

Article

Synthesis of Trithia-Borinane Complexes Stabilized in Diruthenium Core: $[(Cp^*Ru)_2(\eta^1-S)(\eta^1-CS)\{(CH_2)_2S_3BR\}]$ (R = H or SMe)

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Abstract: The thermolysis of *arachno-1* $[(Cp^*Ru)_2(B_3H_8)(CS_2H)]$ in the presence of tellurium powder yielded a series of ruthenium trithia-borinane complexes: $[(Cp^*Ru)_2(\eta^1-S)(\eta^1-CS)\{(CH_2)_2S_3BH\}]$ **2**, $[(Cp^*Ru)_2(\eta^1-S)(\eta^1-CS)\{(CH_2)_2S_3B(SMe)\}]$ **3**, and $[(Cp^*Ru)_2(\eta^1-S)(\eta^1-CS)\{(CH_2)_2S_3BH\}]$ **4**. Compounds **2–4** were considered as ruthenium trithia-borinane complexes, where the central six-membered ring $\{C_2BS_3\}$ adopted a boat conformation. Compounds **2–4** were similar to our recently reported ruthenium diborinane complex $[(Cp^*Ru)\{(\eta^2-SCHS)CH_2S_2(BH_2)_2\}]$. Unlike diborinane, where the central six-membered ring $\{CB_2S_3\}$ adopted a chair conformation, compounds **2–4** adopted a boat conformation. In an attempt to convert *arachno-1* into a *closo* or *nido* cluster, we pyrolyzed it in toluene. Interestingly, the reaction led to the isolation of a capped butterfly cluster, $[(Cp^*Ru)_2(B_3H_5)(CS_2H_2)]$ **5**. All the compounds were characterized by 1H , $^{11}B\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy and mass spectrometry. The molecular structures of complexes **2**, **3**, and **5** were also determined by single-crystal X-ray diffraction analysis.

Keywords: boron-containing heterocycles; thiolato ligand; borinane; metallaborane

1. Introduction

The mutually synergistic interactions between metals and organic ligands often generate compounds of fundamental and practical importance [1–6]. The structure and reactivity of metallaboranes, which features compounds with an M–B bond, is greatly influenced by transition metals as well as organic ligands [7–25]. Previous studies have been carried out to understand the ways in which metal and borane fragments can interact to generate novel geometries [1–4,16–25]. However, there is still little understanding of how a transition metal can be used to vary the chemistry of metallaborane compounds. In this regard, our group was actively involved in the synthesis of various electron-precise transition metal–boron complexes such as σ -borane [26–31], boryl [32,33], triply-bridged trimetallic borylene [34–38], diborane [39], B-agostic [26,27,40–42], and metallaboratrane [26,27,43,44] complexes using of different synthetic precursors. An important aspect is the incorporation of transition metals into the chemistry of p-block elements other than carbon [45–47]. The literature contains numerous examples for boron, but other elements illustrate the possibilities as well [48,49]. The chemistry of transition-metal complexes with main group elements, particularly with chalcogen ligands, are of substantial importance. The homo- and heterometallic sulfido complexes with a wide range of substrates are well-documented in the literature [50–53]. In contrast, thioborates are not regularly seen in the coordination sphere of transition metals, mostly due to the lack of synthetic routes. It is interesting to see how a change of metal or ligand plays an important role in determining the nature of the molecules (Chart 1).

