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Synthesis of the First *hyper-closo*-Type Monocarbon Ruthenacarboranes by Polyhedral Contraction of [*nido*-$B_{10}H_{12}CH$]$^-$ and Molecular Structure of 2-Cl-2,5-(Ph_3P)$_2$-2-H-3,9-(MeO)$_2$-2,1-$RuCB_8H_6$

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*Summary: Treatment of [nido-$B_{10}H_{12}CH$]$^-$$Cs^+$ with $RuCl_2(PPh_3)_3$ in methanol under gentle reflux afforded the two novel 10-vertex monocarbon ruthenacarboranes 2-Cl-2,5-(Ph_3P)$_2$-2-H-3,9-(MeO)$_2$-2,1-$RuCB_8H_6$ (**3**) and 2,2-(Ph_3P)$_2$-2-H-3,9-(MeO)$_2$-2,1-$RuCB_8H_7$ (**4**) along with a small amount of the 8-vertex complex (PPh_3)$_2$-$HRuCB_6H_4(OMe)_3$ (**6**). The 10-vertex clusters **3** and **4** on the basis of their capped-tricapped-trigonal-prismatic geometry, established for **3** by a single-crystal X-ray diffraction study, and the formal Wadian electron-counting arguments can be regarded as hyper-closo species having n rather than n + 1 skeletal electron pairs.*

The [*nido*-$B_{10}H_{12}CH$]$^-$ anion (**1**) is normally used as a convenient source for the π-monocarbollide ligand, which, in turn, is most widely employed for the preparation of 12-vertex monocarbon *closo*-metallacarboranes *via* treatment with transition-metal reagents.[1] In this paper we demonstrate an unprecedented use of **1** as a precursor to smaller cage monocarbon carborane ligands, and, in particular, we report the first example of a polyhedral contraction reaction of **1** where the elimination of 2 and even 4 boron-containing fragments is effected by the action of 16-electron $RuCl_2(PPh_3)_3$ (**2**). Such deep transformations upon treatment with transition-metal reagents have never before been observed for either mono- or dicarbon *nido*-carboranes and may thus be considered as new and efficient synthetic routes at least to the MCB_8 derivatives. The main products of the reaction are found to be the novel 10-vertex monocarbon ruthenacarborane clusters 2-Cl-2,5-(Ph_3P)$_2$-2-H-3,9-(MeO)$_2$-2,1-$RuCB_8H_6$ (**3**) and 2,2-(Ph_3P)$_2$-2-H-3,9-(MeO)$_2$-2,1-$RuCB_8H_7$ (**4**), which may be viewed as rare types of monocarbon *hyper-closo*-metallacarboranes.

Although now a number of super-electron-deficient 10-vertex *hyper-closo*-metallacarborane clusters[2] as well as closely related *iso-closo*-metallaboranes[3] are known, analogous monocarbon metallacarboranes with the *closo* geometry have never been reported. The only structurally related monocarbon metallacarborane species appears to be *iso-nido*-[{$IrC(OH)B_8H_6(OMe)$}($C_6H_4PPh_2$)-(PPh_3)] (**5**),[4] isolated quite unexpectedly as one of the products of the reaction between *trans*-[$Ir(CO)Cl(PPh_3)_2$] and *closo*-[$B_{10}H_{10}$]$^{2-}$. The iridium atom in **5** is coordinated by five rather than six atoms of the six-membered open face. Herein we present a single-crystal X-ray diffraction study of cluster **3** which, in contrast to **5**, proved to have a completely closed deltahedral geometry and, therefore, may be regarded as the first example of a crystallographically characterized 10-vertex monocarbon metallacarborane of *hyper-closo* type.

Treatment of the Cs^+ salt of **1** with 1 equiv of **2** in deoxygenated methanol at reflux temperature for 4 h, followed by column chromatographic separation and fractional crystallization of the reaction products, afforded the two air-stable metallacarborane complexes **3** and **4** as predominant products in isolable moderate yields[5,6] (Scheme 1). In addition, several minor products were formed in the reaction, and one of them was isolated as a colorless crystalline solid (**6**) whose NMR and mass spectrum data were consistent with the formula (PPh_3)$_2$$HRuCB_6H_4(OMe)_3$ based on the $RuCB_6$ rather than the $RuCB_8$ framework.[7]

