

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

Dmitry A. Loginov, Dmitry V. Muratov, Zoya A. Starikova,
Pavel V. Petrovskii, Alexander R. Kudinov *

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow GSP-1, Russian Federation

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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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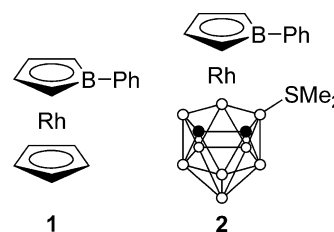
Keywords: Boron; Boron heterocycles; Metallacarboranes; Iridium; Rhodium; Triple-decker complexes

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.

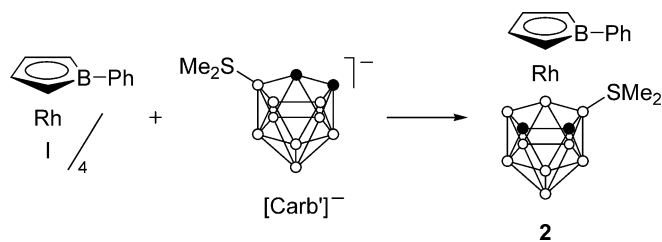
* Corresponding author. Tel.: +7 495 135 9367; fax: +7 495 135 5085.
E-mail address: arkudinov@ineos.ac.ru (A.R. Kudinov).



2. Results and discussion

2.1. Synthesis

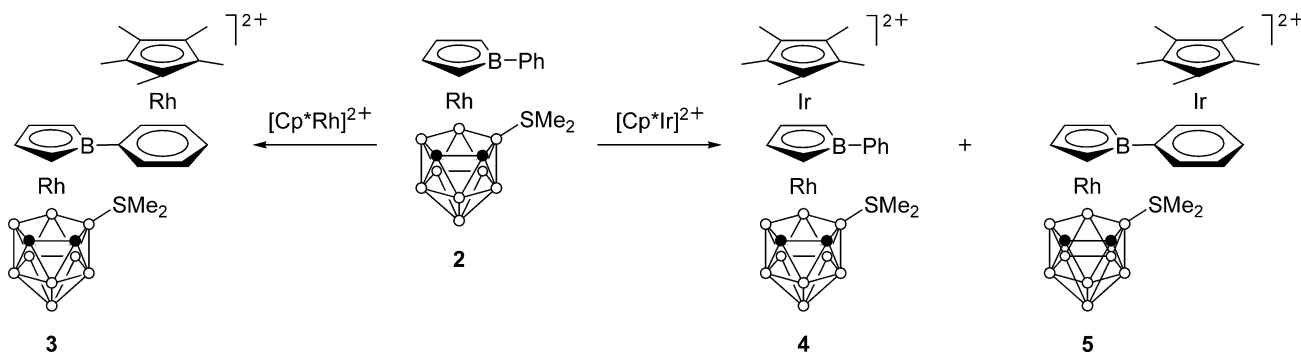
Herberich et al. [14–16] have shown that the (borole)iodide complex $[(\eta^5\text{-C}_4\text{H}_4\text{BPh})\text{RhI}]_4$ is a useful synthon of the $(\eta^5\text{-C}_4\text{H}_4\text{BPh})\text{Rh}$ species. In particular, it reacts with silver salts in acetonitrile giving cation $[(\eta^5\text{-C}_4\text{H}_4\text{BPh})\text{Rh}(\text{MeCN})_3]^+$ [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



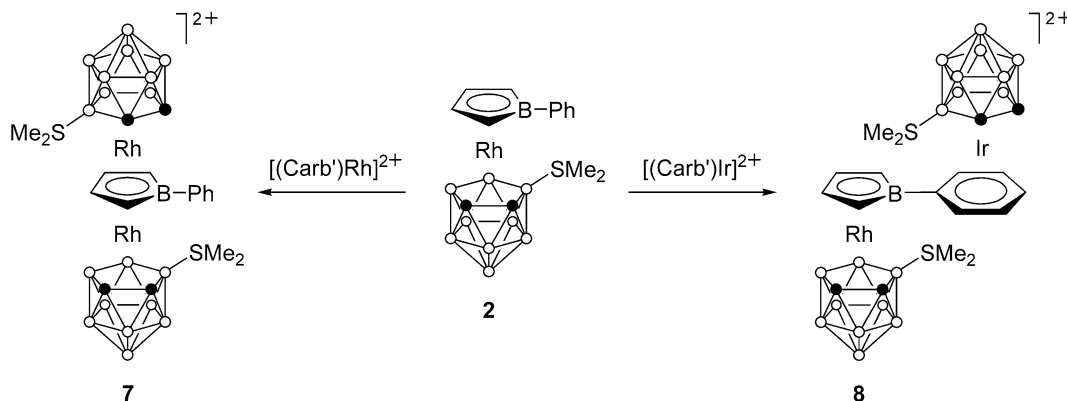
Scheme 1.