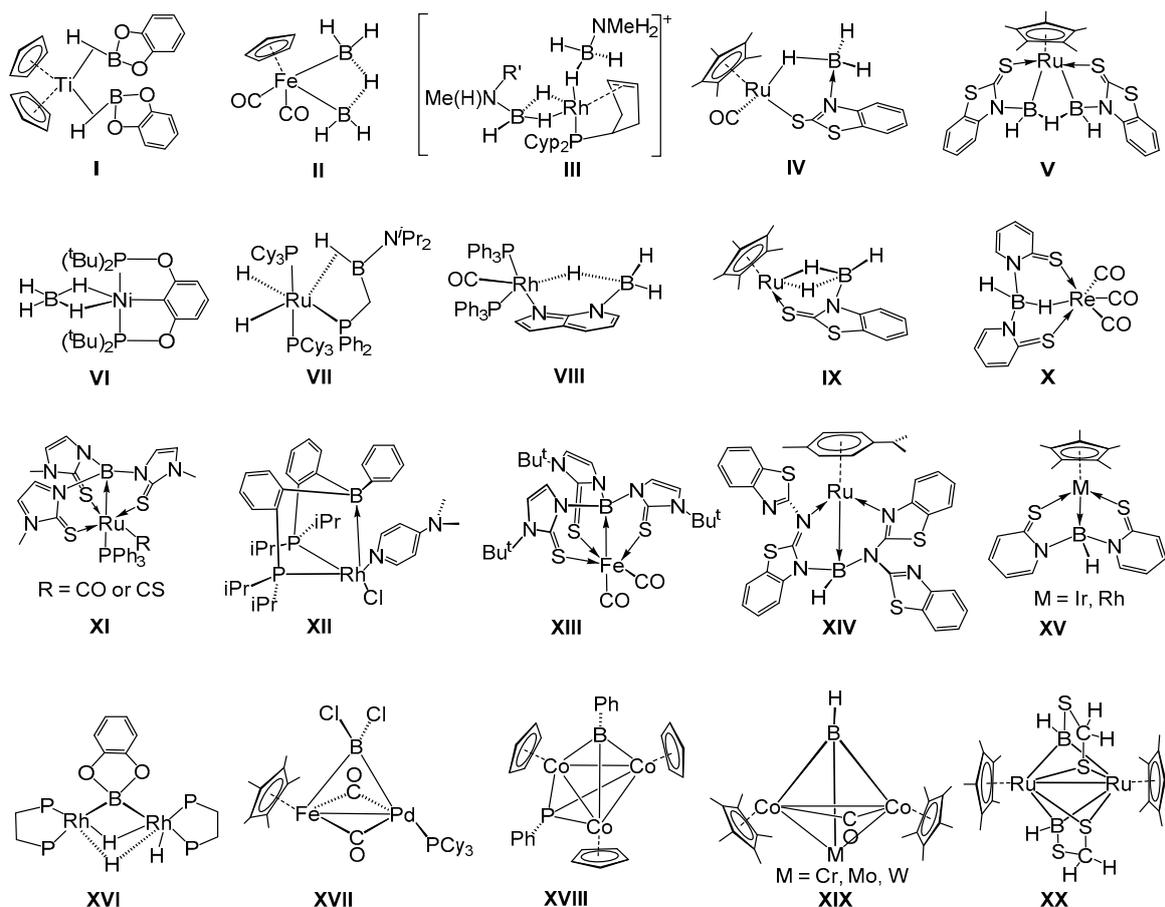


Chart 1. Change in the coordination modes of the molecules with a change in metal or ligand. I–V: borane, borate, and diborane; VI–X: borane, borate, and agostic; XI–XV: metallaboratrane; XVI–XX: boryl and borylene complexes.

Several research groups have explored this idea, which has led to the isolation of unique molecules with interesting bonding interactions [1,54–65]. Here, we have tried to provide a quick overview of several such examples reported by us and others [26,54–65]. Hartwig in 1996 reported the first example of a σ -borane metal complex, **I**, from the reaction of catecholborane and dimethyl titanocene [1]. Following this, several research groups were successful in isolating σ -borane/borate complexes [54–56]. Weller and colleagues synthesized a novel bis(σ -amine–borane) complex of rhodium through the displacement of a labile fluoroarene ligand from $[\text{Rh}(\eta^6\text{-C}_6\text{H}_5\text{F})\{\text{P}(\text{C}_5\text{H}_9)_2(\eta^2\text{-C}_5\text{H}_7)\}][\text{BArF}_4]$ [54]. Inspired by this, our group recently reported a σ -borane complex of ruthenium from the reaction of ruthenium bis(σ)borate and $[\text{Mn}_2(\text{CO})_{10}]$ [26,27]. The first metalladiborane $[(\eta^5\text{-C}_5\text{H}_8)\text{Fe}(\text{CO})_2(\eta^2\text{-B}_2\text{H}_5)]$, **II**, was structurally characterized by Shore in 1989 [57,58]. We recently reported a ruthenium diborane, a derivative of diborane(6) from the reaction of $[(\text{Cp}^*\text{Ru})_2\text{B}_3\text{H}_9]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) and 2-mercaptobenzothiazole [26]. Sabo-Etienne and colleagues have recently shown the formation of a ruthenium agostic complex $[\text{RuH}_2\{\eta^2\text{-H-B}(\text{N}^i\text{Pr}_2)\text{-CH}_2\text{PPh}_2\}(\text{PCy}_3)_2]$, **VII**, by treating phosphinomethyl(amino)borane $[\text{Ph}_2\text{PCH}_2\text{BHN}^i\text{Pr}_2]$ and $[\text{RuH}_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]$ [59]. The reaction of $\text{Na}[(\text{H}_2\text{B})\text{mp}_2]$ ($\text{mp} = 2\text{-mercaptopyridyl}$) and $[\text{Re}_2\text{CO}_{10}]$ enabled us to isolate an agostic complex of rhenium, $[\text{Re}(\text{CO})_3(\mu\text{-H})\text{BH}(\text{C}_5\text{H}_4\text{NS})_2]$, **X** [27]. Hill and colleagues established how scorpionate ligands can be utilized for the formation of complexes that have a direct metal boron bond through the isolation of the first metallaboratrane, $[\text{M}(\text{CO})(\text{PPh}_3)[\text{B}(\text{mt})_3]](\text{M} \rightarrow \text{B})$ ($\text{mt} = \text{methimazolyl}$, $\text{M} = \text{Ru}$ and Os) in 1999 [60]. Following this, Bourissou and Parkin synthesized a Rh^{I} metallaboratrane [61], **XII**, and a ferraboratrane $[\{k^4\text{-B}(\text{mim}^{\text{tBu}})_3\}\text{Fe}(\text{CO})_2]$ ($\text{mim}^{\text{tBu}} = 2\text{-mercapto-1-tert-butylimidazolyl}$) [62], **XIII**, respectively. We successfully isolated a ruthenaboratrane by using $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$ as a

