SYNTHESIS OF TEN-VERTEX *closo*-METALLACARBABORANES FROM 4-CB_8H_{14}

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Nickelocene and 4-$CB_8H_{13}^-Na^+$ react in diglyme at 130–140°C to produce an unstable [6-η^5-C_5H_5Ni-η^5-1-CB_8H_9] complex which rearranges to the isomeric [10-η^5-C_5H_5Ni-η^4-1-CB_8H_9] species. Modification of the synthesis led to the isolation of a bimetallic [(6,7-η^5-$C_5H_5Ni)_2$-η^6-1-CB_7H_8] compound. The [2-η^5-C_5H_5Co-η^5-1-$CB_8H_9]^-$ anion was prepared by treatment of 4-CB_8H_{14} with cyclopentadiene and $CoCl_2.6\,H_2O$ in ethanolic potassium hydroxide. Structures of the complexes were determined by their NMR spectra and X-ray diffraction studies.

The title compounds have been only little investigated. Hawthorne and coworkers[1] isolated the first representative of monometallic 10-vertex carbaboranes, [10-η^5-C_5H_5Ni-η^4-1-CB_8H_9], as a trace by-product in the reaction of nickelocene with the 7-$CB_{10}H_{13}^-$ anion. Polyhedral expansion of the [6-η^5-C_5H_5Co-η^5-1-$CB_7H_8]^-$ complex[2] led to the isolation of a bimetallic 10-vertex[η^5-C_5H_5Co-η^5-C_5H_5Ni-1-CB_7H_8] isomeric species[3]. Our recent high yield preparation of 4-CB_8H_{14} constituted[4] and effective route to the complexes of a general formula [η^5-$C_5H_5M^{n+}$-1-$CB_8H_9]^{n-4}$ (M = Co, Ni) and to the [(η^5-$C_5H_5Ni)_2CB_7H_8$] species[5]. We wish to report herein the relevant experimental details and the structure of the dinickel complex.

Prolonged treatment of 4-$CB_8H_{13}^-Na^+$ with nickelocene in diglyme at 130–140°C produced an orange-yellow complex *I* (R_F 0·34; m/z 236) which slowly rearranged to another isomeric orange-yellow species *II* (R_F 0·58; m/z 236) under the conditions of dry column chromatography on silica gel during the work up of the reaction mixture. Column chromatography allowed us to isolate in moderate yield pure complex *II* the NMR data of which were in agreement with those found[1] for [10-η^5-C_5H_5Ni-η^4-1-CB_8H_9]. We were, however, unable to obtain pure compound *I* due to its progressive rearrangement to complex *II* under relatively mild conditions. The NMR data of the complex *I*, obtained by substracting the signals of *II* from the spectra of the isolated *c.* 1 : 10 mixture of compounds *I* and *II*, were consistent with the [6-η^5-C_5H_5Ni-η^5-1-CB_8H_9) arrangement. For the complex *I* can be smoothly rearranged to compound *II* without any detecable intermediate, the 6,1-arrangement should be preferred to the 2,1-structural alternative.