According to an X-ray diffraction study,[8] cluster **3** adopts the 10-vertex *closo* geometry and involves the CB_8-cage ligand substituted by two MeO and one PPh_3 groups at the boron atoms and coordinated by its 6-membered (CB_5) open face to the Ru atom of the 12-electron $RuHCl(PPh_3)$ moiety (Figure 1). The molecular geometry of **3** seems to be best described as a tricapped trigonal prism with one additional vertex C(1) wherein two axial bonds, B(3)−B(5) (2.746(7) Å) and B(6)−B(9)

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[5] To a suspension of **2** (100 mg, 0.38 mmol) in 30 mL of deoxygenated absolute MeOH was added a stoichiometric amount of **1** (360 mg, 0.38 mmol); the mixture was stirred at ambient temperature for 1 h and thereafter refluxed for 4 h under argon. The resulting claret-colored mixture was filtered through a coarse frit and the filtrate concentrated in vacuo. The remaining dark residue was separated by column chromatography on silica gel using CH_2Cl_2 as eluent into two yellow fractions which were reduced in vacuo and subjected separately to the same chromatographic procedure by using 5−40 mesh silica gel. The resulting separation yielded three principal products, **3** and **6** (as a mixture, R_f 0.42) and the pure solid form of **4** (52 mg, 17% yield, R_f 0.88). In addition, at least three minor products of unidentified structures could be also isolated as crude solids in 2−5% yields. Finally, recrystallization of the mixture of **3** and **6** two times from CH_2Cl_2/*n*-hexane (2:1 mixture) afforded **3** as a yellow solid (140 mg, 45% yield). A small amount of **6** (16 mg, 5.3% yield) was obtained as colorless crystals from the first mother liquor diluted with *n*-hexane.

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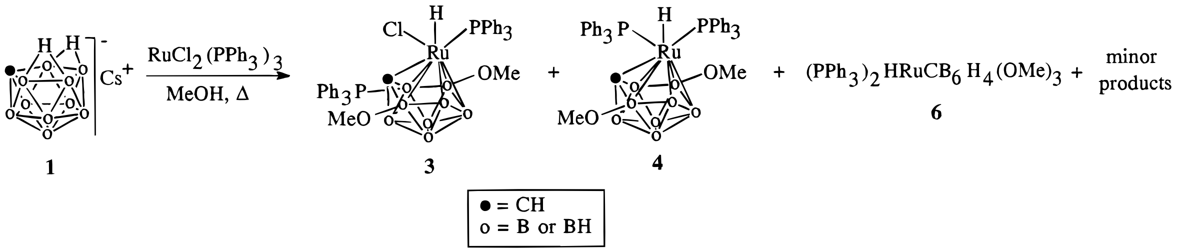
Scheme 1



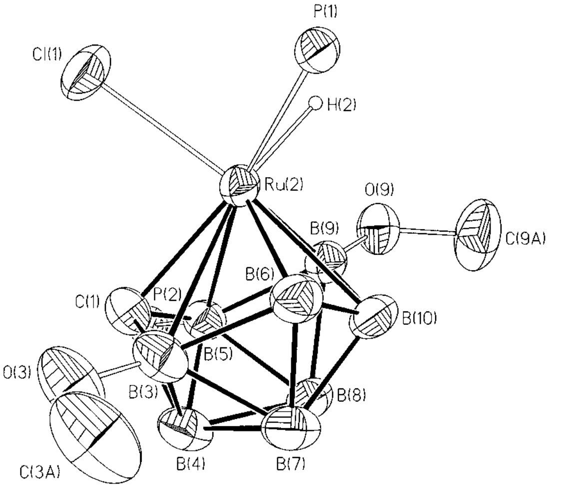


Figure 1. Molecular structure of **3** (thermal ellipsoids are drawn at the 50% probability level); the phenyl group carbon atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(2)−Cl(1), 2.4212(13); Ru(2)−P(1), 2.3243(13); Ru(2)−H(2), 1.63(4); Ru(2)−C(1), 2.157(3); Ru(2)−B(3), 2.502(5); Ru(2)−B(5), 2.436(4); Ru(2)−B(6), 2.095(4); Ru(2)−B(9), 2.083(4); Ru(2)−B(10), 2.346(4); Cl(1)−Ru(2)−P(1), 89.16(4); P(1)−Ru(2)−H(2), 68(2); Cl(1)−Ru(2)−H(2), 94(2).

