Metallacarboranes and triple-decker complexes with the (C₄Me₄)Pt fragment

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ABSTRACT

Complex Cb^*PtCl_2 ($Cb^* = \eta\text{-}C_4Me_4$) reacts with the carborane anions $[7,8\text{-}C_2B_9H_{11}]^{2-}$ and $[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ giving platinacarboranes $Cb^*Pt(\eta\text{-}7,8\text{-}C_2B_9H_{11})$ (**1**) and $[Cb^*Pt(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})]^+$ (**2**), respectively. Reactions of the $[Cb^*Pt]^{2+}$ fragment (as a labile nitromethane solvate) with the sandwich compounds $Cp^*Fe(\eta\text{-}C_5H_3Me_2BMe)$ and $Cp^*Rh(\eta^5\text{-}C_4H_4BPh)$ afford the triple-decker cations $[Cb^*Pt(\mu\text{-}\eta{:}\eta\text{-}C_5H_3Me_2BMe)FeCp^*]^{2+}$ (**3**) and $[Cb^*Pt(\mu\text{-}\eta^5{:}\eta^5\text{-}C_4H_4BPh)RhCp^*]^{2+}$ (**4**) with bridging boratabenzene and borole ligands. The structures of **1** and **3**$(CF_3SO_3)_2$ were determined by X-ray diffraction.

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1. Introduction

The fragments $[Cp^*M]^{2+}$ (M = Rh, Ir) are widely used in organometallic synthesis [1]. In particular, using these fragments a number of metallacarboranes [2–5] and triple-decker complexes [6–8] have been prepared. In contrast, chemistry of the related fragment $[Cb^*Pt]^{2+}$ ($Cb^* = \eta\text{-}C_4Me_4$) is notably less developed. In 1975, Canziani and Malatesta have described a two-step procedure for the preparation of the chloride complex Cb^*PtCl_2 from $(CO)_2PtCl_2$ and 2-butyne in 47% yield [9]. Moreto and Maitlis have synthesized this compound in 60% yield using more available acetonitrile complex $(MeCN)_2PtCl_2$ instead of $(CO)_2PtCl_2$ [10]. The chloride Cb^*PtCl_2 has been proven to be a useful synthon of the $[Cb^*Pt]^{2+}$ fragment [11]. In particular, Herberich et al. have synthesized the sandwich cations $[Cb^*PtCp]^+$ and $[Cb^*Pt(\eta\text{-}C_6Me_6)]^{2+}$ via the intermediate solvate complex $[Cb^*Pt(Me_2CO)_3]^{2+}$ [12]. Herein we report the synthesis and structures of the first Cb^*Pt-containing metallacarborane and triple-decker complexes.

2. Results and discussion

2.1. Synthesis

We found that reactions of Cb^*PtCl_2 with the carborane anions $[7,8\text{-}C_2B_9H_{11}]^{2-}$ and $[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ afford complexes **1**

(71%) and **2** (17%) (Scheme 1).[1] The low yield of **2** may be caused by a side demethylation of the SMe_2 group [13].
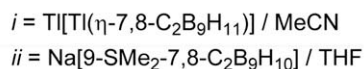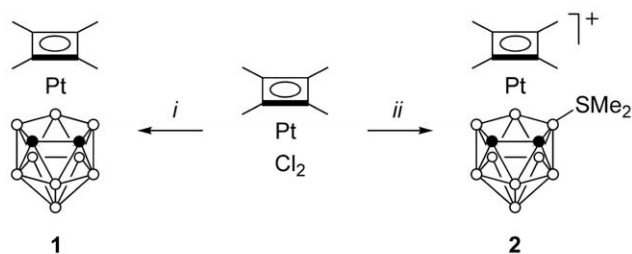
Electrophilic stacking of sandwich compounds with $[(\text{ring})M]^{n+}$ fragments is an effective method for the preparation of cationic triple-decker complexes [14]. In particular, complexes with bifacially-bonded boratabenzene [6,15] and borole [8,16] ligands have been prepared by this way. Using the stacking reaction of $Cp^*Fe(\eta\text{-}C_5H_3Me_2BMe)$ with the labile solvate $[Cb^*Pt(MeNO_2)_3]^{2+}$ we synthesized the μ-boratabenzene triple-decker complex **3** (17%) (Scheme 2). Similar reaction of $Cp^*Rh(\eta^5\text{-}C_4H_4BPh)$ affords the μ-borole cation **4** (64%). The low yield of **3** may be explained by easy oxidation of $Cp^*Fe(\eta\text{-}C_5H_3Me_2BMe)$ in contrast to $Cp^*Rh(\eta^5\text{-}C_4H_4BPh)$. The solvate complex $[Cb^*Pt(MeNO_2)_3]^{2+}$ was generated by treatment of Cb^*PtCl_2 with Ag^+ in nitromethane. It should be emphasized, that cations **3** and **4** are the first examples of stable Cb^*Pt-containing triple-decker complexes. Herberich et al. have described earlier the formation of the thermally unstable μ-cyclopentadienyl cation $[Cb^*Pt(\mu\text{-}\eta{:}\eta\text{-}Cp)FeCp^*]^{2+}$ which was detected only by ^1H NMR spectroscopy at 0 °C [14b]. Greater stability of triple-decker complexes with bridging boron heterocycles is a general tendency associated with favorable balance of donor and acceptor properties of these ligands.
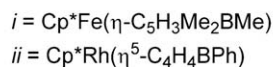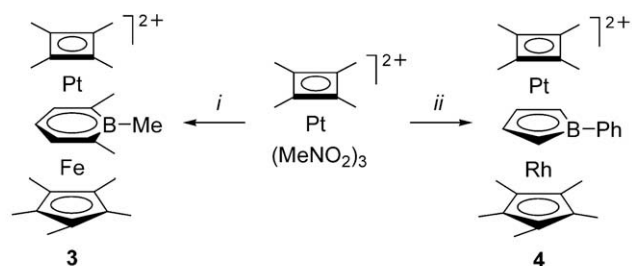
2.2. X-ray diffraction study

