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Modified synthesis of Ru–Rh heterobimetallic metallacarboranes based on ruthenium *exo-nido* complexes and not accompanied by *exo-nido* → *closo* rearrangement

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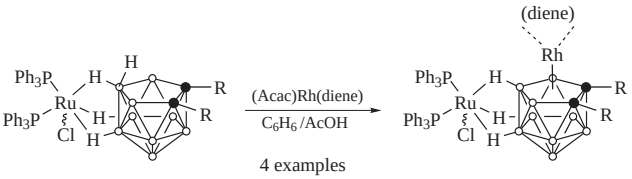
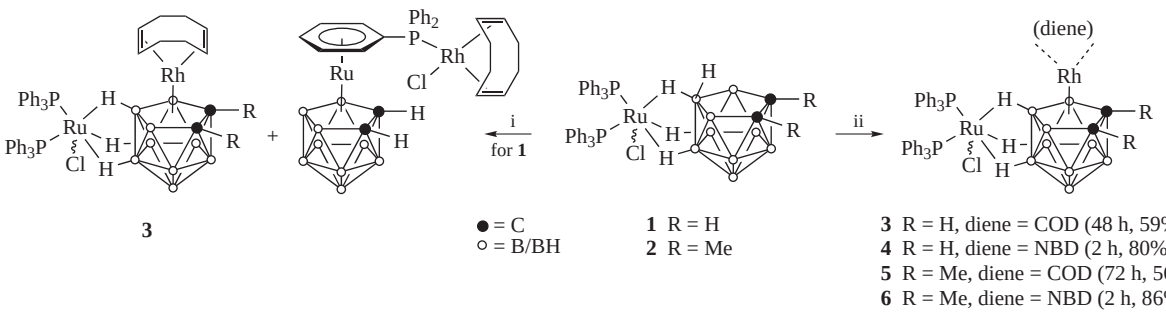
The use of improved protocol for the reaction of rhodium acetylacetonate complexes (diene)RhAcac [diene is 1,5-cyclooctadiene or norbornadiene] with *exo-nido*-ruthenacarboranes 5,6,10-[RuCl(PPh$_3$)$_2$]-5,6,10-(μ-H)$_3$-10-*H*-7,8-R$_2$-7,8-C$_2$B$_8$H$_6$ (R = H or Me) allowed us to synthesize three new binuclear complexes, wherein the ruthenium atom preserved *exo*-position and the rhodium-containing moiety coordinated to the open pentagonal face of *exo-nido*-complex. In addition, one known bimetallacarborane was also prepared for the evaluation of synthetic efficiency of the new procedure.



The synthesis of heterobimetallic carborane complex, wherein the ruthenium atom preserved an exopoliedrical coordination, starting from *exo-nido* complex and an acetylacetonate complex of rhodium has been previously developed by our team.[1] Even though many reports on the preparation of ruthenium-containing binuclear metallacarborane clusters have been already published,[2,3] including ones starting from *exo-nido* ruthenacarboranes,[3] this synthesis is of interest since practically in all cases, the ruthenium atom occupies the *closo*-position either from the starting material or due to the *exo-nido* → *closo* rearrangement during a reaction. Only several Ru–W and Ru–Re complexes with the ruthenium atom at *exo*-position linked to the metallacarborane frame *via* B–Ru (or B–H···Ru) and Ru–W or three B–H···Ru bridges were obtained by the addition of a ruthenium-containig moiety to *closo*-metallacarboranes.[4,5]

It should also be mentioned that such *exo*-ruthena-*closo*-rhodacarborane clusters could be of interest as novel catalysts or their precursors. For example, non-carborane binuclear Ru–Rh complexes could be applied as the catalysts for various organic reactions, such as an oxidation of alcohols, a hydroformylation, *etc*.[6] On the other hand, metallacarborane complexes with exopolyedrically coordinated ruthenium atom as well as rhodacarboranes with *closo*-structure are already known as possessing a high potential in the catalysis of organic processes, in particular, the hydrogenation of unsaturated hydrocarbons.[7]

