the resulting solution was heated at 353 K. The silica source (tetraethylorthosilicate, TEOS) was added gradually under vigorous stirring, then the resulting mixture was aged for 4 h, cooled to room temperature, charged in an oscillating stainless-steel autoclave and heated at 443 K for 336 h. After crystallization the autoclave was cooled to room temperature with cold water. The solid product was collected by filtration, repeatedly washed with demineralized water, and finally dried overnight at 423 K. A fraction of the solid was calcined at 823 K for 4 h to remove the organic molecules trapped in the ERS-10 pores.

Powder data collection: X-ray powder diffraction (XRD) patterns were obtained with a Philips X'PERT diffractometer equipped with a pulse-height analyzer and a secondary curved graphite crystal monochromator. Data were collected stepwise over $3 \leq 2\theta \leq 53°$, with a step size of 0.02° 2θ and an accumulation time of 20 s per step, using $\mathrm{Cu}_{K\alpha}$ radiation ($\lambda = 1.54178$ Å).

Synchrotron X-ray powder diffraction data were collected at room temperature on a sample loaded in a glass capillary mounted in Debye–Scherrer geometry at BM08, GILDA beamline (ESRF, Grenoble) during the experiment 08-02-174. The beamline was set to deliver a wavelength of $\lambda = 0.82714$ Å, and the data was collected on a Fuji Image Plate located at 204.83 mm from the sample and perpendicular to the incident beam; the exposure time was 3 min. Elaboration of the scanned digital images (Fuji BAS2000 scanner) was carried out using the Fit2d software package.[17]

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Direct Electrophilic Insertion into a Twelve-Vertex Metallacarborane**

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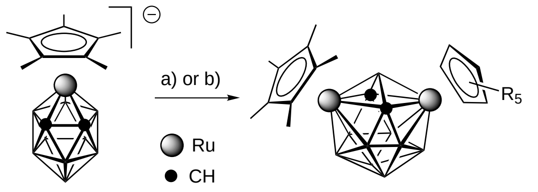
In memory of Margarita I. Rybinskaya

Direct insertion of metal-complex fragments into *closo*-carboranes and metallacarboranes to give polyhedral expansion products is one of the most interesting reactions in metallacarborane chemistry.[1] The nucleophilic insertion into the cage molecules has been well studied.[2] Herein we report the first direct electrophilic insertion[3] into a 12-vertex metallacarborane.

We studied the reaction of ruthenacarborane anion **1** with $[(\eta\text{-C}_5\text{R}_5)\text{Ru(MeCN)}_3]^+$ (R = H, Me) (Scheme 1). The electrophilic attack of the fragments $[(\eta\text{-C}_5\text{R}_5)\text{Ru}]^+$ was expected to proceed at the C_5Me_5 ring to give triple-decker complexes $[(\eta\text{-C}_5\text{R}_5)\text{Ru}(\mu\text{-}\eta\text{:}\eta\text{-C}_5\text{Me}_5)\text{Ru}(\text{C}_2\text{B}_9\text{H}_{11})]$, similar to the formation of $[(\eta\text{-C}_5\text{R}_5)\text{Ru}(\mu\text{-}\eta\text{:}\eta\text{-C}_5\text{Me}_5)\text{Ru}(\eta\text{-C}_5\text{Me}_5)]^+$ by reaction of the same fragments with $[(\eta\text{-C}_5\text{Me}_5)_2\text{Ru}]$.[4] However, electrophilic insertion into the ruthenacarborane cage occurs instead to give 13-vertex diruthenacarboranes **2a**,**b**.



$[(\eta\text{-C}_5\text{Me}_5)\text{Ru}(\text{C}_2\text{B}_9\text{H}_{11})]^-$
1

$[(\eta\text{-C}_5\text{Me}_5)\text{Ru}(\text{C}_2\text{B}_9\text{H}_{11})\text{Ru}(\eta\text{-C}_5\text{R}_5)]$
2a: R = H
2b: R = Me

Scheme 1. Electrophilic insertion into **1** to give **2a**,**b**. Reagents and conditions: a) $[(\eta\text{-C}_5\text{R}_5)\text{Ru(MeCN)}_3]\text{X}$ (X = PF_6 or CF_3SO_3), CH_3NO_2, 100 °C, 4 h, about 50 % yield; b) $[\{(\eta\text{-C}_5\text{Me}_5)\text{RuCl}\}_4]$, THF, 20 °C or even −78 °C, 74 % yield.

