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Synthesis and molecular structure of *exo-nido*-ruthenacarborane containing vinylene bridge group

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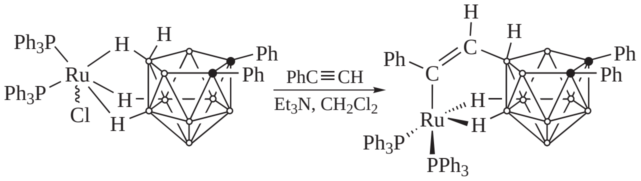
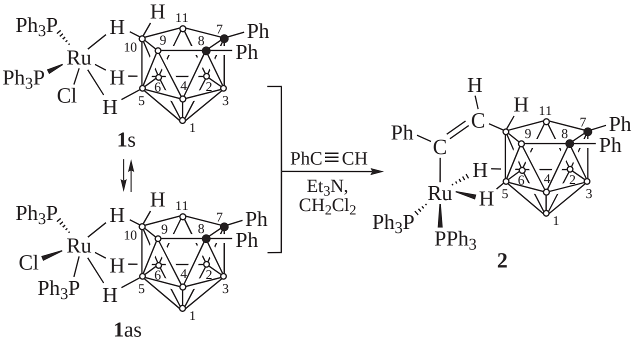
The reaction of the ruthenacarborane *exo-nido*-5,6,10-[Cl(Ph$_3$P)$_2$Ru]-5,6,10-(μ-H)$_3$-10-H-7,8-(Ph)$_2$-7,8-C$_2$B$_9$H$_6$ with phenylacetylene in dichloromethane in the presence of triethylamine at ambient temperature affords *exo-nido*-5,6,10-[(Ph$_3$P)$_2$-Ru]-5,6-(μ-H)$_2$-10-[μ-(PhC=CH)]-10-H-7,8-(Ph)$_2$-7,8-C$_2$B$_9$H$_6$ containing vinylene bridge group between carborane framework and ruthenium atom. Structure of the complex has been determined by X-ray diffraction study.



The progress in the chemistry of carborane complexes with *exo*-coordinated transition metals over the last decades has been associated with their usage for design of pincer ligand systems,[1] constrained geometry compounds,[2] and catalysts for organic reactions.[3] Among the latter there are so-called forced *exo-nido*-metallacarboranes elaborated by Teixidor and co-workers.[4] As a rule, these compounds possess mono- or di-C-substituted {7,8-C$_2$B$_9$} carborane framework with P- or S-donor centers coordinated to an exohedral metal atom. These complexes exhibit catalytic activity in hydrogenation,[4(a),(b)] cyclopropanation,[4(a)] hydrosilylation[4(b)] and show luminescence properties.[4(c)]

Previously, we reported the syntheses of two unusual complexes: with cyclobutenylidene moiety[5(a)] and $\eta^3{:}\eta^2$-phosphacarbocyclic ligand.[5(b)] The latter was obtained by the reaction of *exo-nido*-5,6,10-[Cl(Ph$_3$P)$_2$Ru]-5,6,10-(μ-H)$_3$-10-H-7,8-C$_2$B$_9$H$_8$ with excess of phenylacetylene in the presence of chlorine-eliminating agent. As a result, the ruthenium atom moves from *exo*-position to polyhedral framework to the *closo*-position thus affording two isomeric complexes with allylolefinic cyclic ligands. In the present work we investigate whether such a reaction can bring about complexes with *exo-nido*-structure, and report the synthesis of the B-substituted *exo-nido*-metallacarborane of a new type containing the C-coordination center.



Scheme 1

Since the presence of substituents on carbon atoms of metallacarborane promotes *exo*-coordination of metal atom[6] (*exo-nido* → *closo* rearrangement is sterically hindered), we first synthesized diphenyl-substituted *exo-nido*-5,6,10-[Cl(Ph$_3$P)$_2$Ru]-5,6,10-(μ-H)$_3$-10-H-7,8-(Ph)$_2$-7,8-C$_2$B$_9$H$_6$ **1**.[‡] For the synthesis of this compound, the known method[7(a)] was used, namely, the reaction of Cl$_2$Ru(PPh$_3$)$_3$ with potassium salt of 7,8-diphenyl-7,8-dicarba-*nido*-undecaborate in benzene. Similar to the known *exo-nido*-ruthena-[7(c)] and osmacarboranes,[7(b)] complex **1** exists as a mixture of two isomers **1**(s) and **1**(as) in a 3 : 2 ratio, which are in dynamic equilibrium (Scheme 1).

[†] Deceased.

