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(Indenyl)rhodacarboranes. Electronic *versus* steric effects on the conformation of cyclic ligands

Mikhail A. Arsenov [a], Vladimir B. Kharitonov [a], Elizaveta R. Sovdagarova [a], Alexander F. Smol'yakov [a, b], Dmitry A. Loginov [a, *]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, 119991 Moscow, Russian Federation*
[b] *Faculty of Science, RUDN University, 6 Miklukho-Maklaya St., Moscow 117198, Russian Federation*

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Dedicated to the 70th anniversary of Prof. Narayan Hosmane in recognition of his great contribution to the metallacarborane chemistry.

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ABSTRACT

(Indenyl)rhodacarboranes 1,2-R_2-3-(η^5-indenyl)-3,1,2-$RhC_2B_9H_9$ (**2a**: R = H; **2b**: R = Me) and 3-(η^5-indenyl)-4-SMe-3,1,2-$RhC_2B_9H_{10}$ (**3**) were synthesized by reactions of the iodide complex [(η^5-indenyl)RhI_2]$_n$ (**1b**) with Tl[Tl(η-7,8-R_2-7,8-$C_2B_9H_9$)] or Tl[9-SMe_2-7,8-$C_2B_9H_{10}$]. The formation of **3** is accompanied by monodemethylation of the SMe_2 substituent. The structures of rhodacarboranes **2b**, **3** and the half-sandwich complex (η^5-indenyl)$RhBr_2$(dmso) were determined by X-ray diffraction. Rhodacarborane **2b** has the sterically unfavorable eclipsed *cisoid* conformation, in which the bridgehead carbon atoms of the indenyl ligand are arranged close to the carborane cage carbon atoms. The thermal stability of conformers for **2b** was analyzed by the DFT calculations.

1. Introduction

Applicability of metallacarboranes in transition-metal catalysis, materials science and medicine is well-known [1,2]. In particular, they can be used for design of effective molecular machines and switches [3]. The dicarbollide anion $[C_2B_9H_{11}]^{2-}$ has two carbon atoms and three boron atoms in open pentagonal face that results in energy nonequivalence for the different rotamers in its transition-metal complexes. The conformers of the bis(dicarbollide)cobalt anion $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ are most investigated and well-known [4]. Differences in the rotamer energies are rather small and less than 3 kcal mol^{-1} [5]. Interestingly, the *transoid* conformation, in which two pairs of carbon vertices reflected through a center of symmetry, is most stable, that can be explained by *trans* effect of metal molecular orbitals [6]. Introduction of halogen or methyl sulfide substituents at the 8- and 8′-positions of the metallacarborane cages leads to the following stabilization of *transoid* conformation up to 10 kcal mol^{-1} [3,7]. This stabilization was attributed by the formation of intramolecular $C_{carb}H\cdots XB$ (X = Cl, Br, I, SMe) hydrogen bonds between the ligands.

The indenyl anion has close symmetry with dicarbollide dianion because two carbon atoms of its cyclopentadienyl ring are involved in the conjugation with benzene ring [8]. This nonequivalence of carbon atoms introduces the possibility of different conformers in the sandwich indenyl compounds. Earlier, Welch with coworkers showed that (indenyl)cobalta- and rhodacarboranes (containing both, indenyl and dicarbollide ligands) usually adopts the staggered *cisoid* conformation, in which the bridgehead carbon atoms of the indenyl ligand are arranged close to the carborane cage carbon atoms [9]. This conformation is controlled by electronic factors, which arise from *trans* effect of metal molecular orbitals. Interestingly, the introduction of bulky aryl- and alkyl substituents to the cage carbon atoms leads to displacement of the six-membered ring of the indenyl ligand to the next best staggered conformation in the case of cobaltacarboranes [10], whereas the rhodium complexes preserve the staggered *cisoid* geometry [11]. Probably, this different

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* Corresponding author.
E-mail address: dloginov@ineos.ac.ru (D.A. Loginov).
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behavior is caused by a stronger steric hindrance in the case of cobalt in accordance with smaller covalent radius of Co *vs.* Rh. In support of this suggestion, iridacarborane 3-(η^5-indenyl)-3,1,2-$IrC_2B_9H_{11}$ has the almost eclipsed *cisoid* conformation [12].

In the present work we report the synthesis and structure of novel (indenyl)rhodacarboranes including the strongly sterically hindered compound 1,2-Me_2-3-(η^5-indenyl)-3,1,2-$RhC_2B_9H_9$, which adopts the eclipsed *cisoid* conformation.