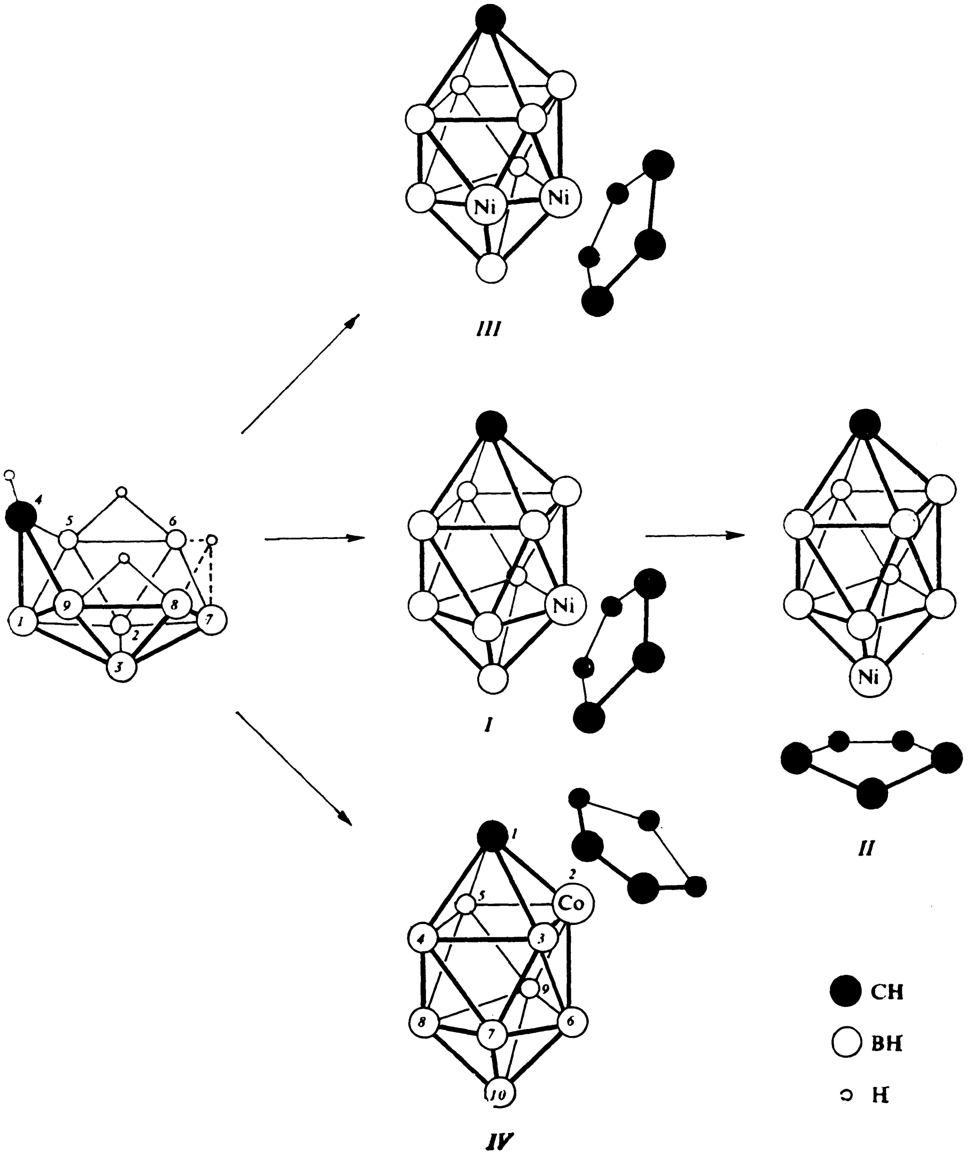
Another product was isolated, besides complexes *I* and *II*, on treatment of the 4-$CB_8H_{13}^-N(CH_3)_4^+$ salt (preheated to 160°C after partial hydrolysis) with nickelocene in acetonitrile as a dark green paramagnetic species the mass spectrum of which (*m*/*z* 347) was consistent with a bimetallic [$(C_5H_5Ni)_2CB_7H_8$] complex *III*. The species did not give normal NMR spectra due to its paramagnetism and therefore an X-ray diffraction study was used to resolve the structure. The relevant study[6] clearly confirmed the [6,7-$(\eta^5$-$C_5H_5Ni)_2$-η^6-1-CB_7H_8] arrangement for *III* (see Scheme 1), involving a Ni–Ni bond; the complex being thus isostructural with the heterometallic [6-η^5-C_5H_5Co-7-η^5-C_5H_5Ni-η^6-1-CB_7H_8] compound[3]. Isolation of compound *III* is another example of high stability of the metallaborane complexes with a metal–metal bonding, which seems to be a general feature of these types of compounds[3,4,7,8]. Considering the electron count arguments[9,10], complex *III* should contain the two nickel atoms in different oxidation states, Ni^{4+} and Ni^{3+}, or better in an average +3·5 oxidation state, which is likely responsible for the observed paramagnetism.