The structures of the metallacarborane complex **1** and the triple-decker cation **3** are shown in Figs. 1 and 2. Selected bond

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[1] All the cationic complexes described here were isolated as salts with the PF_6, BF_4, or CF_3SO_3 anions.

Scheme 1.

$i = \text{Tl}[\text{Tl}(\eta\text{-}7,8\text{-}C_2B_9H_{11})] / \text{MeCN}$
$ii = \text{Na}[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}] / \text{THF}$

Scheme 2.

$i = \text{Cp*Fe}(\eta\text{-}C_5H_3Me_2BMe)$
$ii = \text{Cp*Rh}(\eta^5\text{-}C_4H_4BPh)$

lengths and angles are given in Tables. 1 and 2. The dihedral angle between the C_4 and C_2B_3 planes in **1** is equal to 4.7°. In the case of **3** the crystallographic cell contains two independent molecules; data for only one of them will be used in further discussion. Cation **3** is formed by three cyclic frames (C_4, C_5B, and C_2B_3); the dihedral angle C_4/C_5B (6.3°) is somewhat larger than C_5B/C_5 (2.7°). We have shown earlier, that the metal-to-ring $Co \cdots C_4$ distance in Cb*Co complexes is strongly dependent on donor–acceptor ability of other ligands at the Co atom [17]. In contrast, the $Pt \cdots C_4$ distance
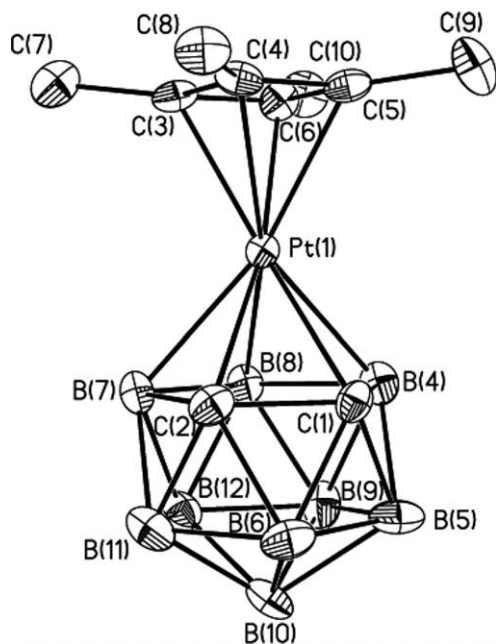

Fig. 1. Structure of complex **1**. Atoms are represented by 50% thermal ellipsoids.
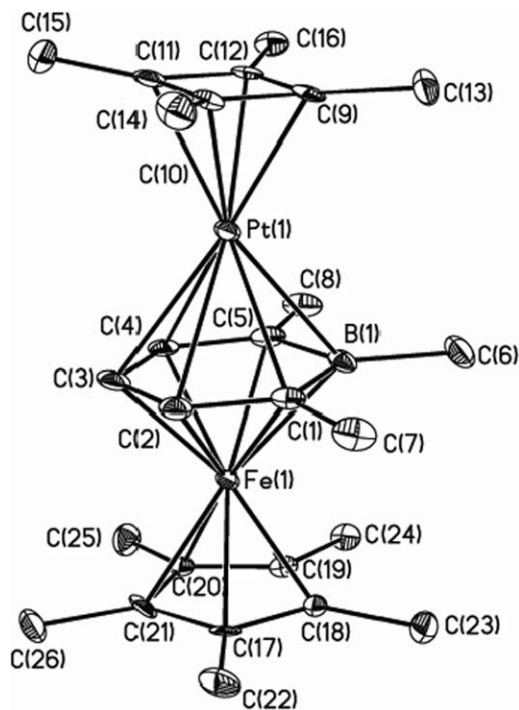

Fig. 2. Structure of cation **3**. Atoms are represented by 50% thermal ellipsoids.