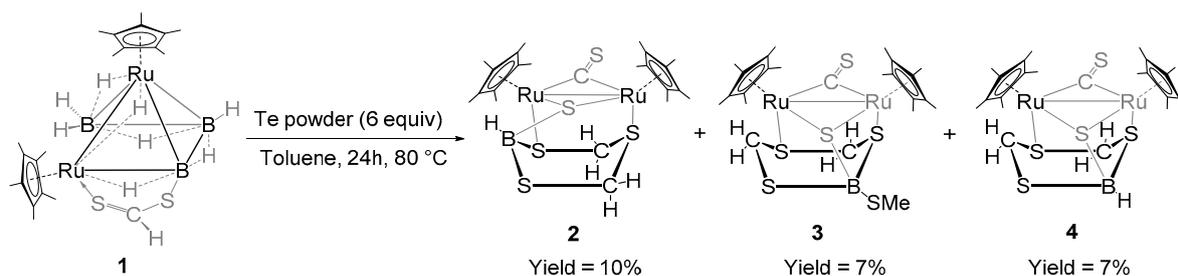
precursor **XIV** [43], whereas a rhoda/irida boratrane, $[\text{Cp}^*\text{M}(\text{BHL}_2)]$, ($\text{L} = \text{C}_5\text{H}_4\text{NS}$, $\text{M} = \text{Rh}$ or Ir) [43], **XV**, could be synthesized from the reaction of $[\text{Cp}^*\text{MCl}_2]_2$ with $\text{Na}[\text{H}_2\text{B}(\text{mp})_2]$. Marder and colleagues synthesized metal-bridged-boryl complexes by using catecholborane [63]. In 2005, Braunschweig reported a heterometallic Fe–Pd bridged-boryl complex from the reaction of $[\text{Cp}^*\text{Fe}(\text{CO})_2\text{BCl}_2]$ and $[\text{Pd}(\text{Cy}_3)_2]$ [64]. Later, our group successfully synthesized a homometallic ruthenium bridged-boryl complex from the reaction of HBCat (catecholborane, $\text{cat} = 1,2\text{-O}_2\text{C}_6\text{H}_4$) and $[\{\text{Ru}(\text{CO})\}_2\text{B}_2\text{H}_6]$ [32]. Following this, we recently reported a bis(bridging-boryl) complex, $[\{\text{Cp}^*\text{Ru}(\mu, \eta^2\text{-HBS}_2\text{CH}_2)_2\}]_2$, from the thermolysis of $[\text{Cp}^*\text{Ru}(\mu\text{-H})_2\text{BH}(\text{S-CH}=\text{S})]$ with chalcogen powder [33]. Fehlner and colleagues reported a homometallic bridging borylene complex **XVIII** [65] from the reaction of $[\text{CpCo}(\text{PPh}_3)_2]$ and $\text{BH}_3 \cdot \text{THF}$. Our group was successful in synthesizing heterometallic triply bridged borylene complexes $[\{\text{Cp}^*\text{Co}\}_2(\mu_3\text{-BH})(\mu\text{-CO})\{\text{M}(\text{CO})_5\}]$ ($\text{M} = \text{W}, \text{Mo}, \text{Cr}$) from the reaction of $[\{\text{Cp}^*\text{CoCl}\}_2]$ and $\text{LiBH}_4 \cdot \text{THF}$ with $[\text{M}(\text{CO})_3(\text{MeCN})_3]$ [34–38].

Ligands such as COS , CS_2 , and CO_2 interact with transition metal complexes, showing a wide range of chemical transformations, such as insertion, dimerization, disproportionation, coupling, and catalytic reactions [66–68]. On the basis of the general concern of the electron donating/accepting properties of CS_2 and CO_2 , various binding modes with one or more metal atoms have been recognized [69]. However, reactivities of these ligands towards polyhedral metallaborane clusters have been sparsely explored [70–74]. In this context, Fehlner and colleagues described the reactivity of CS_2 with an unsaturated chromaborane cluster $[(\text{Cp}^*\text{Cr})_2\text{B}_4\text{H}_8]$, which underwent metal-assisted hydroboration and successively converted to a methanedithiolato ligand [71]. Following this, our group reported the reaction of CS_2 with *nido*- $[(\text{Cp}^*\text{Ru})_2(\mu\text{-H})_2\text{B}_3\text{H}_7]$, which subsequently transformed into $[(\text{Cp}^*\text{Ru})_2(\text{B}_3\text{H}_8)(\text{CS}_2\text{H})]$, **1**, containing a dithioformato ligand (CHS_2) [69]. Recently, we reported for the first time a ruthenium trithia-diborinane complex, 1-thioformyl-2,6-tetrahydro-1,3,5-trithia-2,6-diborinane $[(\text{Cp}^*\text{Ru})\{\eta^2\text{-SCHS}\}\text{CH}_2\text{S}_2(\text{BH}_2)_2]$, from the reaction of $[\{\text{Cp}^*\text{RuCl}(\mu\text{-Cl})\}_2]$ and $\text{Na}[\text{BH}_3(\text{SCHS})]$ [33]. Encouraged by these results, we became interested in exploring the reactivity of **1** under different reaction conditions, especially with heavier chalcogen ligands. Thus, we performed the reaction of **1** in the presence of chalcogen powder. As expected, the reaction enabled us to isolate some interesting ruthenium trithia-borinane complexes.

2. Results and Discussion

Synthesis of Ruthenium Borinane Complexes, 2–4

As shown in Scheme 1, the pyrolysis of **1** in the presence of tellurium powder in toluene yielded compounds **2–4** along with compounds $[\{\text{Cp}^*\text{Ru}(\mu, \eta^3\text{-SCHS})\}_2]$ and $[\text{Cp}^*\text{Ru}(\mu\text{-H})_2\text{BH}(\text{SCHS})]$ [33]. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectra at room temperature display single resonance at $\delta = -4.1, 7.4,$ and 4.9 ppm for compounds **2, 3,** and **4**, respectively, indicating the presence of a single boron atom. While the ^1H NMR spectrum of compounds **2** and **4** shows the presence of a terminal B–H proton at $\delta = 3.75$ and 2.58 ppm, respectively, compound **3** does not show any indication of a B–H terminal. Instead, it shows a resonance at $\delta = 2.06$ ppm, indicating the presence of a (SCH_3) unit. Apart from that, both **2** and **3** display resonances in the region $\delta = 3.96\text{--}1.69$ ppm, which may be attributed to the presence of methylene protons. Both compounds display signals for two sets of Cp^* protons around 1.79 and 1.72 ppm in a 1:1 ratio. The presence of the Cp^* ligands, methylene, and SCH_3 units are also supported by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. Apart from that, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra also show a resonance at $\delta = 288.6$ and 285.8 ppm, indicating the presence of a C=S group in the molecules of **2** and **3** respectively. Furthermore, the mass spectra show molecular ion peaks (ESI^+) at $m/z = 686.9603, 732.9479,$ and 686.9604 for compounds **2, 3,** and **4** respectively. Although we isolated the majority of Te powder after workup, we are not in a position to comment on the exact role of chalcogen powder, in particular Te powder, in the formation of complexes **2–4** from **1**.