[‡] *exo-nido*-5,6,10-[Cl(Ph$_3$P)$_2$Ru]-5,6,10-(μ-H)$_3$-10-H-7,8-(Ph)$_2$-7,8-C$_2$B$_9$H$_6$ **1**. A mixture of Cl$_2$Ru(PPh$_3$)$_3$ (508 mg, 0.53 mmol), [7,8-Ph$_2$-7,8-*nido*-C$_2$B$_9$H$_{10}$]$^-$K$^+$ (190 mg, 0.59 mmol) and benzene (15 ml) was stirred at ambient temperature for 3 h. The solution was concentrated *in vacuo.* The residue was chromatographed on a silica gel column with benzene–hexane mixture (2 : 1) as an eluent. Recrystallization from the benzene–hexane mixture afforded orange microcrystals of analytically pure complex **1** (360 mg, 71%). In solution compound **1** exists as a mixture (3 : 2) of symmetric (s) and asymmetric (as) isomers, which are in dynamic equilibrium.

^{1}H NMR (400.13 MHz, CD$_2$Cl$_2$) δ: –16.50 (m, H^{10}, s), –15.35 (m, H^6, as), –6.28 (m, H^{10}, as), –4.39 (m, H^{5,6}, s), –3.24 (m, H^5, as), –0.95 to 0.01 (m, extra-H, s + as), 6.87–7.40 (m, Ph, s + as). ^{1}H{^{11}B} NMR (400.13 MHz, CD$_2$Cl$_2$) δ: –16.50 (q, H^{10}, s, J 11.6 Hz), –15.35 (t, H^6, as, J 10.1 Hz), –6.28 (td, H^{10}, as, J_t 9.6 and J_d 45.3 Hz), –4.39 (d, H^{5,6}, s, J 36.0 Hz), –3.24 (d, H^5, as, J 40.9 Hz), –0.61 (d, extra-H, as, J 13.5 Hz), –0.32 (d, extra-H, s, J 11.6 Hz), 1.83, 1.88, 2.46 and 3.10 (all br. s, 1H, 2H, 2H, 1H, B–H, s), 0.30, 1.45, 2.18, 2.29, 2.96 and 3.26 (all br. s, all 1H, B–H, as), 6.87–7.40 (m, Ph, s + as). ^{31}P{^{1}H} NMR (161.98 MHz, CD$_2$Cl$_2$) δ: 44.92 (d, as, J 31.22 Hz), 48.80 (s, **1**s), 52.82 (br. s, as). Found (%): C, 65.80; H, 5.74; B, 9.76. Calc. for C$_{50}$H$_{50}$B$_9$P$_2$ClRu·C$_6$H$_6$ (%): C, 65.63; H, 5.51; B, 9.49.

Ruthenacarborane **1** reacts with phenylacetylene in the presence of triethylamine to give complex *exo-nido*-5,6,10-[$(Ph_3P)_2Ru$]-5,6-(μ-H)$_2$-10-[μ-(PhC=CH)]-10-H-7,8-(Ph)$_2$-7,8-$C_2B_9H_6$ **2**[§] in 33% yield (see Scheme 1).

The structure of complex **2** was established by NMR and X-ray diffraction methods.[¶] The unit cell contains two crystallographically independent molecules of similar geometry. Five-coordinated ruthenium atom in each of these two molecules has a distorted square pyramidal configuration and is located in an *exo*-position of the carborane polyhedron (Figure 1). Metal center in **2** is connected to the carborane ligand *via* two-electron three-center Ru–H–B bonds and vinylene bridge group [–(Ph)C=C(H)–]. The Ru–C(vinyl) interatomic distances [2.041(5) and 2.060(6) Å in two independent molecules] are close to the average value 2.048 Å of similar distances in σ-vinyl ruthenium complexes.[8] In particular, in five-coordinated compound Ru(CO)Cl(PhC=CHPh)$(PPh_3)_2$ it is 2.03(1) Å.[9] The distances between metal atom and hydrogen atoms [1.73(5)–1.81(5) Å] or boron atoms [2.394(7)–2.428(7) Å] in the Ru–H–B bonds of **2** are similar to the analogous ones of known *exo-nido*-5,6,10-[$Cl(Ph_3P)_2Ru$]-5,6,10-(μ-H)$_3$-10-H-7,8-$C_2B_9H_8$ [1.82(5)–1.85(4) and 2.394(6)–2.399(6) Å, respectively].[7(a)]

The structure of complex **2** conforms with NMR spectroscopic data. The $^1H\{^{11}B\}$ NMR spectrum contains a set of phenyl groups signals with total intensity of 45 H and a peak from the vinyl hydrogen atom with intensity of 1H at 6.18 ppm. There are a series of signals related to terminal B–H and bridge Ru–H–B protons as well as a peak at 0.35 ppm from ‘extra’-hydrogen atom located above an open pentagonal face of $\{C_2B_3\}$ of the carborane framework.

