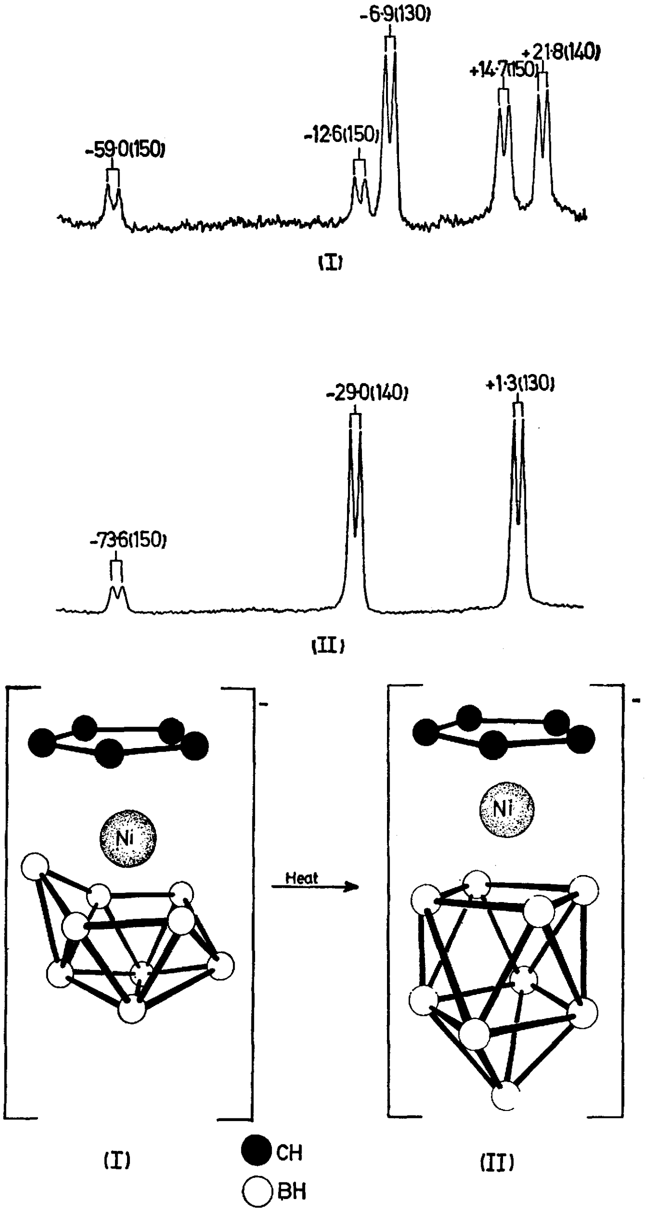

FIGURE. The proposed structures of (I) and (II) shown with their 80·5 MHz ^{11}B n.m.r. spectra.

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