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Isolation and characterization of the chelate *exo-nido*-ruthenacarborane intermediates formed in the thermal *exo-nido-to-closo* conversion of [*exo-nido*-5,6,10-$\{Cl(Ph_3P)_2Ru\}$-5,6,10-(μ-H)$_3$-10-H-7,8-R_2-7,8-$C_2B_9H_6$] (R = H or Me) upon the triphenylphosphine ligand displacement with the chiral (2*S*,4*S*)-(−)-2,4-bis(diphenylphosphino)pentane

Dmitri N. Cheredilin [a], Fedor M. Dolgushin [a], Alexander A. Korlyukov [a], Ivan A. Godovikov [a], Renat Kadyrov [b], Elena V. Balagurova [a], Stanislav P. Solodovnikov [a], Igor T. Chizhevsky [a,*]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds of the RAS, 28 Vavilov Street, 119991 Moscow, Russian Federation*
[b] *Degussa AG, Degussa Homogeneous Catalysis, Rodenbacher Chaussee 4, 63457 Hanau, Germany*

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Abstract

Reactions of [*exo-nido*-5,6,10-$\{Cl(Ph_3P)_2Ru\}$-5,6,10-(μ-H)$_3$-10-H-7,8-R_2-7,8-$C_2B_9H_6$] (**1**, R = H; **2**, R = Me) with the chiral (2S,4S)-2,4-bis(diphenylphosphino)pentane (**3**,*S*,*S*-bdpp) ligand proceed in benzene with replacement of both PPh_3 ligands on the metal center with the diphosphine affording the chelate *exo-nido* complexes [*exo-nido*-5,6,10-{Cl(*S*,*S*-bdpp)Ru}-5,6,10-(μ-H)$_3$-10-H-7,8-R_2-7,8-$C_2B_9H_6$] (**7**, R = H) and (**8**, R = Me), respectively. A relatively fast and irreversible rearrangement of **7** into its *closo* isomer [*closo*-3,3-(*S*,*S*-bdpp)-3-Cl-3-H-3,1,2-$RuC_2B_9H_{11}$] (**4**) occurs in solution already at room temperature. On the contrary, *exo-nido*-to-*closo* conversion of **8** proceeds in benzene (or much faster in toluene) only on heating and yields 17-electron paramagnetic complex [*closo*-3,3-(*S*,*S*-bdpp)-3-Cl-1,2-Me_2-3,1,2-$RuC_2B_9H_9$] (**9**). All *exo-nido*- and *closo*-ruthenacarboranes obtained were characterized by a combination of analytical, multinuclear NMR or EPR spectroscopic data and, in addition, by X-ray diffraction studies of both dimethylated complexes **8** and **9**.

Keywords: Metallacarborane clusters; *exo-nido-to-closo* conversion; Paramagnetic *closo*-ruthenacarboranes; Chirality; Crystal structures; NMR spectroscopy; EPR spectroscopy; CD spectroscopy

1. Introduction

In the context of our investigation on the chemical [1–3] and catalytic [4] properties of "three-bridge" *exo-nido*-metallacarboranes of ruthenium and osmium in which the exopolyhedral metal center is bonded to the cage carborane ligand via three two-electron, three-center B–H···M bonds, we became interested in extending the range of the known *exo-nido* derivatives. Such an extension could, in principle, be accomplished by varying of either the phosphine ligands attached to the metal atom or the carborane cage substituents. For this reason, we have recently examined the room-temperature phosphine–diphosphine displacement reactions of [*exo-nido*-5,6,10-$\{Cl(Ph_3P)_2Ru\}$-5,6,10-(μ-H)$_3$-10-H-7,8-R_2-7,8-$C_2B_9H_6$] (**1**, R = H; **2**,

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[*] Corresponding author. Tel.: +7 495 1359334; fax: +7 495 1355085.
E-mail address: chizbor@ineos.ac.ru (I.T. Chizhevsky).

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R = Me) using chelating diphosphines $Ph_2P(CH_2)_2PPh_2$ and $Ph_2P(CH_2)_3PPh_2$ [5] as well as thermal reaction of **1** with the chiral diphosphine (2*S*,4*S*)-(−)-2,4-bis(diphenylphosphino)pentane (**3**, *S*,*S*-bdpp) [6]. From the latter reaction, in refluxing toluene, a series of 18- and 17-electron *closo*-(*S*,*S*-bdpp)ruthenacarborane species were isolated, of which two were formulated as [*closo*-3,3-(*S*,*S*-bdpp)-3-Cl-3-H-3,1,2-$RuC_2B_9H_{11}$] (**4**) and [*closo*-3,3-(*S*,*S*-bdpp)-3-Cl-3,1,2-$RuC_2B_9H_{11}$] (**5**), and the third was *ortho*-cycloboronated derivative of **5**, [*closo*-3-Cl-3,3-{(*S*,*S*)-$Ph_2PCH(CH_3)CH_2CH(CH_3)PPh$-*ortho*-$C_6H_4$}-3,1,2-$RuC_2B_9H_{10}$] (**6**). It seemed probable that these chiral diphosphine *closo* products **4**–**6** could be produced either via spontaneous *exo*-*nido*-*to*-*closo* thermal conversion of *exo*-*nido* intermediate [*exo*-*nido*-5,6,10-{Cl(*S*,*S*-bdpp)Ru}-5,6,10-(μ-H)$_3$-10-H-7,8-$C_2B_9H_8$] (**7**) or, alternatively, in the course of PPh_3-diphosphine displacement reaction of *closo* precursor [*closo*-3,3-$(PPh_3)_2$-3-Cl-3-H-3,1,2-$RuC_2B_9H_{11}$] which might initially be formed from **1** at elevated temperature [7]. Of particular importance was therefore to determine the structure of real intermediate complexes of these phosphine–diphosphine displacement reactions.