Table 1
Selected bond lengths (Å) and angles (°) for compound **1**

Pt(1)–C(1)	2.246(6)	C(3)–C(4)	1.457(9)
Pt(1)–C(2)	2.247(7)	C(4)–C(5)	1.471(10)
Pt(1)–C(3)	2.108(6)	C(5)–C(6)	1.466(9)
Pt(1)–C(4)	2.188(6)	C(3)–C(6)	1.467(10)
Pt(1)–C(5)	2.160(7)	C(1)–C(2)	1.622(10)
Pt(1)–C(6)	2.099(7)	C(1)–B(4)	1.736(10)
Pt(1)–B(4)	2.219(8)	C(2)–B(7)	1.737(10)
Pt(1)–B(7)	2.240(8)	B(4)–B(8)	1.827(12)
Pt(1)–B(8)	2.226(7)	B(7)–B(8)	1.844(10)
C(3)–C(4)–C(5)	89.8(5)	C(2)–B(7)–B(8)	104.7(5)
C(4)–C(5)–C(6)	90.0(6)	B(7)–B(8)–B(4)	106.1(5)
C(5)–C(6)–C(3)	89.6(5)	B(8)–B(4)–C(1)	104.7(5)
C(6)–C(3)–C(4)	90.6(6)	B(4)–C(1)–C(2)	112.6(6)
C(1)–C(2)–B(7)	111.8(5)		

Table 2
Selected bond lengths (Å) and angles (°) for cation **3**

Pt(1)–C(1)	2.364(4), 2.392(4)	Fe(1)–C(17)	2.058(4), 2.073(4)
Pt(1)–C(2)	2.457(4), 2.475(4)	Fe(1)–C(18)	2.073(4), 2.071(4)
Pt(1)–C(3)	2.489(5), 2.483(5)	Fe(1)–C(19)	2.071(4), 2.062(4)
Pt(1)–C(4)	2.462(4), 2.418(4)	Fe(1)–C(20)	2.068(4), 2.068(4)
Pt(1)–C(5)	2.373(4), 2.326(4)	Fe(1)–C(21)	2.068(4), 2.074(5)
Pt(1)–B(1)	2.376(5), 2.373(5)	C(1)–C(2)	1.436(6), 1.450(6)
Pt(1)–C(9)	2.116(4), 2.109(4)	C(2)–C(3)	1.454(6), 1.443(6)
Pt(1)–C(10)	2.147(4), 2.130(4)	C(3)–C(4)	1.447(6), 1.452(6)
Pt(1)–C(11)	2.179(5), 2.176(5)	C(4)–C(5)	1.445(6), 1.428(6)
Pt(1)–C(12)	2.134(4), 2.125(4)	B(1)–C(1)	1.557(6), 1.547(7)
Fe(1)–C(1)	2.136(4), 2.146(4)	B(1)–C(5)	1.564(7), 1.573(6)
Fe(1)–C(2)	2.079(4), 2.088(4)	C(9)–C(10)	1.459(6), 1.462(6)
Fe(1)–C(3)	2.059(5), 2.060(5)	C(10)–C(11)	1.460(6), 1.456(6)
Fe(1)–C(4)	2.070(5), 2.079(4)	C(11)–C(12)	1.459(6), 1.443(6)
Fe(1)–C(5)	2.140(4), 2.139(4)	C(9)–C(12)	1.480(6), 1.460(6)
Fe(1)–B(1)	2.218(5), 2.219(5)		
C(1)–C(2)–C(3)	120.9(4), 121.0(4)	B(1)–C(1)–C(2)	122.5(4), 122.1(4)
C(2)–C(3)–C(4)	120.8(4), 120.9(4)	C(9)–C(10)–C(11)	90.9(4), 89.6(4)
C(3)–C(4)–C(5)	121.5(4), 121.2(4)	C(10)–C(11)–C(12)	89.9(4), 90.5(4)
C(4)–C(5)–B(1)	121.5(4), 122.0(4)	C(11)–C(12)–C(9)	90.1(3), 90.2(4)
C(1)–B(1)–C(5)	112.8(4), 112.8(4)	C(12)–C(9)–C(10)	89.1(4), 89.6(4)