(2.944(6) Å) are disrupted and one extra bond, Ru(2)−B(10) (2.346(4) Å), is formed. The C(1) vertex bridges one of the broken axial bonds, B(3)−B(5), and is simultaneously bonded to two capping atoms, Ru(2) and B(4) (the C(1)−Ru(2) and C(1)−B(4) distances are equal to 2.157(3) and 1.664(6) Å, respectively).

It can be seen from Figure 1 that an alternative description of the polyhedron as a bicapped Archimedian square antiprism, which is normally found for electron-precise 10-vertex monocarbon metallacarboranes of the *closo* type,[9] seems much less appropriate in this case. In particular, the B(6)···B(9) distance within the basal prism face B(6)B(7)B(8)B(9) is too long to be considered as bonding and, in contrast, one extra bond, B(10)−Ru(2), which does not comply to the bicapped antiprismatic geometry is formed. One of the basal fragments of the antiprism, B(3)B(4)B(5)Ru(2), shows quite significant deviations from planarity, the folding angle along the B(5)···B(3) line being equal to 20.2°. Moreover, the mean plane of this cycle is not quite parallel to another basal plane of the antiprism, B(6)B(7)B(8)B(9), forming with the latter the dihedral angle of 9.5°.

The structure of **3** has revealed several specific geometrical features typical of the 10-vertex *hyper-closo* polyhedra. The 6-membered open face coordinating by the Ru atom has an almost ideal chair conformation. Thus, the signs of the torsion angles about the bonds of the six-membered cycle are alternating with their absolute values in the range of 48.7−57.2°. The Ru(2) atom is located in the vicinity of the approximate 3-fold axis of the 6-membered ring, so that the atoms with low cluster connectivity of 4, C(1), B(6), and B(9), turned out to be much closer to the ruthenium center (2.157(3), 2.095(4), and 2.083(4) Å, respectively) as compared

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(6) Characterization data for **3** and **4** are as follows. **3**: IR (KBr) ν_{BH} 2527 cm^{-1} ν_{RuH} 1955 cm^{-1}; ^{1}H NMR (400.13 MHz, CD_2Cl_2, J (Hz)) 7.81−7.40, 7.06 (m + d br, 29H + 1H, Ph, J_d = 12), 3.60 (s br, 1H, *CH_{Cb}), 3.46 (s, 3H, MeO), 3.13 (s, 3H, MeO), −4.68 (d, 1H, H_{Ru}, J_{H-P} = 57) (the asterisk indicates that the resonance was assigned by ^{13}C-{^{1}H}−^{1}H correlation); ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6, J_{P-B} (Hz)) 52.1 (s, 1P, P_{Ru}), 3.9 (q-like, 1P, P_B, 152 (av)); ^{13}C{^{1}H} NMR (100.51 MHz, CD_2Cl_2, J_d = J_{C-P} (Hz)) 134.8, 133.0, 130.3 (s v br + d br, s br, $C_{Ph-o,m,p(k?)}$(B−PPh_3), $J_d \approx 4$), 134.7, 129.3, 127.9, 122.8 (d, $C_{Ph-o,m,p,k}$(Ru−PPh_3),^1J_d = 7, ^2J_d = 12, ^3J_d = 12, ^4J_d = 65 (C_k)), 57.5 (s, MeO), 56.2 (s, MeO), 48.9 (q-like br, C_{Cb}); ^{11}B NMR (128.33 MHz, CD_2Cl_2, J_{B-H} (Hz)) 77.0 (d br, 1B, B6, 122), 70.2 (s, 1B, B9), 15.1 (d, 1B, B7(8), 160), 13.8 (d, 1B, B8(7), 160), 11.7 (s, 1B, B3), −4.1 (d, 1B, B4, 145), −25.8 (d, 1B, B5, J_{B-P} = 150), −29.0 (d, 1B, B10, 145). Anal. Calcd for $C_{39}H_{43}B_8ClO_2P_2Ru{\cdot}CH_2Cl_2$: C, 52.58; H, 4.71; P, 6.79. Found: C, 52.99; H, 4.52; P, 6.54. **4**: IR (KBr) ν_{BH} 2530 cm^{-1}, ν_{RuH} 1950 cm^{-1}; ^{1}H NMR (400.13 MHz, CD_2Cl_2, J (Hz)) 7.37, 7.35−7.10 (t-like + m, 31H, Ph + CH_{Cb}(?), J_t = 8), 4.07 (s, 3H, MeO), 3.70 (s, 3H, MeO), −5.36 (d d, 1H, J_{H-P1} = 22.1, J_{H-P2} = 45.3); ^{31}P{^{1}H} NMR (161.98 MHz, CD_2Cl_2, J_{P-P} (Hz)) 50.7 (d, 1P, P1, 16), 38.7 (d, 1P, P2, 16); ^{13}C{^{1}H} NMR (100.51 MHz, CD_2Cl_2, J_d = J_{C-P} (Hz)) 135.2, 134.5, 133.3, 130.8, 130.0, 128.4, 127.5 (s br + 6 d (partly overlapped), $C_{Ph-o,m,p,k}$(Ru−PPh_3), J_d= 48.2 (C_k), 32.0 (C_k), $J_d \approx 8$), 132.1 (s v br, C_{Cb}?), 59.5 (s br, MeO), 57.7 (s, MeO); ^{11}B NMR (128.33 MHz, CD_2Cl_2, J_{B-H} (Hz)) 82.4 (s, 1B, B9), 78.8 (s br, 1B, B6), 19.8 (d, 1B, B4(7 or 8), 124), 12.7 (s br + s, 3B, B7,8(4,7 or 4,8), B3), −23.7 (d br, 1B, B5(10), 120), −28.7 (d br, 1B, B10(5), 120). Anal. Calcd for $C_{39}H_{44}B_8O_2P_2Ru$: C, 58.94; H, 5.54, Found: C, 59.30; H, 5.59. FAB MS (positive ion, *m*/*e*): calcd for $^{12}C_{39}{}^1H_{44}{}^{11}B_8{}^{16}O_2{}^{31}P_2{}^{101}Ru$ 794.3, found 794.6 [M]$^+$, 717.3 [M − Ph]$^+$, 530.3 [M − PPh_3 − H_2]$^+$, 456.2 [M − PPh_3 − Ph]$^+$.