Herein, we report our results for the reactions of *exo*-*nido* complexes **1** and **2** with the chiral (*S*,*S*)-bdpp ligand, focusing mainly on the isolation and the NMR spectroscopic and/or solid-state structural characterization of the chelate *exo*-*nido*-ruthenacarborane intermediates. In addition, thermal reactivity studies in solution of these chelate *exo*-*nido*-ruthenacarborane complexes with respect to *exo*-*nido* → *closo* conversion are reported.

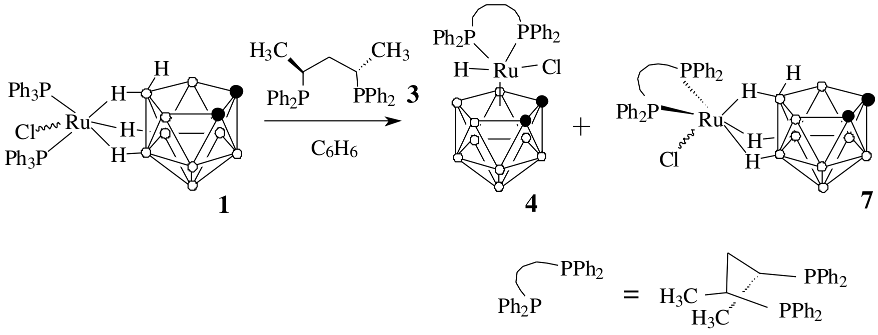
2. Result and discussion

2.1. Synthesis and characterization of the chelate exo-nido- (7) and closo- (4) isomeric ruthenacarborane complexes

Previously, from the thermal PPh_3/(*S*,*S*)-bdpp displacement reaction of *exo*-*nido* complex **1** with **3** in refluxing toluene [6], we were unable to isolate the chelate *exo*-*nido*-ruthenacarborane complex **7**, the probable first step intermediate of this process. One may reasonably suggest that species **7** is very short-lived and quite reactive towards *exo*-*nido*-*to*-*closo* isomerization under the thermal conditions used in the reaction. In the present work we have found that the replacement of PPh_3 ligands in **1** with diphosphine **3** to form the diamagnetic *closo* complex **4** could be achieved even at room temperature upon treatment of starting reagents in benzene for ca 2 days. Interestingly, when this reaction was monitored by TLC, an additional band of a new complex was observed after the first 2 h. The new species slowly disappeared during the conversion of **1** to **4**, exhibiting properties of an apparent intermediate. In an attempt to isolate such an intermediate complex we terminated the reaction of **1** with **3** at an earlier stage and this afforded, after column chromatography, an orange crystalline complex **7**, along with some amount of **4** (Scheme 1). The ruthenacarborane species thus isolated, on the basis of multinuclear NMR spectral data, has been identified as having an *exo*-*nido* cluster structure.

Interestingly, complex **7** in solution proved to be reactive toward *exo*-*nido*-*to*-*closo* conversion. Thus, the ^1H NMR spectrum of a pure fraction of **7**, taken for the NMR analysis immediately after the chromatographic separation, displays a sharp seven-line multiplet at δ −8.30 ppm, which is indicative of the chlorohydrido–ruthenium *closo* complex **4** [6]. The ^1H NMR spectrum of this fraction also displays in the high-field region a set of broad and partly overlapping multiplets grouped into two groups, with one of these groups between δ −0.55 and −4.75 ppm and another one at higher field between δ −14.7 and −16.8 ppm as expected [8–10] for B···H···B and B–H···Ru bonds of *exo*-*nido* species **7**. Note, the relative intensity of the resonance at δ −8.30 ppm is increased in time, so that after few hours complex **4** is seen in the spectrum as the predominant species. The comparison of this ^1H NMR spectrum with that initially observed for the mixture of **7** and **4** allowed us to identify all basic aliphatic resonances of the diphosphine ligand in **7** (see Section 3). Moreover, from a set of upfield B–H···Ru and B···H···B resonances it can be concluded that **7** exists in solution as a mixture of geometrical isomers [10]. Indeed, due to the chirality of (*S*,*S*)-bdpp ligand **3**, three geometrical isomers would have been expected to exist for the *exo*-*nido* complex **7** of which each has no mirror symmetry (Chart 1).

Owing to the observed overlapping of principal resonances in the high-field region of the ^1H NMR spectrum



Scheme 1.