Scheme 1. Reaction of $[(Cp^*Ru)_2(B_3H_8)(CS_2H)]$, **1**, in the presence of tellurium powder.

The single-crystal X-ray diffraction study disclosed the core geometry (C_2S_3B ring) of compounds **2** and **3** to be very similar to each other (Figure 1a,b). The only difference between the two is the position of the boron atom in the central six-membered ring $\{C_2S_3B\}$. Compounds **2** and **3** can be called as 1,3,5-trithia-4-borinane and 1,3,5-trithia-2-borinane complexes of ruthenium, respectively, which is similar to our recently reported diborinane $[(Cp^*Ru)\{\eta^2-SCHS\}CH_2S_2(BH_2)_2]$ [33]. Unlike diborinane, compounds **2** and **3** have only one boron atom in the six-membered ring $\{C_2S_3B\}$ and are the monoborane derivatives of $[(Cp^*Ru)\{\eta^2-SCHS\}CH_2S_2(BH_2)_2]$. While the central six-membered ring adopts a chair conformation in diborinane [33], **2** and **3** adopt a boat conformation. A significant difference between **2** and **3** is the presence of the $\{SMe\}$ moiety instead of a terminal hydrogen attached to the boron atom in compound **3**. The B–S bond length (av. 1.921 Å) in **2** and **3** is within the B–S single bond distance and is in accord with the ruthenium diborinane complex [33]. One of the interesting features observed in these molecules is the presence of the thioformyl unit bonded to the ruthenium atoms. While the diborinane has only one ruthenium atom, compounds **2** and **3** have two ruthenium atoms bridged by one thiocarbonyl unit on one side and B–S on the other side. The C–S distance in the thiocarbonyl unit (1.612(15) Å in **2** and 1.617(7) Å in **3**) is found to be shorter than that of **1**. The Ru1–Ru2 distances of 2.759(6) Å in **2** and 2.759(6) Å in **3** are significantly shorter when compared to **1**, but are well within the reported Ru–Ru single bond distance [69]. The ruthenium atoms are connected to two sulfur atoms S2 and S4 present in the (C_2S_3B) ring and the bridging sulfur is connected to the ring boron atom B1. Although we failed to crystallize compound **4**, it was characterized in comparison to its spectroscopic data with **2** and **3**. Based on the spectroscopic data, compound **4** is expected to have a structure similar to that of compound **3** where instead of the SMe group, a terminal H is attached to the B atom (Scheme 1).

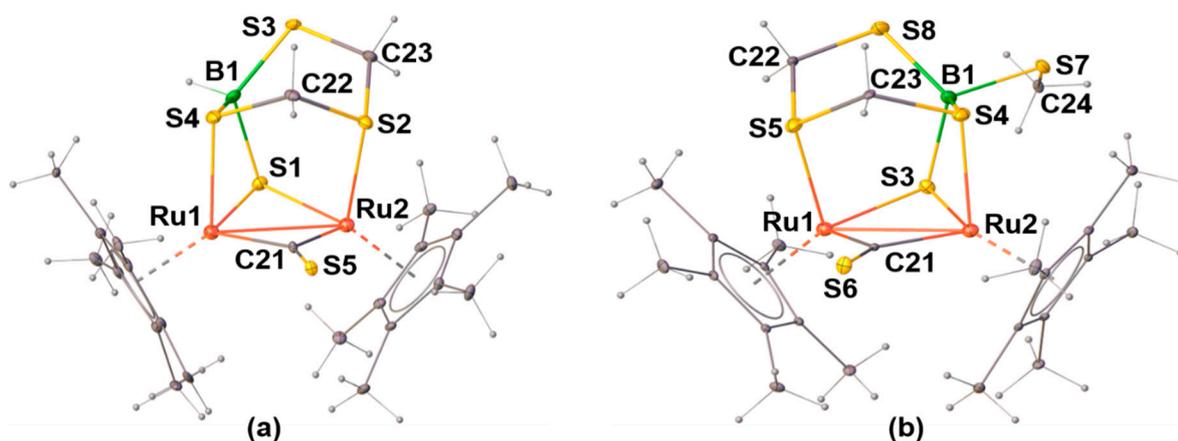
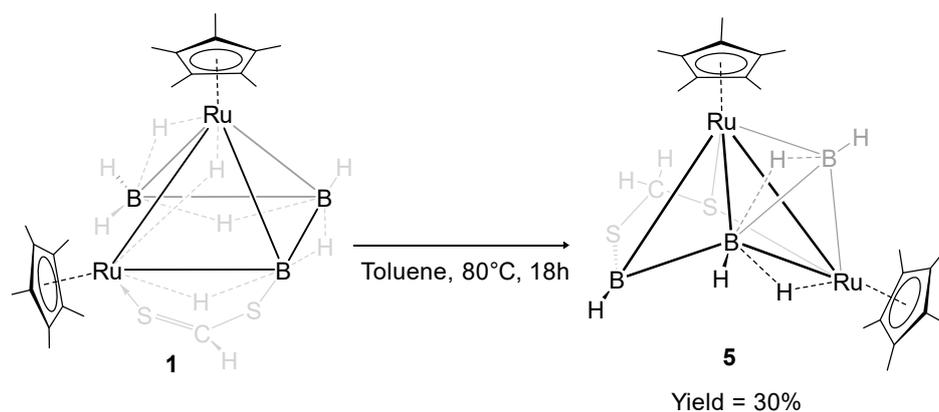