(7) Although complex **6** was not isolated in sufficient quantities to allow complete characterization, the NMR and mass spectral data available are consistent with the formulation of this species as having an eight-vertex monocarbon metallacarborane structure, $(PPh_3)_2HRuCB_6H_4(OMe)_3$: ^{1}H NMR (400.13 MHz, C_6D_6, J (Hz)) 7.51, 6.97, (m + m 12H + 18H, Ru$(PPh_3)_2$), 4.17 (s, 3H, MeO), 3.05 (s, 6H, 2 MeO), 2.99 (s br, 1H, CH_{Cb}), −9.02 (t, 1H, H_{Ru}, J_{H-P} = 20.7); ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6) 49.4 (s, P_{Ru}); ^{11}B NMR (128.33 MHz, CD_2Cl_2, J_{B-H} (Hz)) 68.9 (s br, 1B), 33.7 (s, 2B), 12.8 (d, 1B, 140), −31.8 (d, 2B, 150); FAB MS (positive ion, *m*/*e*): calcd for $^{12}C_{40}{}^1H_{44}{}^{11}B_6{}^{16}O_3{}^{31}P_2{}^{101}Ru$ 801.2, found 801.6 [M]$^+$, 724.4 [M − Ph]$^+$, 647.3 [M − 2Ph]$^+$, 570.2 [M − 3Ph]$^+$, 539.4 [M − PPh_3]$^+$, 462.4 [M − PPh_3 − Ph]$^+$. Since this species seems to have a *hyper-closo* structure (there is the characteristic low-field resonance at 68.9 ppm in the ^{11}B NMR spectra which could be ascribed to the low-coordinate boron atom), a detailed investigation of its formation and structure as well as those of other minor products of the above reaction is planned.

(8) Crystal data for **3**: $RuC_{39}H_{43}B_8ClO_2P_2{\cdot}CH_2Cl_2$, M_r = 913.60, triclinic, space group $P\bar{1}$, a = 9.968(2) Å, b = 12.269(3) Å, c = 19.455(4) Å, α = 94.83(3)°, β = 90.39(3)°, γ = 111.68(3)°, V = 2201.1(8) Å^3 for Z = 2, d(calcd) = 1.378 g/cm^3, F(000) = 932, μ = 6.45 cm^{-1}. Data collection was carried out with an Enraf-Nonius CAD-4 diffractometer: λ(Mo Kα) = 0.710 73 Å, T = 293 K; 10 585 independent reflections with $2.0° < 2\theta < 56.0°$ collected and used in refinement; $R1$ = 0.0397 (on F for 6513 observed reflections with $I > 2.0\sigma(I)$), w$R2$ = 0.1281 (on F^2 for all data); 677 variables refined. Hydrogen atoms were refined isotropically, except for the solvent molecule.