It should be emphasized that the electrophilic insertion reactions were previously unknown. Parent *ortho*-carborane $\text{C}_2\text{B}_{10}\text{H}_{12}$ as well as neutral metallacarboranes $[(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})]$ and $[(\eta\text{-C}_5\text{Me}_5)\text{Rh}(\text{C}_2\text{B}_9\text{H}_{11})]$ were proved to be unreactive towards $[(\eta\text{-C}_5\text{R}_5)\text{Ru}]^+$. In contrast, in the case of **1** the insertion can be carried out even at −78 °C by reaction of Tl-**1** with $[\{(\eta\text{-C}_5\text{Me}_5)\text{RuCl}\}_4]$ (**3**) in THF. The high reactivity of anion **1** is evidently connected with its greater nucleophilicity.

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The precursor salt Tl-**1** was obtained by reaction of **3** with the thallium derivative of the dicarbollide anion Tl[Tl($C_2B_9H_{11}$)]. Since Tl-**1** reacts with **3** to give the symmetrical compound **2b**, the latter can be prepared by direct reaction of Tl[Tl($C_2B_9H_{11}$)] with two equivalents of **3**.

All the compounds were characterized by ^{1}H and ^{11}B NMR spectroscopy and elemental analysis. The ^{1}H NMR spectra of **2a** and **2b** display narrow signals for the C_5H_5 and C_5Me_5 ligands which supports the diamagnetism of the compounds. It should be mentioned that the cage CH protons appear as a broad singlet at $\delta = -0.67$ ppm (**2a**) or -1.27 ppm (**2b**), dramatically up-field shifted in comparison with the corresponding signals of the precursor anion **1** ($\delta = 2.72$ ppm). The ^{11}B NMR spectra show downfield signals at $\delta = 95.10$ ppm (**2a**) or 97.03 ppm (**2b**), characteristic for the presence of a low-coordinate boron atom adjacent to metal atoms.[5] These spectral data are in good agreement with that reported by Hawthorne and Salentine for the 13-vertex diferracarborane [(η-$C_5H_5)_2Fe_2C_2B_9H_{11}$],[6] proposed to have a structure similar to **2a,b**.

The structures of PPN-**1** (PPN = $(Ph_3P)_2N$) (Figure 1) and **2b** (Figure 2) were determined by X-ray structure analysis.[7] The anion **1** has a sandwich geometry with almost parallel C_5 and C_2B_3 rings in staggered conformation. One of the carbon atoms in the cage is disordered leading to the superposition of the C(2) and B(2) or B(4) atoms. The Ru···C_5Me_5 plane distance (1.82 Å) is almost the same as the corresponding distance in [(η-$C_5Me_5)_2$Ru] (1.81 Å).[8]

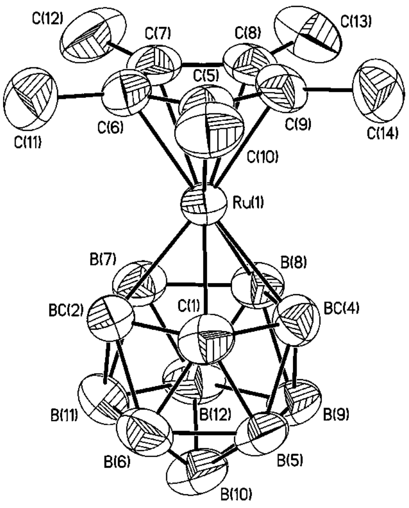

Figure 1. Structure of anion **1**. Atoms are represented as 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. The disordered carbon atoms are signed as BC(2) and BC(4).

Compound **2b** possesses nearly ideal C_{2v} symmetry for a 13-vertex dimetallacarborane cage (Figure 2). The Ru···C_5Me_5 plane distance (1.88 Å) is considerably longer than that in anion **1**. Both ruthenium atoms are bonded to C_2B_4 faces with a common C_2B frame in the bridging position. The distances from the Ru atoms to the bridging boron atom B(1) (2.070(3) and 2.063(3) Å, av 2.07 Å) are much shorter than other Ru–B distances (2.191(4)–2.213(3) Å, av 2.20 Å). The distance Ru(1)···Ru(2) (3.5307(5) Å) suggests that there is no direct interaction between the ruthenium atoms.