Figure 1. Molecular structures and labelling diagrams of **2** (a) and **3** (b). Selected bond lengths (Å) and angles ($^\circ$): **2**: B1–S3 1.885(8), S1–Ru1 2.3436(14), Ru1–Ru2 2.7590(6), C21–S5 1.612(5), C23–S3 1.789(6), C23–S2 1.826(5); Ru1–C21–Ru2 86.75(18), S3–C23–S2 118.4(3), S3–B1–S1 119.0(4), Ru1–S1–Ru2 72.36(4). **3**: B1–S3 1.922(8), B1–S8 1.879(8), B1–S4 1.968(9), Ru2–S3 2.3364(17), Ru1–Ru2 2.7590(7), C21–S6 1.617(7), C22–S8 1.803(7), C22–S5 1.802(7); Ru2–C21–Ru1 87.2(3), S8–B1–S3 119.7(4), S8–B1–S4 112.5(5), S3–B1–S4 98.9(4), Ru1–S3–Ru2 72.44(5).

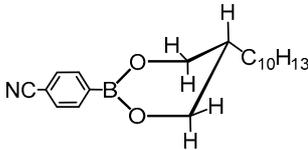
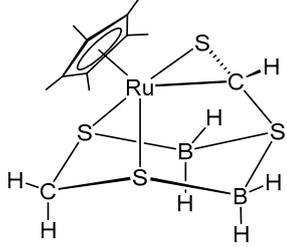
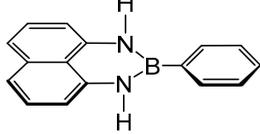
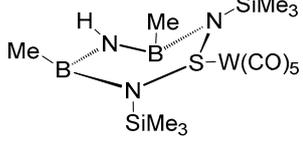
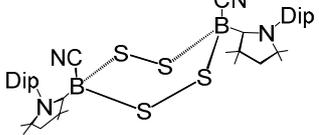
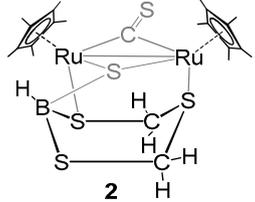
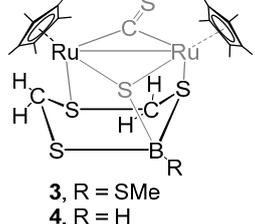
The six-membered ring containing a $\{C_2BS_3\}$ moiety adopts a boat conformation, similar to the reported diborinanes, such as bis(cAAC)-stabilized 3,6-dicyano-1,2,4,5-tetrasulfa-3,6-diborinane reported by Braunschweig et al. where the central $\{B_2S_4\}$ ring displayed a boat conformation and was the first example of a structurally and NMR-spectroscopically characterized $\{B_2S_4\}$ -heterocycle [75]. Meller et al. reported the synthesis and characterization of a diborinane-tungsten adduct, $[(BMe)_2(NH)\{N(SiMe_3)_2(S)\{W(CO)_5\}]]$ [76]. In contrast, the structurally characterized dioxaborinane, $[CN(C_6H_5)(BO_2C_3H_5)(C_6H_4)(C_4H_9)]$, adopted the half-chair conformation [77]. Recently, our group reported for the first time a trithia-diborinane stabilized ruthenium complex, $[(Cp^*Ru)\{\eta^2-SCHS\}CH_2S_2(BH_2)_2]$ [33]. Although some examples of trithia-diborinane compounds have been reported, there are no examples of metal complexes of such trithia-diborinane species except the one reported by us [33]. Compounds **2–4** are the monoborinane derivatives, and are a novel entry to the class of transition metal borinane complexes. The few structurally characterized borinane and diborinane derivatives are listed in Table 1.

In order to check whether *arachno*- $[(Cp^*Ru)_2(B_3H_8)(CS_2H)]$, **1**, can be converted to a *nido* or *closo* geometry with the release of hydrogen, we pyrolyzed **1**. Interestingly, the reaction led to the formation of **5** having a capped butterfly geometry, instead of a *nido* or *closo* geometry (Scheme 2). The mass spectrometry of the new compound gives a molecular ion peak at $m/z = 613.0588$ that corresponds to $C_{21}H_{37}Ru_2B_3S_2Na$. The room-temperature $^{11}B\{^1H\}$ NMR spectrum of **5** rationalizes the presence of two boron environments, which appear at $\delta = 43.6$ and -24.1 ppm. Besides the BH terminal protons, one B–H–B and one Ru–H–B proton is observed in the 1H NMR spectrum. Furthermore, the 1H NMR spectrum implies the presence of two equivalent Cp^* ligands in **5**.



Scheme 2. Thermolysis of $[(Cp^*Ru)_2(B_3H_8)(CS_2H)]$, **1**.

Table 1. Selected structural and spectroscopic data of borinane derivatives and complexes [33,75–78].