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



Scheme 2.



Scheme 3.

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**.

lar to that of the cyclopentadienyl analogue **1**. Indeed, its reaction with the $[\text{Cp}^*\text{Rh}]^{2+}$ fragment yields the arene-type complex **3** (Scheme 2).¹ On the contrary, similar reaction with $[\text{Cp}^*\text{Ir}]^{2+}$ affords the triple-decker complex **4** which, according to ^1H NMR spectroscopy, contains an admixture of the arene-type complex **5** (ca. 7%). The admixture content can be decreased to ca. 1–2% by lowering the reaction temperature to -15°C . The exclusive formation of the arene-type complex in the case of the reaction with $[\text{Cp}^*\text{Rh}]^{2+}$ is probably caused by low stability of the corresponding Rh_2 triple-decker complex $[(\text{Carb}')\text{Rh}(\mu\text{-}\eta^5\text{:}\eta^5\text{-C}_4\text{H}_4\text{BPh})\text{RhCp}^*]^{2+}$ (**6**).² Greater stability of the RhIr analogue is in accordance with stronger bonding of iridium with π -ligands.

In contrast to $[\text{Cp}^*\text{Rh}]^{2+}$, the dicationic rhodacarborane fragment $[(\text{Carb}')\text{Rh}]^{2+}$ reacts with **2** giving the Rh_2 triple-decker complex **7** isolated as a diastereomeric mixture (Scheme 3).³ The formation of **7** suggests its greater stability compared with **6**, apparently due to its higher symmetry. Lower stability of asymmetric triple-decker complexes in comparison with symmetric analogues is a general tendency [18] and is explained by asymmetric distribution of electron density in the triple-decker fragment $\text{M}(\mu\text{-ring})\text{M}'$ resulting in loosening of one of two $\text{M}(\mu\text{-ring})$ bonds.

Interestingly, the behavior of the iridacarborane fragment $[(\text{Carb}')\text{Ir}]^{2+}$ is also different from that of the cyclopentadienyl analogue $[\text{Cp}^*\text{Ir}]^{2+}$. It reacts with **2** giving the arene-type complex **8**. Possibly, the corresponding RhIr triple-decker structure is unstable owing to its low symmetry.

2.2. NMR spectroscopy

General features of ^1H NMR spectra for **2–5**, **7** and **8** are close to those for the cyclopentadienyl analogues [9,19] (Table 1). In particular, the signals of borole ring protons for triple-decker complexes **4** and **7** are strongly downfield shifted ($\Delta\delta = 0.8\text{--}1.3$ ppm) from the corresponding signals for the sandwich compound **2**. For the arene-type complexes **3** and **8** these signals are shifted in the same direction but in lower extent ($\Delta\delta = 0.1\text{--}0.4$ ppm), thus allowing to distinguish between triple-decker and arene-type structures. The determination of the structural type can be also made using the value of downfield shift (relative to **2**) of the signals of cage CH-protons. For the triple-decker complexes **4** and **7** this shift amounts to 1.6–

1.8 ppm, whereas for the arene-type complexes **3** and **8** it is 0.3–0.8 ppm.

There are four signals of borole ring protons in ^1H NMR spectra of complexes **2–5**, **7** and **8**, which can be explained by their C_1 symmetry. Another possible explanation is the absence of free rotation in solution owing to low orbital symmetry of the carborane and borole ligands [20] as well as to sterical effect of bulky SMe_2 and Ph substituents. However, this explanation is unlikely since the preliminary DFT calculations (at PBE/TZV level) revealed that the rotation barrier is very small (18.0 kJ mol^{-1}).