Reaction of 4-CB_8H_{14} with $CoCl_2.6\,H_2O$ and cyclopentadiene in concentrated ethanolic potassium hydroxide afforded a dark red anionic complex *IV* characterized as its tetramethylammonium salt the NMR data of which correspond well to the [2-η^5-C_5H_5Co-η^5-1-$CB_8H_9]^-N(CH_3)_4^+$ structure recently determined by an X-ray diffraction study[11].

Formation of the discussed monometallic complexes may consist in an insertion of the metal atom above the $B_{(6,7,8)}$ triangular face of the 4-$CB_8H_{13}^-$ anion to form compounds *I* and *IV* upon a dehydrogenative closure and reorganization of the skeleton. Similar mechanism has also been postulated to explain the formation of the recently reported[12] *closo*-[10-$P(C_6H_5)_3$-6-H/$P(C_6H_5)_3/_2$Ir-1-CB_8H_8] structurally analogous to compound *I*. In contrast to the cobalt complex *IV*, the nickel species *I* is unstable due to unfavourable location of the $(Ni^{IV}C_5H_5)^{3+}$ group in the equatorial belt[13], which accounts for the observed *I* → *II* rearrangement. Similar facile equatorial-apex rearrangement of the skeletal nickel atom was observed with the isoelectronic [2-η^5-C_5H_5Ni-η^5-$B_9H_9]^-$ anion[13].

EXPERIMENTAL

^1H (200 MHz) and ^{11}B (64·18 MHz) NMR spectra were recorded on a Varian XL-200 equipment, chemical shifts are given in δ (ppm related to tetramethylsilane and $BF_3.O(C_2H_5)_2$, positive values downfield). Mass spectra were obtained on a GC/MS HP-5985 spectrometer. Purity of individual complexes was monitored by TLC on Silufol (silica gel on aluminium foil, starch as binder, producer Kavalier, Votice, Czechoslovakia). Melting points were measured in sealed capillaries and are uncorrected. All reactions were performed under dry nitrogen, unless otherwise stated. Diglyme was purified by shaking with solid potassium hydroxide, dried over calcium hydride and distilled *in vacuo* with $NaAlH_2(OC_2H_4OCH_3)_2$ prior to use.



SCHEME 1

10-η^5-cyclopentadienyl-10-nickela-1-carba-*closo*-decaborane(9) (*II*)

To a stirred suspension of sodium hydride (0·25 g; 0·01 mol) in diglyme (30 ml) was added dropwise a solution of 4-CB_8H_{14} (0·6 g; 5·3 mmol) in diglyme (10 ml). The hydrogen evolution having ceased, nickelocene (2 g; 0·01 mol) was added and the mixture was heated to 130—140°C for 8 h. Excess sodium hydride was decomposed with methanol (3 ml), the mixture was exposed to air for 30 min, placed on a 2·5 × 30 cm column of silica gel and eluted with benzene–hexane (1 : 2) to isolate two orange-yellow fractions (R_F 0·58 and 0·35) which were washed with several 30 ml portions of water to remove the diglyme. After removing the organic solvents *in vacuo*, the solid residues were sublimed at 120—130°C/1·3 Pa. The first fraction yielded 0·15 g (12%) of a orange-yellow complex *II*; *m*/*z* 236 (corresponding to $^{12}C_6{}^{11}B_8{}^1H_{14}{}^{62}Ni^+$); ^1H NMR spectrum (deuteriochloroform): δ 5·96 (5 H, s, C_5H_5), 8·07 (1 H, s, CH skel.); ^{11}B NMR spectrum (deuteriochloroform) δ_B −2·35 (4 B, d, 160), −26·87 (4 B, d, 145). The above data are consistent with those obtained for [10-η^5-C_5H_5Ni-η^4-1-CB_8H_9] by Hawthorne[1]. After an analogous work up of the second fraction, 0·2 g (16%) of a *c*. 1 : 10 mixture of *I* and *II* were isolated. The NMR data of the compound *I* were obtained by substracting the signals of compound *II* from the spectra of the mixture; ^1H NMR spectrum (deuteriochloroform): δ 5·01 (5 H, s, C_5H_5), 5·48 (1 H, s, CH skel.); ^{11}B NMR spectrum (deuteriochloroform): δ_B 76·5 (1 B, d), 2·0 (2 B, d), −1·4 (1 B, d), −17·0 (2 B, d), −19·1 (2 B, d).