Entry	^{11}B NMR (ppm) ^a	$d_{\text{av}}[\text{B-E}]$ ^b [Å]	Conformations ^c
	8.3 ^d	1.352	half chair
	−5.0 and −15.6	1.915	chair
	f	1.414	planar
	37.6	1.433	boat
	−11.2 ^e	1.943	boat
	−4.1	1.919	boat
	7.3 (3) 4.9 (4)	1.923 f	Boat f
3, R = SMe 4, R = H			

^a NMR spectra were recorded in a CDCl_3 solvent unless stated. ^b E = hetero atom in the central ring. ^c conformation of the central six-membered ring. ^d In $[\text{D}_6]$ -acetone. ^e In CD_2Cl_2 . ^f Data not available.

The identity of **5** is confirmed by its solid-state X-ray crystal analysis. The asymmetric unit of **5** contains two independent molecules and the structural data presented here are from one of the units (Figure 2). In one of the units, the B5–B4–B3–S4–C43–S3 moiety is disordered over two positions with occupancy factors 0.602 and 0.398. As shown in Figure 2, the molecular structure of **5** can be viewed as a capped butterfly cluster, where one of the triangular faces (Ru1–B2–Ru2) is capped by a BH fragment (B1 in Figure 2). The Ru1–Ru2 distance in **5** is shorter than that observed

in **1** by 0.258 Å. While the Ru–B distances in both **1** and **5** is comparable, the B–B distances show considerable variation. It is worth noting that the B1–B2 bond distance of 1.679(11) Å in **5** is shorter than the normal B–B single bond, but it is comparable to that of a manganese hexahydridodiborate complex $[\{(\text{OC})_4\text{Mn}\}(\eta^6\text{-B}_2\text{H}_6)\{\text{Mn}(\text{CO})_3\}_2(\mu\text{-H})]$ [39]. The interatomic separation between B3 and S1 (3.029 Å) is significantly longer for the formation of a direct B–S bond, and is bridged via the {S–CH₂} unit. With seven-skeletal-electron-pairs (sep), compound **5** satisfies the electron count for a BH capped *arachno*-butterfly structure. By the fused polyhedral model of Mingos [79–82], **5** should have 44 electrons [Ru_2B_2 (butterfly); $42 + \text{Ru}_2\text{B}_2$ (tetrahedron); $40 - \text{Ru}_2\text{B}$ (face); 38], which is also supported by the cve count of 44 electrons [$2 (\text{Cp}^*\text{Ru}) \times 13 + 1 (\mu_2\text{-S}) \times 1 + 1 \times (\mu_3\text{-S}) \times 3 + 3 (\text{BH}) \times 4 + 2 (\text{H}) \times 1$]. Compound **5** thus obeys the Wade–Mingos rule for an *arachno* system [79–82].

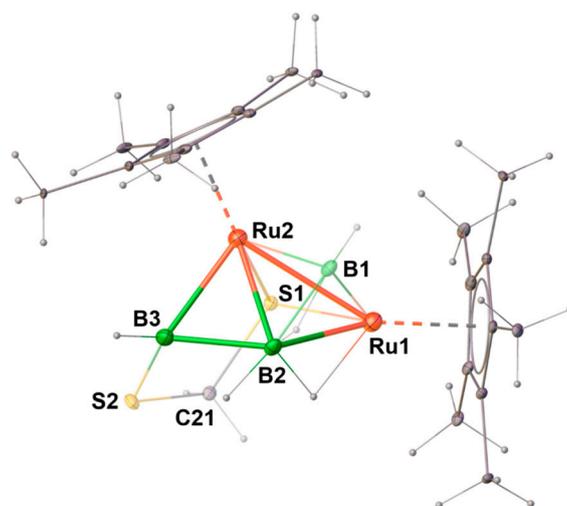


Figure 2. Molecular structure and labelling diagram of **5**: B1–B2 1.679(11), B1–Ru2 2.098(7), B1–Ru1 2.116(7), B2–Ru2 2.174(6), B2–Ru1 2.231(7), S1–Ru2 2.3017(15), S1–Ru1 2.3035(15), Ru1–Ru2 2.7157(6); Ru2–B1–Ru1 80.2(2), Ru2–B2–Ru1 76.1(2), B1–Ru1–S1 103.2(2), B2–Ru1–S1 83.16(19), B1–Ru1–Ru2 49.59(19), B2–Ru1–Ru2 50.98(16).

3. Materials and Methods

3.1. General Procedures and Instrumentation

All manipulations were conducted under an Ar/N₂ atmosphere using standard Schlenk techniques or glove box techniques. The solvents were distilled prior to use under argon. Compound *arachno*-**1** was prepared according to the literature method [69], while other chemicals were obtained commercially and used as received. The external reference $[\text{Bu}_4\text{N}][\text{B}_3\text{H}_8]$ for the ¹¹B NMR was synthesized with the literature method [83]. Preparative thin layer chromatography was performed with Merck 105554 silica-gel TLC plates (Merck, Darmstadt, Germany). The NMR spectra were recorded on a 400 or 500 MHz Bruker FT-NMR spectrometer (Bruker, Billerica, MA, USA). Residual solvent protons were used as reference (δ , ppm CDCl₃, 7.26), while a sealed tube containing $[\text{Bu}_4\text{N}(\text{B}_3\text{H}_8)]$ in [d₆]-benzene (δ_{B} , ppm, −30.07) was used as an external reference for the ¹¹B NMR. The FT-IR spectrum was recorded using a Jasco FT/IR-4100 spectrometer (JASCO, Easton, MD, USA). The HRMS (ESI) spectra were obtained using a Bruker Micro TOF-II instrument (Bruker, Billerica, MA, USA). Note that all the reported compounds were isolated by the preparative thin layer chromatographic technique (TLC), using silica-gel-coated aluminum TLC plates. The impure reaction mixture was slowly loaded on the TLC and eluted by using the hexane/CH₂Cl₂ mixture in inert atmosphere. Elution with the particular solvent mixture allowed us to separate the compounds in pure form.

