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Different reactivity of cyclooctadiene complexes 3,3-(cod)-8-SMe₂-*closo*-3,1,2-RhC₂B₉H₁₀ and 1,8-Me₂-2,2-(cod)-11-SMe₂-2,1,8-*closo*-RhC₂B₉H₈ toward iodine[☆]

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ABSTRACT

Reaction of the thallium salt Tl[7,8-Me₂-10-SMe₂-7,8-*nido*-C₂B₉H₈] with [(cod)RhCl]₂ in THF furnishes new rhodacarborane 1,2-Me₂-3,3-(cod)-8-SMe₂-3,1,2-*closo*-RhC₂B₉H₈ (**1**). The latter undergoes 1,2 → 1,7 carbon atom isomerization upon reflux in *o*-xylene for 5 h producing complex 1,8-Me₂-2,2-(cod)-11-SMe₂-2,1,8-*closo*-RhC₂B₉H₈ (**2**). Reaction of complex **2** with 1 equiv of I₂ in benzene results in a loss of the cod ligand and formation of product **3**, consisting of cationic [(1,8-Me₂-11-SMe₂-*closo*-2,1,8-RhC₂B₉H₈)₂I₃]⁺ (**3a**⁺) and anionic [(1,8-Me₂-11-SMe₂-*closo*-2,1,8-RhC₂B₉H₈)₂I₃]⁻ (**3b**⁻) iodide species. In contrast, unisomerized analog 3,3-(cod)-8-SMe₂-*closo*-3,1,2-RhC₂B₉H₁₀ reacts with I₂ affording dimeric iodide [3,3-I₂-8-SMe₂-*closo*-3,1,2-RhC₂B₉H₁₀]₂ (**5**). The structures of **2** and **5** were determined by a single crystal X-ray diffraction.

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1. Introduction

Halide complexes [Cp^{*}MX₂]₂ (M = Rh, Ir; X = Cl, Br, I) are widely used in organometallic synthesis as a source of Cp^{*}M fragment [1]. Rhodium(III) catalysts have been proven to be highly efficient for the chelation-assisted C–H functionalizations with high activity, selectivity, broad substrate scope and high functional group tolerance [2]. This approach has become a highly efficient and reliable synthetic method for constructing C–C [3], C–N [4], and C–O [5] bonds. Recently rhodium complexes with carborane ligands [(Carb)RhX₂]₂ (Carb – dicarbollides or tricarbollides) were applied in catalytic oxidative coupling of benzoic acids with internal alkynes [6] and their iridium analogs were shown to efficiently catalyze the reductive amination reaction of aldehydes (or ketones) with primary (or secondary) amines in the presence of carbon monoxide as a reductant [7]. Thus, investigation of influence of the structural parameters (e.g. cage isomerism) on the physical and chemical properties of metallacarboranes with potential catalytic activity [8] is in demand.

Previously we reported the reaction of iridium ethene complex 1,8-Me₂-2,2-(C₂H₄)₂-7-SMe₂-2,1,8-IrC₂B₉H₈ with iodine which led to decomplexation of ethene ligand and formation of iodide complex [(1,8-Me₂-7-SMe₂-2,1,8-IrC₂B₉H₈)₂I₃]⁺[(1,8-Me₂-7-SMe₂-2,1,8-IrC₂B₉H₈)₂I₃]⁻ [9]. The anionic species in that compound had a dimeric structure with the bridged methylthio group as the result of spontaneous demethylation of SMe₂ substituent in metallacarborane cage. We decided to investigate if the similar rhodacarborane olefin complexes react with iodine in the similar manner. It is known that cyclooctadiene ligand in CpRh(cod) is easily substituted [10] upon the reaction with I₂, while iridium analog CpIr(cod) forms cationic complex [CpIr(cod)]⁺ [11]. That fact allows us to study the substitution of olefin ligand by I₂ in cyclooctadiene rhodium complexes instead of less stable ethene congeners. Herein we report different reactivity of the parent rhodacarboranes 3,3-(cod)-8-SMe₂-*closo*-3,1,2-RhC₂B₉H₁₀ and 1,8-Me₂-2,2-(cod)-11-SMe₂-2,1,8-*closo*-RhC₂B₉H₈ (**2**) in the reaction with iodine.