However, the mentioned synthetic method[1] (Scheme 1, conditions i) contains significant drawbacks, *viz*., a long reaction time and a low yield of the desired product due to the side reaction. Thus, the present work was aimed at the further improvement of our previous results *via* increasing the reaction rate of binuclear complex formation. This was achieved by the addition of acetic acid to the reaction mixture, which is known as a promotor of elimination of the acetylacetonate ligand.[8] This modification (see Scheme 1, conditions ii) allowed us to decrease the reaction time and isolate the desired bimetallacarboranes as the only reaction products in significantly higher yields. For instance, the



3

1 R = H
2 R = Me

3 R = H, diene = COD (48 h, 59%)
4 R = H, diene = NBD (2 h, 80%)
5 R = Me, diene = COD (72 h, 56%)
6 R = Me, diene = NBD (2 h, 86%)

Scheme 1 *Reagents and conditions*: i, (Acac)Rh(COD), THF, 7 days; ii, (Acac)Rh(diene), C$_6$H$_6$/AcOH. COD is 1,5-cyclooctadiene, NBD is norbornadiene.

† Deceased.

yield increased from 18 to 59% in the case of reaction of ruthenacarborane **1** with (Acac)Rh(COD).

In addition, three new complexes **4**–**6** were obtained and characterized in this work. Already known bimetallacarborane **3** was also synthesized in order to evaluate the growth of the yield under the proposed conditions. Thus, complexes **3**–**6** bearing different diene ligands at the rhodium atom and substituents at the carbon atoms of carborane cage were prepared from ruthenacarboranes **1**, **2** using the improved procedure.‡

NMR spectroscopic data§ revealed that all the binuclear complexes exist in solution as a mixture of two inseparable isomers which, moreover, are in the equilibrium. This is indicated by a double set of signals of the bridging hydrogen atoms, diene ligand, and substituents at the carbon atoms of carborane cage in ^{1}H NMR spectra as well as by a doubled set of signals in ^{31}P NMR. The comparative analysis of spectra of the synthesized binuclear metallacarboranes with those of 'three-bridged' *exo-nido*-ruthenacarboranes allowed us to presume that in this case, a geometric *cis-trans* isomerism of ligand arrangement at the six-coordinated ruthenium atom[9] takes place similar to *exo-nido*-ruthenacarboranes (Figure 1).

In conclusion, the modification improving the known synthetic method has been elaborated and used for the synthesis of three new bimetallacarboranes. These results can be of general interest for researchers working in the area of metallacarborane chemistry.

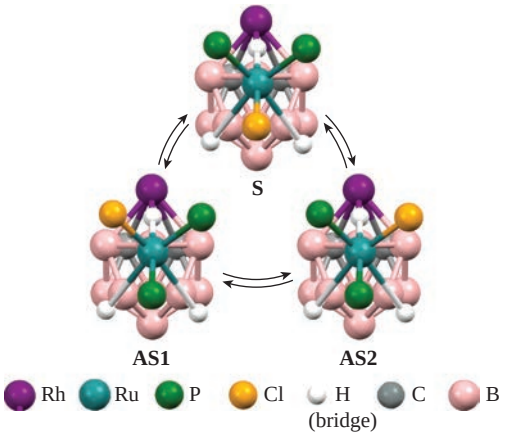


Figure 1 Schematic representation of the structures and mutual transition of symmetric (**S**) and asymmetric (**AS1** and **AS2**) isomers of *exo-closo*-metallacarboranes.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.01.023.

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‡ *General procedure.* Acetic acid (~1 equiv.) was added to the equimolar solution of *exo-nido*-ruthenacarborane **1** or **2** and acetylacetonate rhodium complex dissolved in minimum amount of benzene and the resulting solution was stirred for several hours (see Scheme 1). The obtained mixture was loaded onto a chromatographic column, and the product was eluted with a benzene–*n*-hexane (2 : 1) mixture in order to collect orange-red fraction. The products were recrystallized from a benzene–*n*-hexane mixture to isolate the analitically pure bimetallacarboranes **3**–**6**. Yields are shown in Scheme 1.

§ See Online Supplementary Materials.