In the case of cations **7** and **8** existing as diastereomeric mixtures, there is a double set of signals of SMe_2 protons. Comparison of their intensities allows to estimate the ratio of *meso*- and *DD/LL*-isomers as 1:1.

Unfortunately, the signal of the boron atom of the borole ring in $^{11}\text{B}\{^1\text{H}\}$ NMR spectra often overlap with signals of cage boron atoms, lowering usefulness of these spectra.

2.3. Structure of the triple-decker complex **4**(BF_4)₂

The molecular structure of complex **4**(BF_4)₂ consists of separated cation **4** and two BF_4^- anions. The crystallographic cell contains two independent molecules; data for only one of them will be used in further discussion. Cation **4** is formed by three cyclic frames (C_5 , C_4B and C_2B_3), between which two metal atoms are located (Fig. 1). Selected bond lengths and angles are given in Table 2. The planes of the C_5 and C_4B rings are approximately parallel (the dihedral angle is equal to 2.3°). The C_2B_3 plane of the carborane ligand is inclined to the borole ring for 5.3° , that is possibly connected with steric repulsion of the Ph and SMe_2 groups. The borole ring is only slightly folded along the line $\text{C}(1)\text{C}(4)$ (0.2°), which is less than in other

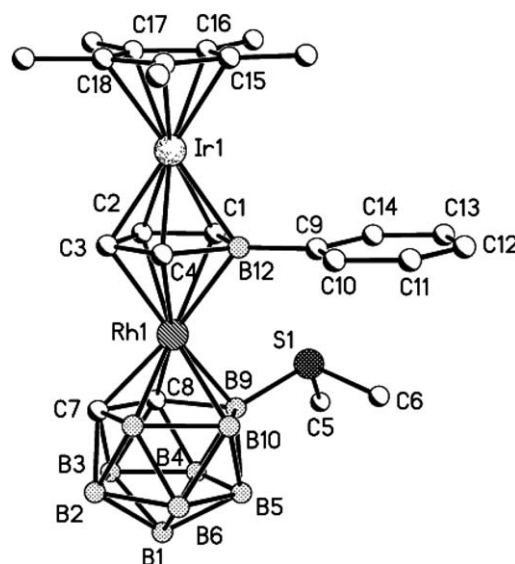


Fig. 1. Structure of cation **4**.

¹ The fragments $[\text{Cp}^*\text{M}]^{2+}$ ($\text{M} = \text{Rh}, \text{Ir}$) were generated as labile solvates $[\text{Cp}^*\text{M}(\text{Sol})_3]^{2+}$ ($\text{Sol} = \text{MeNO}_2, \text{Me}_2\text{CO}$) by treatment of $[\text{Cp}^*\text{MCl}_2]_2$ with AgBF_4 . All the cationic complexes described here were isolated as salts with the BF_4^- anion.

² An intermediate formation of the cyclopentadienyl analogue $[\text{Cp}^*\text{Rh}(\mu\text{-}\eta^5\text{:}\eta^5\text{-C}_4\text{H}_4\text{BPh})\text{RhCp}^*]^{2+}$ has been detected by ^1H NMR spectroscopy [9].

³ Solvates $[(\text{Carb}')\text{M}(\text{MeNO}_2)_3]^{2+}$ ($\text{M} = \text{Rh}, \text{Ir}$) were generated *in situ* by treatment of $[(\text{Carb}')\text{MBr}_2]_2$ with AgBF_4 in MeNO_2 . Their preliminary generation is inapplicable owing to low stability.