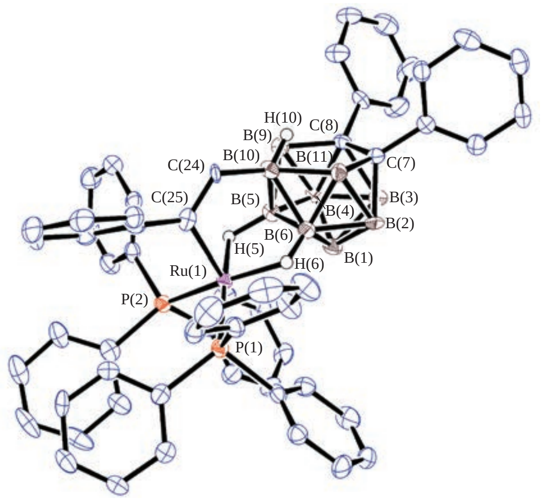


Figure 1 Molecular structure of one of two independent molecules of **2** with thermal ellipsoids drawn at the 50% probability level [excluding H(5), H(6), and H(10) atoms, the rest H-atoms are omitted for clarity]. Selected bond lengths (Å) (the values for two independent molecules are slashed): Ru(1)–P(1) 2.2745(17)/2.2964(17), Ru(1)–P(2) 2.2913(16)/2.2637(17), Ru(1)–C(25) 2.041(5)/2.060(6), Ru(1)–B(5) 2.419(7)/2.394(7), Ru(1)–B(6) 2.405(6)/2.428(7), Ru(1)–H(5) 1.74(5)/1.79(5), Ru(1)–H(6) 1.73(5)/1.81(5), B(10)–C(24) 1.556(9)/1.551(8), C(24)–C(25) 1.328(8)/1.329(8); selected bond angles (°): P(1)–Ru(1)–H(5) 162.8(17)/173.5(17), P(2)–Ru(1)–H(6) 172.5(18)/165.6(17), P(1)–Ru(1)–P(2) 107.11(6)/104.04(6), H(5)–Ru(1)–H(6) 95(2)/98(2), C(25)–Ru(1)–P(1) 104.55(16)/97.25(17), C(25)–Ru(1)–P(2) 93.00(16)/103.16(17), C(25)–Ru(1)–H(5) 91.6(17)/88.9(17), C(25)–Ru(1)–H(6) 86.6(17)/87.5(17).

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[§] *exo-nido*-5,6,10-[$(Ph_3P)Ru$]-5,6-(μ-H)$_2$-10-[μ-(PhC=CH)]-10-H-7,8-(Ph)$_2$-7,8-$C_2B_9H_6$ **2**. Triethylamine (0.1 ml) and phenylacetylene (0.02 ml) were added to the solution of complex **1** (72 mg, 0.076 mmol) in CH_2Cl_2 (4 ml, freshly predistilled under argon). The mixture was stirred at ambient temperature for 5.5 h. Then it was evaporated and dried *in vacuo* to remove the amine. The resulting residue was dissolved in minimal amount of CH_2Cl_2 and chromatographed on a silica gel column with CH_2Cl_2–hexane (1 : 1) mixture as the eluent. Recrystallization from benzene–hexane mixture afforded red microcrystals of analytically pure complex **2** (25 mg, 33%). Compound **2** slowly decomposes in solution on air.

$^1H\{^{11}B\}$ NMR (400.13 MHz, $CDCl_3$) δ: –3.52 (d, 2 H, Ru–H–B, *J* 24.7 Hz), 0.35 (br. s, extra-H), 0.75, 2.76, 3.37 and 3.68 (all br. s, 2 H, 1H, 2 H, 1H, B–H), 6.18 (br. s, 1H, PhC=C*H*), 6.70 (t, 2 H, Ph, *J* 7.6 Hz), 6.84–7.07 (m, 26 H, Ph), 7.16 (d, 2 H, Ph, *J* 7.2 Hz), 7.40 (br. s, 11 H, Ph), 7.57 (d, 4 H, Ph, *J* 7.2 Hz). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$) δ: 49.68 (s). ^{11}B NMR (192.57 MHz, $CDCl_3$) δ: –9.56 (br. s), –14.24 (br. s), –19.29 (s), –20.16, –27.11 and –35.72 (all br. s). Found (%): C, 69.52; H, 5.64; B, 9.52. Calc. for $C_{58}H_{55}B_9P_2Ru \cdot 0.5\,C_6H_6$ (%): C, 69.68; H, 5.56; B, 9.25.

[¶] *Crystal data for* **2**: $C_{58}H_{55}B_9P_2Ru \cdot 1.5\,C_6H_6$, $M = 1129.48$, triclinic, space group $P\bar{1}$, $a = 17.238(3)$, $b = 18.041(3)$ and $c = 20.202(4)$ Å, $\alpha = 73.840(4)$, $\beta = 72.100(4)$, $\gamma = 82.857(4)$°, $V = 5737.0(18)$ Å^3, $d_{calc} = 1.308$ g cm^{-3}, $Z = 4$, μ(MoKα) = 0.372 mm^{-1}, [λ(MoKα) = 0.71073 Å], $T = 120(2)$ K, $2\theta_{max} = 54°$, $R_1 = 0.0774$ for 12732 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.1601$ for all 25037 unique reflections ($R_{int} = 0.1504$). All calculations were performed using the SHELXT program package[10].

CCDC 1523017 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.