

The first metallacarborane triple-decker complexes with a bridging borole ligand

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Abstract

The (borole)iodide complex $[(\eta^5\text{-C}_4\text{H}_4\text{BPh})\text{RhI}]_4$ reacts with the carborane anion $[\text{Carb}']^-$ ($\text{Carb}' = 9\text{-SMe}_2\text{-7,8-C}_2\text{B}_9\text{H}_{10}$) giving $(\text{Carb}')\text{Rh}(\eta^5\text{-C}_4\text{H}_4\text{BPh})$ (**2**). Reactions of **2** with dicationic fragments $[\text{LM}]^{2+}$ afford the μ -borole triple-decker complexes $[(\text{Carb}')\text{Rh}(\mu\text{-}\eta^5\text{:}\eta^5\text{-C}_4\text{H}_4\text{BPh})\text{ML}]^{2+}$ [$\text{LM} = \text{Cp}^*\text{Ir}$ (**4**), $(\text{Carb}')\text{Rh}$ (**7**)] or the arene-type complexes $[(\text{Carb}')\text{Rh}(\mu\text{-}\eta^5\text{:}\eta^6\text{-C}_4\text{H}_4\text{BPh})\text{ML}]^{2+}$ [$\text{LM} = \text{Cp}^*\text{Rh}$ (**3**), $(\text{Carb}')\text{Ir}$ (**8**)]. The structure of **4**(BF_4)₂ was determined by X-ray diffraction.
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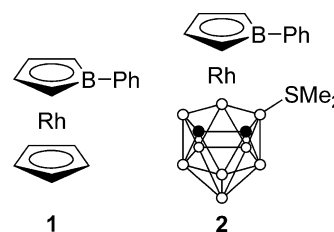
Keywords: Boron; Boron heterocycles; Metallacarboranes; Iridium; Rhodium; Triple-decker complexes

1. Introduction

Metallacarborane triple-decker complexes are still rare. Siebert et al. have prepared compounds with a bridging diborole ligand [1–6]. We have described previously two μ -cyclopentadienyl nickelacarborane complexes [7,8].

Recently, we have shown that the reactions of the B-phenylborole complex $\text{CpRh}(\eta^5\text{-C}_4\text{H}_4\text{BPh})$ (**1**) with dicationic fragments $[(\text{ring})\text{M}]^{2+}$ afford either triple-decker or arene-type complexes $[\text{CpRh}(\mu\text{-}\eta^5\text{:}\eta^5\text{-C}_4\text{H}_4\text{BPh})\text{M}(\text{ring})]^{2+}$ and $[\text{CpRh}(\mu\text{-}\eta^5\text{:}\eta^6\text{-C}_4\text{H}_4\text{BPh})\text{M}(\text{ring})]^{2+}$ [9]. The monoanionic carborane ligand $[\text{Carb}']^-$ ($\text{Carb}' = 9\text{-SMe}_2\text{-7,8-C}_2\text{B}_9\text{H}_{10}$) is analogous with Cp^- in coordinating ability [10–13]. It allows to assume that the (borole)rhodacarborane complex $(\text{Carb}')\text{Rh}(\eta^5\text{-C}_4\text{H}_4\text{BPh})$ (**2**) should react with $[(\text{ring})\text{M}]^{2+}$ fragments similar to **1**. Herein we report the use of such reactions for the synthesis of the first metallacarborane triple-decker complexes with a bridging borole ligand.

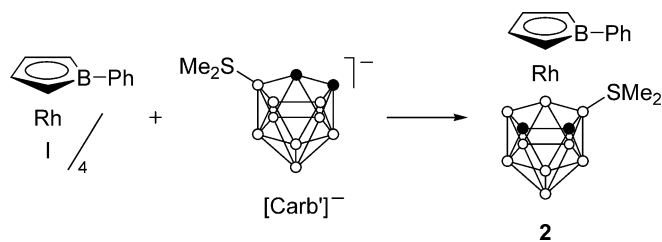
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2. Results and discussion

2.1. Synthesis

Herberich et al. [14–16] have shown that the (borole)iodide complex $[(\eta^5\text{-C}_4\text{H}_4\text{BPh})\text{RhI}]_4$ is a useful synthon of the $(\eta^5\text{-C}_4\text{H}_4\text{BPh})\text{Rh}$ species. In particular, it reacts with silver salts in acetonitrile giving cation $[(\eta^5\text{-C}_4\text{H}_4\text{BPh})\text{Rh}(\text{MeCN})_3]^+$ [16]. The latter reacts with mesitylene and hexamethylbenzene giving the arene complexes $[(\eta^5\text{-C}_4\text{H}_4\text{BPh})\text{Rh}(\eta^6\text{-arene})]^+$. We found that the reaction of $[(\eta^5\text{-C}_4\text{H}_4\text{BPh})\text{RhI}]_4$ with the carborane anion $[\text{Carb}']^-$ yields the rhodacarborane complex **2** (Scheme 1). Similar



reaction of $[\text{Carb}'^-]$ with $[\text{Cp}^*\text{RuCl}]_4$ has been shown earlier to give $\text{Cp}^*\text{Ru}(\text{Carb}')$ [7,17].