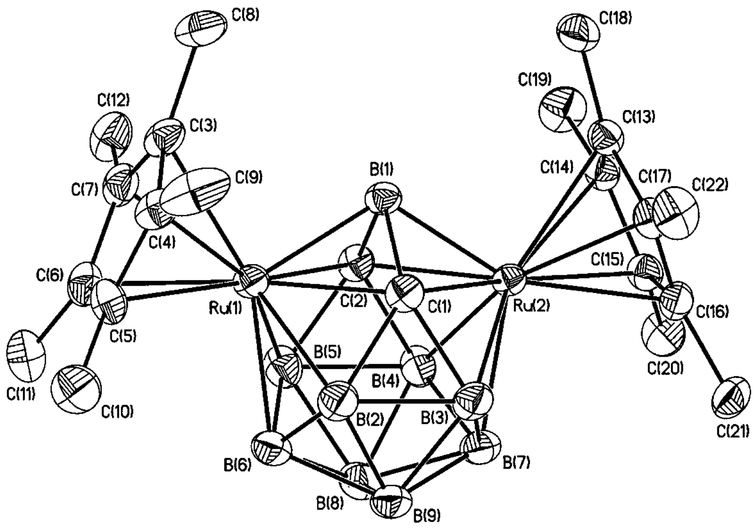

Figure 2. Structure of **2b**. Atoms are represented as 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Compounds **2a,b** belong to $2n$ skeletal electron (*hypercloso*)[9] systems (where n is the number of vertexes) which violate Wade's rules.[10] Nevertheless, they are stable over 200 °C even in air. To explain this violation, one might suggest that the ruthenium atoms are in the oxidation state III, but diamagnetism of the compounds rules out this speculation. According to the extended Hückel calculations by Fowler,[11] neutral $B_{13}H_{13}$ (C_{2v} symmetry, $2n$-electron system) has a nearly nonbonding LUMO, suggesting that $B_{13}H_{13}$ and $[B_{13}H_{13}]^{2-}$ should be almost equally stable. Analogously, two series of stable 13-vertex dimetallacarboranes, having $2n$ and $2n+2$ skeletal electrons, could be suggested, exemplified by **2a,b** and [(η-$C_5H_5)_2Co_2C_2B_9H_{11}$],[4b] respectively.

The reactions presented here illustrate a novel approach to the synthesis of dimetallacarboranes. We are currently studying applicability limits of this method.

Experimental Section

All the reactions were carried out under an argon atmosphere, whereas isolation of products was conducted in air.

Tl[(η-C_5Me_5)Ru($C_2B_9H_{11}$)] (Tl-**1**): Acetonitrile (8 mL) was added to a mixture of [{(η-C_5Me_5)RuCl}$_4$] (109 mg, 0.1 mmol) and Tl[Tl($C_2B_9H_{11}$)] (227 mg, 0.42 mmol) and the resulting suspension was stirred for 72 h. The reaction mixture was diluted with acetone (10 mL), filtered, and evaporated to dryness in vacuo. The residue was redissolved in THF and reprecipitated by addition of diethyl ether to give Tl-**1** (182 mg, 79%) as a white air-stable solid. ^{1}H NMR (400.13 MHz, [D$_6$]acetone, 25 °C): $\delta = 1.89$ (s, 15H; C_5Me_5), 2.72 ppm (bs, 2H; cage CH); ^{11}B{^{1}H} NMR (128.38 MHz, [D$_6$]acetone, 25 °C): $\delta = -28.12$ (1B), -24.65 (2B), -15.41 (2B), -9.96 (1B), -8.87 (2B), -1.48 ppm (1B); elemental analysis (%) calcd: C 25.15, H 4.57, B 16.98; found: C 24.94, H 4.66, B 17.04.