Table 2
Selected bond lengths [Å] and angles [°] for cation **4**

Ir(1)–C(1)	2.206(4)	Rh(1)–C(8)	2.134(4)
Ir(1)–C(2)	2.191(4)	Rh(1)–B(9)	2.149(5)
Ir(1)–C(3)	2.178(4)	Rh(1)–B(10)	2.192(5)
Ir(1)–C(4)	2.180(4)	Rh(1)–B(11)	2.166(4)
Ir(1)–B(12)	2.261(4)	C(1)–C(2)	1.444(6)
Ir(1)–C(15)	2.161(4)	C(2)–C(3)	1.478(6)
Ir(1)–C(16)	2.151(4)	C(3)–C(4)	1.460(6)
Ir(1)–C(17)	2.167(4)	B(12)–C(1)	1.581(7)
Ir(1)–C(18)	2.177(4)	B(12)–C(4)	1.598(6)
Ir(1)–C(19)	2.157(4)	B(12)–C(9)	1.558(6)
Rh(1)–C(1)	2.234(4)	C(7)–C(8)	1.634(6)
Rh(1)–C(2)	2.223(4)	B(11)–C(7)	1.725(7)
Rh(1)–C(3)	2.192(4)	B(9)–C(8)	1.737(7)
Rh(1)–C(4)	2.189(4)	B(9)–B(10)	1.793(7)
Rh(1)–B(12)	2.270(5)	B(10)–B(11)	1.831(7)
Rh(1)–C(7)	2.138(4)	B(9)–S(1)	1.908(5)
C(1)–C(2)–C(3)	109.4(4)	C(7)–C(8)–B(9)	109.7(3)
C(2)–C(3)–C(4)	109.1(3)	C(8)–B(9)–B(10)	107.6(3)
C(3)–C(4)–B(12)	110.2(3)	B(9)–B(10)–B(11)	104.8(3)
B(12)–C(1)–C(2)	111.2(4)	B(10)–B(11)–C(7)	105.7(3)
C(1)–B(12)–C(4)	100.1(3)	B(11)–C(7)–C(8)	112.2(3)
C(1)–B(12)–C(9)	128.4(4)	C(5)–S(1)–C(6)	101.5(3)
C(4)–B(12)–C(9)	131.4(4)		

structurally characterised μ -borole triple-decker complexes [21].

The Rh–C(C₄B) bonds in **4** (2.189–2.234 Å, av. 2.21 Å) are somewhat longer than the corresponding bonds in the cyclopentadienyl analogue [CpRh(μ - η^5 : η^5 -C₄H₄BPh)-IrCp*]²⁺ (av. 2.19 Å) [9]. This elongation may be caused by stronger acceptor ability of [Carb'][–] (compared to Cp[–]) leading to lower back donation from the rhodium atom to the borole ring. Strengthening of the Ir–C(C₄B) bonds and bonds within the borole ring is also observed. For example, the bonds B–C (1.598 and 1.581 Å, av. 1.591 Å) and C–C (1.444, 1.478 and 1.460 Å, av. 1.461 Å) in the borole ring of **4** are shorter than the corresponding bonds in [CpRh(μ - η^5 : η^5 -C₄H₄BPh)IrCp*]²⁺ (B–C av. 1.605 Å; C–C av. 1.491 Å).

3. Conclusion

Reactions of (borole)rhodacarborane **2** with cationic fragments [Cp*M]²⁺ (M = Rh, Ir) proceed similar to the cyclopentadienyl analogue **1** giving triple-decker (Ir) or arene-type (Rh) complexes. The replacement of Cp* by Carb' in the cationic fragments changes the reaction pathway. Using these reactions the first metallacarborane μ -borole triple-decker complexes were prepared.

4. Experimental

4.1. General

The reactions were carried out under an inert atmosphere in dry solvents. The isolation of products was conducted in air. Starting materials [(η^5 -C₄H₄BPh)RhI]₄ [14], Na[Carb'] [12], [Cp*RhCl₂]₂, [Cp*IrCl₂]₂ [22], [(Carb')RhBr₂]₂ [10],

[(Carb')IrBr₂]₂ [23] and AgBF₄ · 3dioxane [24] were prepared as described in the literature. ¹H and ¹¹B{¹H} NMR spectra (δ in ppm) were recorded on a Bruker AMX-400 spectrometer (¹H 400.13; ¹¹B 128.38 MHz) relative to residual protons of the solvents (¹H) or BF₃ · Et₂O (¹¹B, external standard).