3.2. Synthesis

3.2.1. Synthesis of Compounds 2, 3, and 4

In a flame-dried Schlenk tube, compound **1** (0.1 g, 0.169 mmol) was suspended in toluene (20 mL), and Te powder (0.58 g, 0.97 mmol) was added. The reaction mixture was stirred for 24 h at 80 °C. The solvent was evaporated in vacuum, then the residue was extracted into hexane/CH₂Cl₂ (60:40 *v/v*) and passed through Celite. After the removal of the solvent from the filtrate, the residue was subjected to chromatographic workup using silica-gel TLC plates. Elution with hexane/CH₂Cl₂ (60:40 *v/v*) yielded pink solid **2** (0.012 g, 10%), pink solid **3** (0.009 g, 7%), and pink solid **4** (0.008 g, 7%) along with the compounds [(Cp**Ru*(μ,η³-SCHS))₂] (0.002 g, 2%) and [Cp**Ru*(μ-H)₂BH(SCHS)] (0.003 g, 4%).

2: HR-MS (ESI+) calcd. for C₂₃H₃₆S₅BRu₂⁺ [M + H]⁺ *m/z* 686.9601, found 686.9603; ¹¹B{¹H} NMR (160 MHz, CDCl₃, 22 °C): δ = −4.1 ppm (br, 1B); ¹H NMR (500 MHz, CDCl₃, 22 °C): δ = 3.81, 2.94, 2.01, 1.70 (d, 4H, CH₂S₂), 3.75 (br, 1H, BH_t), 1.74, 1.72 (s, 30H, 2 × Cp*); ¹³C{¹H} NMR (125 MHz, CDCl₃, 22 °C): δ = 288.6 (s, CS), 96.5, 96.4 (s, C₅Me₅), 28.7, 11.8 (s, CH₂S₂), 9.8, 9.4 ppm (s, C₅Me₅); IR (CH₂Cl₂): $\tilde{\nu}$ = 2494 (BH_t), 1089 cm^{−1} (μ-CS).

3: HR-MS (ESI+) calcd for C₂₄H₃₈BS₆Ru₂⁺ [M + H]⁺ *m/z* 732.9478, found 732.9479; ¹¹B{¹H} NMR (160 MHz, CDCl₃, 22 °C): δ = 7.4 ppm (br, 1B); ¹H NMR (500 MHz, CDCl₃, 22 °C): δ = 3.97, 3.17, 2.19, 1.82 (d, 4H, CH₂S₂), 2.05 (s, 3H, SCH₃), 1.79, 1.73 (s, 30H, 2 × Cp*); ¹³C{¹H} NMR (125 MHz, CDCl₃, 22 °C): δ = 285.8 (s, CS), 97.3, 96.5 (s, C₅Me₅), 35.3, 17.1 (s, CH₂S₂), 12.7 (s, SCH₃), 10.1, 9.4 ppm (s, C₅Me₅); IR (CH₂Cl₂): $\tilde{\nu}$ = 1085 cm^{−1} (μ-CS).

4: HR-MS (ESI+) calcd for C₂₃H₃₆BS₅Ru₂⁺ [M + H]⁺ *m/z* 686.9601, found 686.9604; ¹¹B{¹H} NMR (160 MHz, CDCl₃, 22 °C): δ = 4.9 ppm (br, 1B); ¹H NMR (500 MHz, CDCl₃, 22 °C): δ = 3.93, 3.17, 2.20, 1.76 (d, 4H, CH₂S₂), 2.58 (br, 1H, BH_t), 1.80, 1.73 (s, 30H, 2 × Cp*); ¹³C{¹H} NMR (125 MHz, CDCl₃, 22 °C): δ = 97.3, 96.5 (s, C₅Me₅), 35.3, 17.1 (s, CH₂S₂), 10.1, 9.4 ppm (s, C₅Me₅); IR (CH₂Cl₂): $\tilde{\nu}$ = 2383 cm^{−1} (BH_t), 1081 cm^{−1} (μ-CS).

3.2.2. Synthesis of Compound 5

In a flame-dried Schlenk tube, compound **1** (0.1 g, 0.169 mmol) was suspended in toluene (20 mL), and was stirred at 80 °C for 18 h. The solvent was evaporated in vacuum, and the residue was extracted into hexane/CH₂Cl₂ (70:30 *v/v*) and passed through Celite. After the removal of the solvent from the filtrate, the residue was subjected to chromatographic workup using silica-gel TLC plates. Elution with hexane/CH₂Cl₂ (70:30 *v/v*) yielded orange **5** (0.030 g, 30%).

5: HR-MS (ESI+) calcd for C₂₁H₃₇B₃NaS₂Ru₂⁺ [M + Na]⁺ *m/z* 613.0601, found 613.0588; ¹¹B{¹H} NMR (160 MHz, CDCl₃, 22 °C): δ = 43.6, −24.1 ppm (br, 2B); ¹H NMR (500 MHz, CDCl₃, 22 °C): δ = 5.09 (br, 3H, BH_t) 3.89, 2.94 (d, 2H, CH₂S₂), 1.86, 1.81 (s, 30H, 2 × Cp*), −2.08 (br, 1H, B–H–B), −13.41 (br, 1H, Ru–H–B); ¹³C{¹H} NMR (125 MHz, CDCl₃, 22 °C): δ = 95.8, 92.2 (s, C₅Me₅), 41.1 (s, CH₂S₂), 11.7, 11.1 ppm (s, C₅Me₅); IR (CH₂Cl₂): $\tilde{\nu}$ = 2450 (BH_t), 2046 (Ru–H–B).