The reaction of **1** with the $[\text{Cp}^*\text{Ir}]^{2+}$ fragment has been shown to give the triple-decker complex $[\text{CpRh}(\mu\text{-}\eta^5\text{:}\eta^5\text{-C}_4\text{H}_4\text{BPh})\text{IrCp}^*]^{2+}$ contaminated with the arene-type complex $[\text{CpRh}(\mu\text{-}\eta^5\text{:}\eta^6\text{-C}_4\text{H}_4\text{BPh})\text{IrCp}^*]^{2+}$ whereas similar reaction with $[\text{Cp}^*\text{Rh}]^{2+}$ gives the arene-type complex $[\text{CpRh}(\mu\text{-}\eta^5\text{:}\eta^6\text{-C}_4\text{H}_4\text{BPh})\text{RhCp}^*]^{2+}$ as a sole product [9]. The behavior of rhodacarborane **2** proved to be very simi-

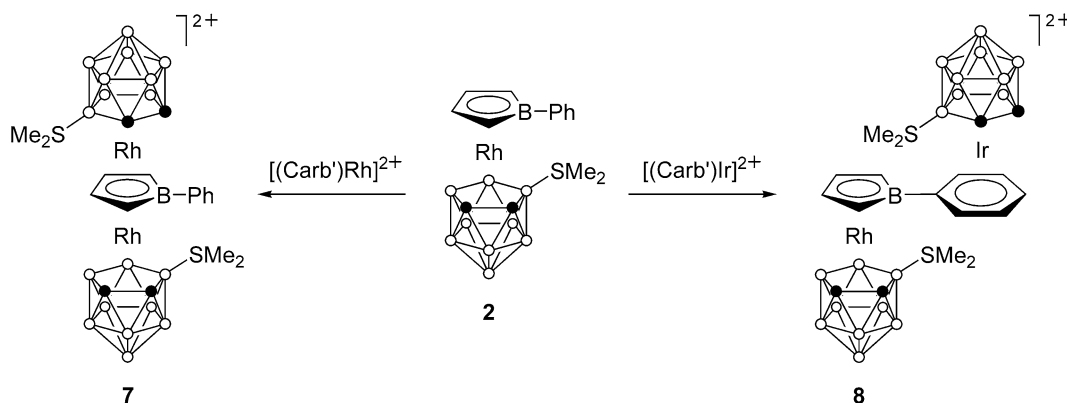
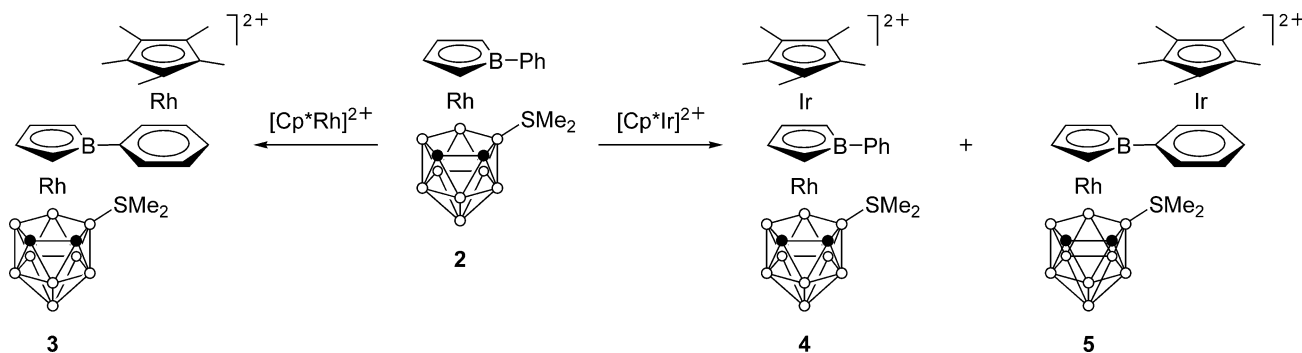


Table 1
 ^1H NMR spectroscopic data for complexes **2–5**, **7** and **8** in nitromethane- d_3 ^a

Complex	$\alpha\text{-H}^b$	$\beta\text{-H}^b$	SMe_2^c	CH-cage^d	Cp^{*c}	Ph^b
2	4.82, 4.75	5.70, 5.64	2.39, 2.37	4.08, 3.41		7.74 (<i>o</i> -H), 7.27 (<i>m</i> -H), 7.22 (<i>p</i> -H)
3	5.14, 5.06	5.94, 5.90	2.52	4.47, 3.74	2.22	7.49 (<i>o</i> -H), 7.28 (<i>m</i> -H, <i>p</i> -H)
4	5.58, 5.48	6.54, 6.43	2.72, 2.45	5.72, 5.15	1.95	7.79 (<i>o</i> -H), 7.55 (<i>m</i> -H), 7.43 (<i>p</i> -H)
5^e	—_f	—_f	—_f	—_f	2.34	—_f
7	6.19 (0.5H), 6.06 (1H), 6.01 (0.5H)	7.04 (0.5H), 6.95 (1H), 6.90 (0.5H)	2.77 (6H), 2.55 (3H), 2.50 (3H)	5.77, 5.22		7.98 (<i>o</i> -H), 7.55 (<i>m</i> -H), 7.45 (<i>p</i> -H)
8	5.16, 5.11	5.82, 5.80	2.85 (3H), 2.83 (3H), 2.56 (6H)	6.15, 5.49, 4.86, 4.14		7.97 (<i>o</i> -H), 7.82 (<i>m</i> -H), 7.75 (<i>p</i> -H)

^a Chemical shifts in ppm.

^b Multiplets.

^c Singlets.

^d Broad singlets.

^e Detected in a mixture with complex **4**.

^f Difficult to measure owing to overlap with signals of **4**.

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