4.2. Synthesis of (Carb')Rh(η^5 -C₄H₄BPh) (**2**)

A solution of Na[Carb'] in THF (2 ml of 0.22 M solution, 0.44 mmol) was added to [(η^5 -C₄H₄BPh)RhI]₄ (150 mg, 0.10 mmol) in THF (10 ml). The reaction mixture was stirred for 24 h and the solvent was removed in vacuo. The residue was dissolved in CH₂Cl₂ and filtered. After evaporation in vacuo, the crude product was washed with MeOH and reprecipitated by petroleum ether from acetone to give a yellow solid. Yield 111 mg (63%). Anal. Calc. for C₁₄H₂₅B₁₀RhS: C, 38.53; H, 5.77; B, 24.77. Found: C, 38.78; H, 5.62; B, 24.93%. ¹¹B{¹H} NMR (acetone-*d*₆): δ = –25.5 (bs, 1B), –23.0 (bs, 1B), –21.1 (bs, 1B), –14.0 (bs, 1B), –10.2 (bs, 1B), –9.0 (bs, 1B), –6.9 (bs, 1B), –4.3 (bs, 1B), 0.4 (bs, 1B), 20.9 (bs, 1B, C₄H₄B).

4.3. Synthesis of the arene-type complex [(Carb')Rh(μ - η^5 : η^6 -C₄H₄BPh)RhCp*](BF₄)₂ (**3**(BF₄)₂)

A mixture of [Cp*RhCl₂]₂ (28 mg, 0.05 mmol) and AgBF₄ · 3dioxane (84 mg, 0.18 mmol) in MeNO₂ (1 ml) was stirred for ca. 0.5 h. The precipitate of AgCl was centrifuged off and the solution obtained was added to **2** (40 mg, 0.09 mmol). The reaction mixture was stirred for 2 h. Ether (10 ml) was added to precipitate complex **3**(BF₄)₂ as a yellow solid which was reprecipitated twice from acetone by ether. Yield 74 mg (96%). Anal. Calc. for C₂₄H₄₀B₁₂F₈Rh₂S: C, 33.99; H, 4.75; B, 15.29. Found: C, 33.60; H, 4.73; B, 14.90%. ¹¹B{¹H} NMR (nitromethane-*d*₃): δ = –25.1 (bs, 1B), –22.4 (bs, 1B), –21.2 (bs, 1B), –14.2 (bs, 1B), –9.7 (bs, 1B), –8.0 (bs, 1B), –4.1 (bs, 2B), –1.4 (s, 2B, BF₄), 1.0 (bs, 1B), 12.5 (bs, 1B, C₄H₄B).

4.4. Synthesis of the triple-decker complex [(Carb')Rh(μ - η^5 : η^5 -C₄H₄BPh)IrCp*](BF₄)₂ (**4**(BF₄)₂)

Me₂CO (1 ml) was added to a mixture of [Cp*IrCl₂]₂ (36 mg, 0.05 mmol) and AgBF₄ · 3dioxane (83 mg, 0.18 mmol). The reaction mixture was stirred for ca. 0.5 h and the precipitate of AgCl was centrifuged off. The solution obtained was added to **2** (40 mg, 0.09 mmol) and left for 2 h at –15 °C. After warming to room temperature, the solvent was removed in vacuo and the residue was reprecipitated twice by ether from CH₂Cl₂ to yield complex **4**(BF₄)₂ (60 mg, 71%) as a yellow solid. Anal. Calc. for C₂₄H₄₀B₁₂F₈IrRhS · CH₂Cl₂: C, 29.37; H, 4.14; B, 12.69. Found: C, 29.42; H, 4.43; B, 12.77%. ¹¹B{¹H} NMR (nitromethane-*d*₃): δ = –20.8 (bs, 1B), –15.9 (bs, 1B), –14.0 (bs,

1B), -7.2 (bs, 1B), -3.5 (bs, 1B), -1.4 (s, 2B, BF₄), 2.9 (bs, 2B), 8.5 (bs, 1B), 13.3 (bs, 1B).

4.5. Synthesis of the triple-decker complex $[(\text{Carb}')\text{Rh}]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-C}_4\text{H}_4\text{BPh})(\text{BF}_4)_2$ (**7**(BF₄)₂)

MeNO₂ (1.5 ml) was added to a mixture of **2** (50 mg, 0.11 mmol), [(Carb')RhBr₂]₂ (52 mg, 0.06 mmol) and AgBF₄ · 3dioxane (104 mg, 0.23 mmol), and the suspension was stirred for 2 h. The precipitate of AgBr was centrifuged off and ether (10 ml) was added to the solution obtained. The resulting red solid was reprecipitated twice by ether from CH₂Cl₂ to yield complex **7**(BF₄)₂ (82 mg, 80%). Anal. Calc. for C₁₈H₄₀B₂₁F₈Rh₂S₂: C, 23.88; H, 4.45; B, 25.07. Found: C, 23.94; H, 4.50; B, 24.25%. ¹¹B{¹H} NMR (nitromethane-*d*₃): $\delta = -21.2$ (bs, 2B), -15.2 (bs, 2B), -13.4 (bs, 2B), -6.7 (bs, 2B), -3.0 (bs, 2B), -1.4 (s, 2B, BF₄), 3.4 (bs, 4B), 9.7 (bs, 2B), 13.9 (bs, 2B).