3.3. X-ray Crystallography

The crystal data for compounds **2**, **3**, and **5** were collected and integrated using a Bruker APEX II CCD diffractometer (Bruker, Billerica, MA, USA), with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation at 296 K (**2** and **3**) and 293 K (**5**). The structures were solved by heavy atom methods using SHELXS-97 [84] and refined using SHELXL-2013 for compound **2** and SHELXL-2014 [85] for compound **3**. The structure of compound **5** was solved by heavy atom method using SIR-92 [86] and SHELXL-2014. The crystallographic data were deposited at the Cambridge Crystallographic Data Centre as Supplementary Materials no. CCDC-1856640 (**2**), CCDC-1828322 (**3**), and CCDC-1407806 (**5**). These data can be obtained free-of-charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for compound (**2**): C₂₃H₃₅BRu₂S₅, *M_r* = 684.76, monoclinic, space group C2/*c*, *a* = 31.732(2) Å, *b* = 10.7145(7) Å, *c* = 17.6302(14) Å, β = 116.019(3), *V* = 5386.5(7) Å³, *Z* = 8, ρ_{calcd} = 1.689 g

cm^{-3} , $\mu = 1.520 \text{ mm}^{-1}$, $F(000) = 2768$, $R_1 = 0.0409$, $wR_2 = 0.0772$, 3120 independent reflections [$\theta \leq 24.999^\circ$] and 283 parameters.

Crystal data for compound (3): $\text{C}_{24}\text{H}_{37}\text{BRu}_2\text{S}_6$, $M_r = 730.84$, orthorhombic, space group $Pbcn$, $a = 34.1570(11) \text{ \AA}$, $b = 8.5558(3) \text{ \AA}$, $c = 19.8431(8) \text{ \AA}$, $V = 5799.0(4) \text{ \AA}^3$, $Z = 8$, $\rho_{\text{calcd}} = 1.674 \text{ g cm}^{-3}$, $\mu = 1.487 \text{ mm}^{-1}$, $F(000) = 2960$, $R_1 = 0.0457$, $wR_2 = 0.0884$, 2850 independent reflections [$\theta \leq 24.93^\circ$] and 309 parameters.

Crystal data for compound (5): $\text{C}_{21}\text{H}_{37}\text{B}_3\text{Ru}_2\text{S}_2$, $M_r = 588.19$, monoclinic, space group $P2_1/n$, $a = 8.5681(2) \text{ \AA}$, $b = 39.1432(9) \text{ \AA}$, $c = 15.1808(3) \text{ \AA}$, $\beta = 95.9220(10)$, $V = 5064.21(19) \text{ \AA}^3$, $Z = 8$, $\rho_{\text{calcd}} = 1.543 \text{ g cm}^{-3}$, $\mu = 1.363 \text{ mm}^{-1}$, $F(000) = 2384$, $R_1 = 0.0420$, $wR_2 = 0.1018$, 6613 independent reflections [$\theta \leq 23.02^\circ$] and 580 parameters.

4. Conclusions

The present work describes the synthesis of various borinane complexes of a group-8 heavier transition metal (i.e., ruthenium) from a dithioformato stabilized *arachno*-diruthenium pentaborane cluster. The new molecules have similar structures, but they differ in terms of the boron atom's position in the central six-membered ring $\{\text{C}_2\text{S}_3\text{B}\}$. With a single boron atom in the six-membered ring $\{\text{C}_2\text{S}_3\text{B}\}$, these mono-borinanes can be called 1,3,5-trithia-4-borinane and 1,3,5-trithia-2-borinane complexes of ruthenium. In all the mono-borinane complexes, the six-membered ring $\{\text{C}_2\text{BS}_3\}$ adopt a boat confirmation, which is in contrast to our previously reported trithia-diborinane complexes of ruthenium, $[(\text{Cp}^*\text{Ru})\{\eta^2\text{-SCHS}\}\text{CH}_2\text{S}_2(\text{BH}_2)_2]$, which adopt a chair conformation. The method reported in this article describing the synthesis of trithia-borinane complexes is unique and may be further utilized to introduce one or more boron atoms to the six-membered ring $\{\text{C}_2\text{BS}_3\}$. The isolation of these complexes opens up a gateway for the synthesis of early and late transition metal trithia-borinane complexes. Furthermore, in an attempt to convert *arachno*- $[(\text{Cp}^*\text{Ru})_2(\text{B}_3\text{H}_8)(\text{CS}_2\text{H})]$, **1**, to a *closo* or *nido* geometry, we performed the pyrolysis of **1** that led to the formation of a capped butterfly cluster. With seven-skeletal-electron-pairs (sep), it satisfies the electron count for a BH capped *arachno*-butterfly structure. These results demonstrate that both the transition metal and the ligands play an important role in the formation of these complexes. It is interesting to see that the properties and reactivity of molecules can be largely controlled by a variation in the metal or ligand.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2304-6740/7/2/21/s1>. ^1H , $^{11}\text{B}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$ NMR and mass spectra of compounds **2**–**5**; The CIF and the checkCIF output files of compounds **2**, **3** and **5**.

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