6,7-Bis(η^5-cyclopentadienyl-nickela)-η^6-1-carba-*closo*-decaborane(8) (*III*)

The 4-CB_8H_{14} carborane (0·5 g; 4·4 mmol) was dissolved in benzene (20 ml) and the solution formed was shaken three times with 10% K_2CO_3 (10 ml). The aqueous extract was left to stand for 1 h to achieve partial hydrolysis and then it was precipitated with 1M tetramethylammonium chloride (10 ml). The precipitate was sucked off, dried at 20°C/1·3 Pa for 2 h and heated at 160°C/1·3 Pa for additional 2 h. The product from the above procedure (0·8 g) was dissolved in acetonitrile (30 ml), nickelocene (2·2 g; 8·9 mmol) was added and the mixture was refluxed for 8 h. After filtration it was stripped onto silica gel (5 g), placed atop a 2·5 × 35 cm dry column of silica gel and eluted with benzene–hexane (1 : 3) to develop orange-yellow and green bands. The former fraction yielded 0·1 g (10%, based on 4-CB_8H_{14} used) of a mixture of complexes *I* and *II* (*c*. 1 : 10, identified by the ^{11}B NMR spectrum) and, from the latter fraction, 0·2 g (14%) of compound *III* were isolated as green crystals which were crystallized from hexane; m.p. 120°C (decomp.); *m*/*z* 347 (corresponding to $^{12}C_{11}{}^{11}B_7{}^1H_{18}{}^{60}Ni_2^+$).

Tetramethylammonium 2-η^5-cyclopentadienyl-2-cobalta-η^5-1-carba-*closo*-decaborate(1−) (*IV*)

To a solution of potassium hydroxide (25 g) in ethanol (40 ml) cyclopentadiene (2 ml), a solution of $CoCl_2.6\ H_2O$ (2·5 g; 0·011 mol) in ethanol (20 ml) and solid 4-CB_8H_{14} (0·65 g; 5·8 mmol) were added at 0°C under continuous shaking. After shaking for additional 2 h at ambient temperature the temperature was raised to 45—50°C for 1 h. After cooling to room temperature, water (150 ml) was added and the ethanol was removed *in vacuo*. The residual mixture was filtered and the filtrate was treated with 1M tetramethylammonium chloride (10 ml). The precipitate was filtered, washed twice with water (50 ml), stripped as an acetone solution (*c*. 50 ml) onto silica gel (10 g) and placed on a 2·5 × 30 cm dry column of silica gel. Elution with ethyl acetate–2-propanol (4 : 1) developped green and brown-red bands, the former being a mixture of compounds. The latter fraction was reduced in volume to *c*. 10 ml and repeatedly eluted with the same solvent system. After removing the organic solvents from the effluent, a solution of tetramethylammonium chloride (1 g) in water (20 ml) was added to the residue. After sucking off the precipitate and crystallizing it from 50% ethanol, 0·3 g (17%, based on 4-CB_8H_{14} used) of compound *IV* were obtained as red crystals. For $N(CH_3)_4C_5H_5CoCB_8H_9$ (305·8) calcd.: 28·31% B, 4·58% N, 19·27% Co; found: 28·22% B, 4·70% N, 19·4% Co; ^1H NMR spectrum (hexadeuterioacetone): δ 6·56 (1 H, s, CH skel.), 4·75 (5 H, s, C_5H_5), 3·46 (12 H, s, $(CH_3)_4N$); ^{11}B NMR spectrum (hexadeuterioacetone): δ_B 34·20 (1 B, d, 148), 2·31 (1 B, d, 142), 0·39 (2 B, d, 136), −21·33 (2 B, d, 140), −25·52 (2 B, d, 136).

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