4.6. Synthesis of the arene-type complex $[(\text{Carb}')\text{Rh}(\mu\text{-}\eta^5\text{-}\eta^6\text{-C}_4\text{H}_4\text{BPh})\text{Ir}(\text{Carb}')](\text{BF}_4)_2$ (**8**(BF₄)₂)

A mixture of **2** (50 mg, 0.11 mmol), [(Carb')IrBr₂]₂ (62 mg, 0.06 mmol) and AgBF₄ · 3dioxane (104 mg, 0.23 mmol) in MeNO₂ (1.5 ml) was stirred for 2 h. The isolation of product was conducted similarly to **7**. Compound **8**(BF₄)₂ was obtained as an orange solid. Yield 97 mg (86%). Anal. Calc. for C₁₈H₄₀B₂₁F₈IrRhS₂: C, 21.73; H, 4.05; B, 22.82. Found: C, 21.54; H, 4.18; B, 22.66%. ¹¹B{¹H} NMR (nitromethane-*d*₃): $\delta = -25.1$ (bs, 2B), -16.7 (bs, 2B), -12.2 (bs, 4B), -6.9 (bs, 2B), -5.1 (bs, 2B), -2.2 (bs, 2B), -1.4 (s, 2B, BF₄⁻), 6.0 (bs, 2B), 14.2 (bs, 2B).

4.7. X-ray crystallography of **4**(BF₄)₂

Crystals of **4**(BF₄)₂ · 0.75CH₂Cl₂ were grown up by slow diffusion in two-layer system, petroleum ether and a solution of complex in CH₂Cl₂/MeNO₂.

Crystal data: C_{24.75}H_{41.50}B₁₂Cl_{1.50}F₈IrRhS (*M* = 1001.14), triclinic, space group *P* – 1, *a* = 12.913(2), *b* = 17.305(3), *c* = 19.590(3) Å, $\alpha = 114.948(3)$, $\beta = 103.483(3)$, $\gamma = 95.917(3)^\circ$, *V* = 3757.6(11) Å³, *Z* = 2, *D*_{calc} = 1.770 g cm⁻³, $\mu = 4.198$ mm⁻¹, *F*(000) = 1942, crystal size 0.30 × 0.40 × 0.60 mm.

X-ray diffraction experiment was carried out with a Bruker SMART 1000 CCD area detector, using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å, ω -scans with a 0.3° step in ω and 10 s per frame exposure, $2.17 < \theta < 27.00^\circ$) at 120 K. Low temperature of the crystal was maintained with a Cryostream (Oxford Cryosystems) open-flow N₂ gas cryostat. Reflection intensities were integrated using SAINT software [25] and absorption correction was applied semi-empirically using SADABS program (*T*_{max}/*T*_{min} = 0.862/0.160) [26]. The structure was solved by direct method and refined by the full-matrix least-squares technique against *F*² in anisotropic approximation for non-

hydrogen atoms. The hydrogen atoms of the BH groups were found in the difference Fourier synthesis. All H(C) atom positions were calculated. All hydrogen atoms were refined in isotropic approximation in riding model with the *U*_{iso}(H) parameters equal to 1.2*U*_{eq}(C_{*i*}) or 1.5*U*_{eq}(C_{*ii*}), where *U*(C_{*i*}) and *U*(C_{*ii*}) are respectively the equivalent thermal parameters of the methyne and methyl carbon atoms to which the corresponding H atoms are bonded. The refinement converged to *wR*₂ = 0.1113 and Goodness-of-fit = 0.926 for all independent reflections (*R*₁ = 0.0376 was calculated against *F* for 14,056 observed reflections with *I* > 2σ(*I*)). All calculations were performed using the SHELXTL software [27].

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Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 297161 for **4**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.05.014.

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