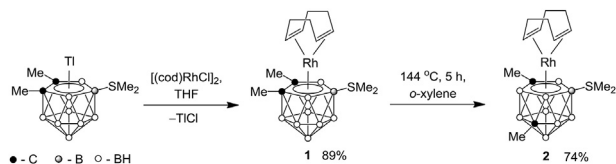
2. Results and discussion

Complex **2** was prepared via two step synthesis (Scheme 1). On the first step thallium salt Tl[10-SMe₂-7,8-Me₂-7,8-*nido*-C₂B₉H₈] was treated with [(cod)RhCl]₂ affording new rhodacarborane 1,2-Me₂-3,3-(cod)-8-SMe₂-3,1,2-*closo*-RhC₂B₉H₈ (**1**) with excellent

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Scheme 1. Synthesis and isomerization of rhodacarborane complex.

yield. The latter undergoes 1,2 → 1,7 carbon atom isomerization upon reflux in *o*-xylene (144 °C, 5 h) producing complex 1,8-Me₂-2,2-(cod)-11-SMe₂-2,1,8-*closo*-RhC₂B₉H₈ (**2**). Noteworthy we were not able to obtain any other isomeric products resulting from this reaction although iridium analog 1,2-Me₂-3,3-(cod)-8-SMe₂-3,1,2-*closo*-IrC₂B₉H₈ forms products of both 1,2 → 1,7 and 1,2 → 1,2 isomerizations upon heating (110 °C, 3 h) [12]. No signs of isomerization reaction of **1** were detected under the same reaction conditions according to the ¹¹B NMR spectrum. The rearrangement reaction of **1** occurs at a higher temperature and leads to the partial decomposition of the starting material. The fact that a product of 1,2 → 1,2 isomerization with 4,1,2-*closo*-RhC₂B₉H₈ architecture is not formed may be due to its low stability at these conditions or instability of intermediates on the reaction pathway.

Complex **1** exhibits two singlets in ¹H NMR spectrum corresponding to the SMe₂ and C_{cage}Me substituents and 1:2:1:2:1:2 pattern in ¹¹B{¹H} NMR spectrum suggesting C₅ molecular symmetry. Cage rearrangement in rhodacarborane **1** leads to the loss of molecular symmetry: complex **2** reveals four singlets corresponding to each methyl group in SMe₂ and C_{cage}Me substituents, the ¹¹B {¹H} NMR spectrum of **2** consists of eight resonances with ⟨δ(¹¹B)⟩ = −10.0 ppm indicative of a *closo*-MC₂B₉ metallacarborane.

According to the single-crystal X-ray diffraction study, complex **2** has 2,1,8-*closo*-RhC₂B₉H₈ configuration of the metallacarborane cage (Fig. 1). Despite of the presence of one methyl substituent in the CB₄ pentagonal face coordinated to the metal atom of the carborane ligand in **2**, the distance from the rhodium atom to the CB₄ plane (1.618 Å) is significantly decreased in comparison with that in the 3,3-(cod)-8-SMe₂-*closo*-3,1,2-RhC₂B₉H₁₀ complex (1.736 Å) where rhodium atom bounds to the C₂B₃ pentagonal face with no methyl substituents. The average distance between the rhodium atom and olefinic carbons in 3,3-(cod)-8-SMe₂-*closo*-3,1,2-RhC₂B₉H₁₀ (2.149 Å) is less than in **2** (2.166 Å). These observations indicate stronger binding of the rhodium atom with carborane ligand and weaker binding with cyclooctadiene in rhodacarboranes with Rh⋯CB₄ connectivity when compared to complexes having Rh⋯C₂B₃ connectivity. We have previously represented the same trends for the series of parent iridacarboranes [12].

Reaction of complex **2** with 1 equiv of I₂ in benzene results in a loss of the cod ligand and formation of product **3** consisting of cationic **3a**⁺ and anionic **3b**[−] iodide species (Scheme 2). It was confirmed by the ESI-MS analysis of product **3** exhibiting the same patterns as the previously studied iridium analog.⁹ The ESI-MS spectra of compound **3** in acetonitrile represent the unfragmented anion **3b**[−] (*m/z* = 999.6) and cation [((Carb)RhI(CH₃CN))₂]²⁺ (*m/z* = 492.3) formed by solvolysis of cation **3a**⁺.