[(η-C_5Me_5)Ru($C_2B_9H_{11}$)Ru(η-C_5H_5)] (**2a**): Nitromethane (5 mL) was added to a mixture of [(η-C_5H_5)Ru(MeCN)$_3$]PF$_6$ (65 mg, 0.15 mmol) and Tl-**1** (86 mg, 0.15 mmol). The solution was stirred under reflux for 4 h leading to a color change from yellow to bright red. The mixture was evaporated to dryness; the residue was dissolved in CH_2Cl_2 and filtered through a thin layer (3 cm) of Al_2O_3. The solution was concentrated to 2 mL and hexane (20 mL) was added to precipitate the product as an orange-red air-stable solid. Yield 38 mg (47 %). ^{1}H NMR (400.13 MHz, [D$_1$]chloroform, 25 °C): $\delta = -0.69$ (bs, 2 H; cage CH), 1.60 (s, 15 H; C_5Me_5), 5.22 ppm (s, 5 H; C_5H_5); $^{11}B\{^1H\}$ NMR (128.38 MHz, [D$_1$]chloroform, 25 °C): $\delta = -5.26$ (2 B), 16.24 (2 B), 17.92 (2 B), 31.94 (1 B), 38.31 (1 B), 95.10 ppm (1 B); elemental analysis (%) calcd: C 38.17, H 5.84, B 18.19; found: C 38.16, H 5.89, B 18.11.

$[(\eta\text{-}C_5Me_5)Ru(C_2B_9H_{11})Ru(\eta\text{-}C_5Me_5)]$ (**2b**): THF (4 mL) was added to a mixture of $[\{(\eta\text{-}C_5Me_5)RuCl\}_4]$ (41 mg, 0.038 mmol) and Tl-**1** (86 mg, 0.15 mmol). The reaction mixture was stirred for 4 h and filtered through a thin layer (3 cm) of Al_2O_3. The solution was concentrated to 2 mL and hexane (20 mL) was added to precipitate the product as a red air-stable solid. Yield 67 mg (74 %). ^{1}H NMR (400.13 MHz, [D$_1$]chloroform, 25 °C): $\delta = -1.27$ (bs, 2 H; cage CH), 1.59 ppm (s, 30 H; C_5Me_5); $^{11}B\{^1H\}$ NMR (128.38 MHz, [D$_1$]chloroform, 25 °C): $\delta = -5.62$ (2 B), 17.78 (4 B), 36.37 (2 B), 97.03 ppm (1 B); elemental analysis (%) calcd: C 43.68, H 6.83, B 16.08; found: C 43.65, H 6.78, B 15.98.

Analogously, direct reaction of $[\{(\eta\text{-}C_5Me_5)RuCl\}_4]$ (82 mg, 0.075 mmol) and $Tl[Tl(C_2B_9H_{11})]$ (81 mg, 0.15 mmol) in THF or Me_2CO gave **2b** (64 mg, 70 %).

Complex **2b** was also prepared in 55 % yield starting from $[(\eta\text{-}C_5Me_5)\text{-}Ru(MeCN)_3]CF_3SO_3$, similar to preparation of **2a**.

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Conformation-Dependent Ionization Energies of L-Phenylalanine[**]

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In recent years there has been an outburst of research interest in small biological molecules in the gas phase.[1] By placing these molecules on the "transparent cover glass" of an isolated environment, one can unravel intrinsic properties usually hidden in the complex medium of a real biological system. The need for such gas-phase studies arises from the anticipation that many biological phenomena can be traced to the fundamental properties of the molecular constituents. Both laser spectroscopy and theoretical methods have made great contributions to elucidating the structures and dynamics of nonrigid biomolecules and their solvated complexes in the gas phase.[2]

Amino acids are known to exist in various conformations resulting from the flexibility of their structures, which comprise a backbone and a side chain or residue. The conformational variety of amino acids plays a crucial role in determining the three-dimensional structure of proteins and controlling their dynamics.[3] The energy barrier that separates different conformers is typically rather small so that thermal energy at room temperature enables the molecule to freely change from one conformation to another. Therefore, it is not generally feasible to isolate a specific conformer experimentally at room temperature. By employing a supersonic expansion, however, one can cool down the molecule to a temperature low enough to isolate it in various frozen forms, in other words, as individual conformers. Numerous exper-

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