2. Results and discussion

2.1. Synthesis and reactivity

The halide complexes [(η^5-indenyl)RhX_2]$_n$ (X = Cl, Br, I) have proved to be useful synthons for introducing of the (η^5-indenyl)Rh fragment in the carborane cage. For example, Welch with co-workers used the heptamethylated complex [(η^5-C_9Me_7)$RhCl_2$]$_2$ for synthesis of rhodacarboranes [11]. This complex was easily synthesized by refluxing of $RhCl_3 \cdot xH_2O$ and heptamethylindene in methanol [13]. However, this chemistry was well developed only for indenyl ligands stabilized by methyl groups. Thus, the reaction of unsubstituted indene with $RhCl_3 \cdot xH_2O$ leads to insoluble polymeric material with composition $C_9H_7RhCl_2$ (according to elemental analysis) in 43% yield [14]. The following reaction of the latter with Tl[Tl(η-7,8-$C_2B_9H_{11}$)] did not give the expected rhodacarborane 3-(η^5-indenyl)-3,1,2-$RhC_2B_9H_{11}$. Besides *nido*-derivatives, the only one *closo*-bis(dicarbollide) complex 3-($C_2B_9H_{11}$)-8-{(C_9H_6)Rh(C_9H_7)}-3,1,2-$RhC_2B_9H_{10}$ was isolated in low yield from this reaction. Recently, we have developed an effective approach to the halide complexes [(η^5-indenyl)RhX_2]$_n$ (**1a**: X = Br; **1b**: X = I) based on the reactions of halogens with bis(ethylene) derivative (η^5-indenyl)Rh(C_2H_4)$_2$ [15]. Complexes **1a**,**b** have proved to be almost insoluble in non-coordinating solvents (e.g., dichloromethane, acetone, acetonitrile) that inhibited detecting of the NMR spectra. Nevertheless, in the present work we found that dimethylsulfoxide dissolves them with decomposition of polymeric structure and formation of adducts (η^5-indenyl)RhX_2(dmso). It should be noted that immediately after dissolution of iodide **1b** in dmso-*d*^{6} there are two multiplet signals of protons of the six-membered ring of the indenyl ligand in the ^{1}H NMR spectrum, whereas for bromide **1a** these protons are observed as only one singlet. Moreover, the storage of the latter in solution for 1 day leads to dramatically changes in the set of signals with splitting of the six-membered ring protons to two multiplets (Fig. 1). This behavior in solution can be attributed to exhaustive replacement of the bromide anions by solvent molecules with formation of salt [(η^5-indenyl)Rh(dmso)$_3$]Br_2. For the iodide complex, the degree of similar transformation is only 20% after 3 days that is in accordance with a stronger bonding of the transition metals with I^- than Br^-. In the case of the bromide derivative we were able to crystallize the intermediate adduct (η^5-indenyl)$RhBr_2$(dmso) from reaction of **1a** with quantitative amount of dimethylsulfoxide in CH_2Cl_2 and confirm its structure by crude X-ray diffraction (Fig. 2). Unfortunately, quality of crystals did not allow us to perform a precise structural analysis.

We found that iodide **1b** reacts with thallium dicarbollides Tl

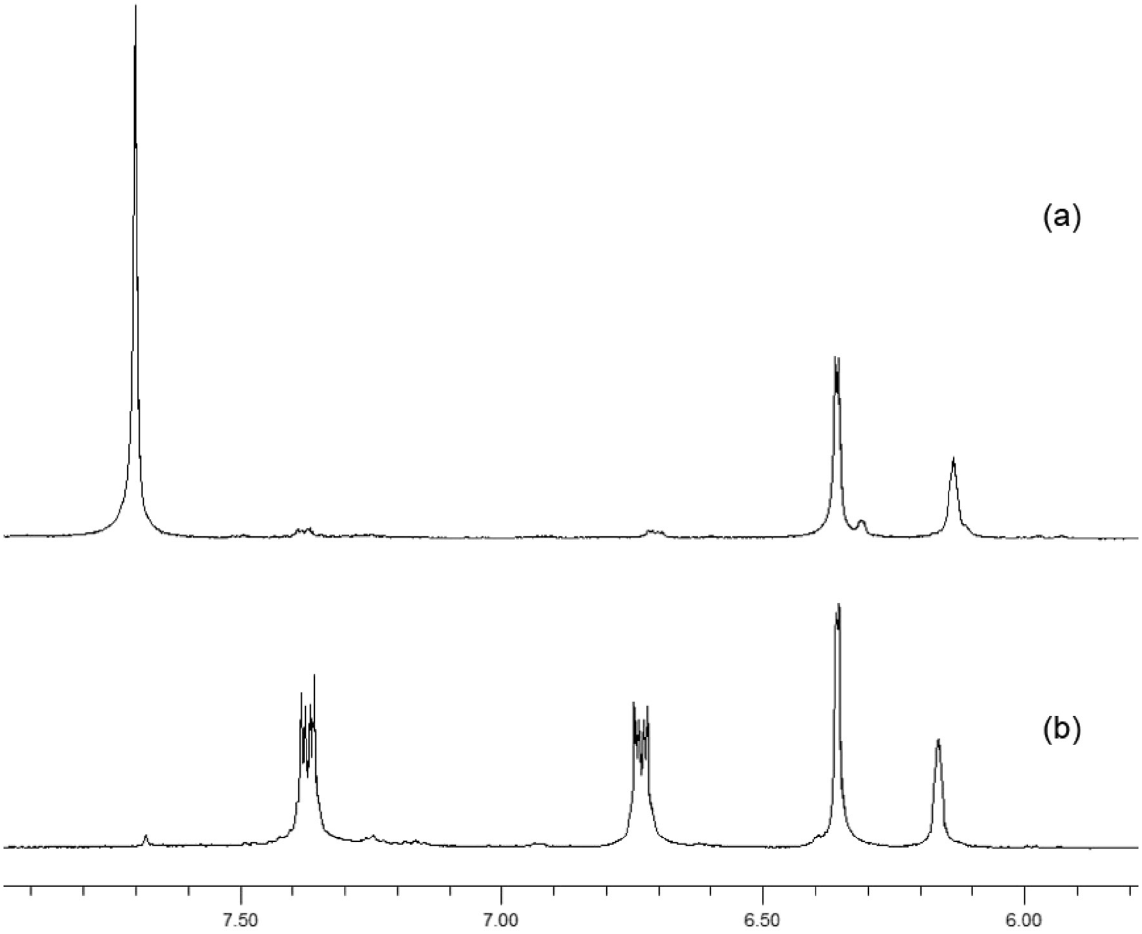

Fig. 1. The ^{1}H NMR spectra for **1a** in dmso-*d*^{6}: a) 5 min after dissolution and b) after 1 day.

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