Interestingly, reaction of **2** with concentrated HI in the AcOH/Ac₂O mixture furnishes a product that devoids peak *m/z* = 999.6 in ESI-MS spectra corresponding to demethylated anion **3b**[−], but the positive ion *m/z* = 492.3 still presents. Based on ESI-MS spectra and elemental analysis, complex **4** appears to be a dimeric iodide represented on Scheme 2. This result indicates that dimer **4** is actually rather stable and is not formed as an intermediate in reaction of **2** with iodine. Thus, we assume that the demethylation reaction with the subsequent formation of dimeric sulphide anion **3b**[−] occurs in

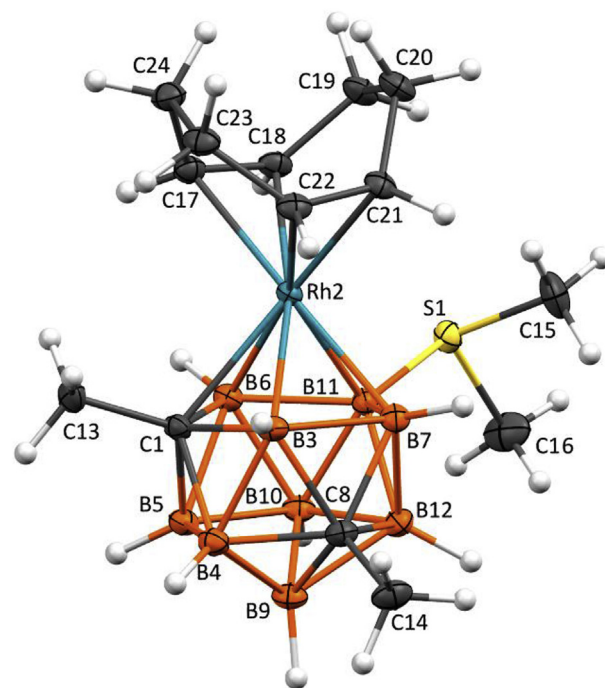
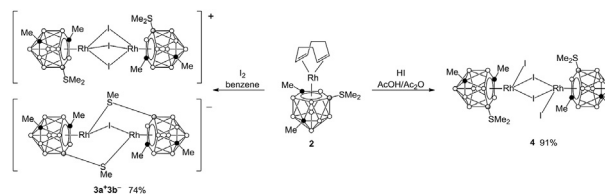


Fig. 1. Structure of complex **2**. Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Rh2–C17 2.179(2), Rh2–C18 2.1895(19), Rh2–C21 2.1461(19), Rh2–C22 2.1485(19), Rh2–C1 2.3070(19), Rh2–B3 2.166(2), Rh2–B6 2.174(2), Rh2–B7 2.188(2), Rh2–B11 2.211(2), S1–C15 1.792(2), S1–C16 1.792(2), S1–B11 1.891(2), C1–C13 1.518(3), C8–C14 1.521(3), C17–C18 1.394(3), C21–C22 1.406(3).



Scheme 2. Reaction of cyclooctadiene complex with iodine and hydroiodic acid.

the intermediate iodide [(Carb)Rh(cod)I]. The external iodide anion may attack cyclooctadiene ligand in [(Carb)Rh(cod)I]⁺ leading to decomposition of diene ligand and formation of dimeric iodide [(Carb)RhI₂]₂ (see below) or methyl group of SMe₂ moiety that will finally furnish **3b**[−] after dimerization and extrusion of cod with excessive iodide anion. Noteworthy, if old HI (containing I₃[−] anion due to oxidation of I[−]) was used in reaction with **2**, another compound, i.e. **3a**⁺I₃[−], could be isolated.

Since rhodium complexes **2** and 3,3-(cod)-8-SMe₂-*closo*-3,1,2-RhC₂B₉H₁₀ had notable structural differences according to the X-ray diffraction study, that was interesting to compare their chemical behaviour under the same reaction conditions. Rhodacarborane 3,3-(cod)-8-SMe₂-*closo*-3,1,2-RhC₂B₉H₁₀ reacts with 1 equiv of I₂ affording new dimeric iodide **5** (Scheme 3). ESI-MS spectra of compound **5** reveal the only peak cluster in the positive ion mode (*m/z* = 464.6, [((Carb)RhI(CH₃CN))₂]²⁺) with no signals in negative ion mode corresponding to the demethylated rhodium dimer of **3b**[−] type. Thus reaction of 3,3-(cod)-8-SMe₂-*closo*-3,1,2-RhC₂B₉H₁₀ with iodine was not complicated by demethylation of the SMe₂ substituent in the metallacarborane cage. Our previous computational study revealed that C_{cage}-methylated derivatives have slightly lower activation barriers of the demethylation reaction

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