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with the remaining three atoms of the coordinating face, each of them having a cluster connectivity of 5, Ru(2)−B(3) = 2.502(5) Å, Ru(2)−B(5) = 2.436(4) Å, and Ru(2)−B(10) = 2.346(4) Å. The RuHCl(PPh_3) moiety in molecule **3** has an almost ideally eclipsed conformation with respect to the three short Ru−C(1), Ru−B(6), and Ru−B(9) bonds which are formed by the cage atoms occupying low-coordinate apical vertices (the torsion angles H(1)C(1)Ru(2)Cl(1), O(9)B(9)Ru(2)H(2), and H(6)B(6)Ru(2)P(1) are equal to 1.9, 14.7, and 15.0°, respectively). Quite identical orientation of the same metal-containing moiety relative to the six-membered cage open face was found in *iso*-*closo*-1,1,1-(PPh_3)HCl-3,5-$(PPh_3)_2$-1-RuB_9H_7.[3b]

The ^{11}B NMR spectra of **3** and **4** both display a set of doublets and singlets in the range −28 to +82 ppm grouped into three distinct groups of signals, with one of these groups of two signals shifted to the extreme low field of about 70−80 ppm. These low-field boron resonances are indicative of a low-coordinate boron atom adjacent to a metal center[3b,10] and may be, therefore, assigned to the B(6) and B(9) atoms. On the basis of the known substituent positions at the cage ligand in cluster **3** and taking into account the obvious similarity in the ^{11}B NMR spectra parameters observed for clusters **3** and **4,** a partial assignment of their boron resonances has been made.[6] In spite of the presence of the two different metal- and boron-bound triphenylphosphine ligands in the molecule of **3**, the terminal metal hydride resonances found in the ^{1}H NMR spectrum at −4.68 ppm splits into a doublet (J_{H-P} = 57 Hz), and no indication of the long-range coupling of hydride to the unique phosphine on B(5) was revealed. The metal−hydride resonance in the ^{1}H NMR spectrum of **4**, by contrast, is observed as a doublet of doublets at −5.36 ppm due to coupling of hydride to phosphorus nuclei of the two nonequivalent metal-coordinated triphenylphosphine ligands. This is confirmed by the observation of two separated 1:1 doublets at 50.7 and 38.7 ppm with $^2J_{P-P}$ = 16 Hz. After selective ^{31}P decoupling of the phosphorus signals the hydride resonance in the ^{1}H NMR spectrum of **4** has collapsed into two doublets with $J_{H-P(1)}$ = 22.1 Hz and $J_{H-P(2)}$ = 45.3 Hz, respectively.

According to the skeletal electron-counting formalism,[11] clusters **3** and **4** cannot be regarded as usual 10-vertex $2n + 2$ electron *closo*-metallacarboranes which normally possess a D_{4d} symmetry.[9] Considering an Ru(PPh_3)HCl unit as contributing zero electrons and three orbitals to the CB_8 cage for bonding, and then taking into account the presence of the pendant phosphine ligand on B(5) which contributes one extra electron to the cluster, **3** would have only 20 framework electrons available for bonding and would, therefore, be considered as a *hyper-closo* cluster. However, earlier discussion[12] concerning the structure and type of bonding in such 10-vertex and other related metallacarborane and metallaborane clusters of "*hyper-closo*" or "*iso-closo*" type based on the geometry of a capped tricapped trigonal prism showed that more experimental evidence will be required to entirely resolve this problem, and any new examples of $2n$ skeletal electron systems such as those presented above would seem to be an important contribution to the area.

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Supporting Information Available: Tables of crystallographic data collection parameters, atomic coordinates and *U* values, bond lengths and angles, and anisotropic parameters for **3** and figures giving ^{1}H and ^{11}B NMR spectra of **6** in CD_2Cl_2 (11 pages). Ordering information is given on any current masthead page.

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