Metallacarboranes

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# Synthesis and Structure of 14- and 15-Vertex Ruthenacarboranes**

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Polyhedral expansion, a method developed by Hawthorne,[1] has proved to be very efficient for the synthesis of increasingly larger metallacarboranes.[2] This method has also been successfully applied to the synthesis of supercarboranes.[3] For example, by using carbon-atoms-adjacent (CAd) carborane anions as starting materials,[4] 13- and 14-vertex carboranes were prepared recently.[5,6] As theoretical calculations suggested that $[B_{14}H_{14}]^{2-}$ and $[B_{15}H_{15}]^{2-}$ have similar stability,[7] one may wonder whether such a cage-opening followed by boron or metal insertion would allow the preparation of 15-vertex clusters. This spurred us to prepare 15-vertex carboranes and metallacarboranes. Unfortunately, the reactions of $Na_2$-*nido*-$[(CH_2)_3C_2B_{12}H_{12}]$ with different borane reagents $RBX_2$ under various reaction conditions did not

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give any 15-vertex carborane, and rather afforded 14-vertex $(CH_2)_3C_2B_{12}H_{12}$ and a mixture of inseparable boron-containing species of high polarity. However, a metal fragment did insert into the 14-vertex *nido*-carborane cage to generate a 15-vertex metallacarborane. On the other hand, redox reactions were observed between *nido*-$[MR_2C_2B_{11}H_{11}]^{2-}$ and $R'BX_2$ or $MX_2$. These results are reported herein.

The starting material 2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$ (**2**) was prepared from $[\{(CH_2)_3C_2B_{11}H_{11}\}\{Na_2(thf)_4\}]_n$ (**1**) by the method developed by us.[6] Single-crystal X-ray analysis[8] revealed that **2** is an isomer of 2,13-$(CH_2)_3$-2,13-$C_2B_{12}H_{12}$[6] (Figure 1). Treatment of **2** with an excess of finely cut sodium metal in THF at room temperature gave, after recrystallization, 14-vertex *nido*-carborane salt $[\{(CH_2)_3C_2B_{12}H_{12}\}\{Na_2(thf)_4\}]_n$ (**3**) that was isolated in 80% yield (Scheme 1). Its $^1H$ NMR spectrum supported a molar ratio of four THF molecules per cage. The $^{11}B\{^1H\}$ NMR spectrum displayed a 1:2:2:3:2:1:1 pattern in the range 0.2 to −50.6 ppm, which was also observed in the reaction of **2** with an excess of lithium metal in THF. This result indicated that Group 1 metals can only reduce *closo*-$(CH_2)_3C_2B_{12}H_{12}$ to *nido*-$[(CH_2)_3C_2B_{12}H_{12}]^{2-}$, which suggests that *nido*-$[(CH_2)_3C_2B_{12}H_{12}]^{2-}$ is a stronger reducing reagent than *nido*-$[(CH_2)_3C_2B_{10}H_{10}]^{2-}$, as the latter can be reduced to *arachno*-$[(CH_2)_3C_2B_{10}H_{10}]^{4-}$ by lithium metal.[4e] This high reducing power of **3** may prevent its capitation with $HBBr_2{\cdot}SMe_2$.

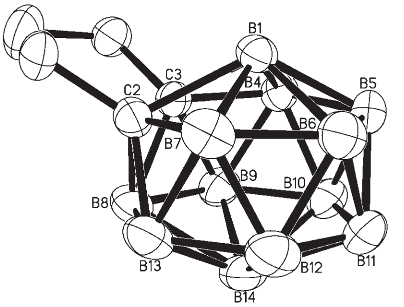
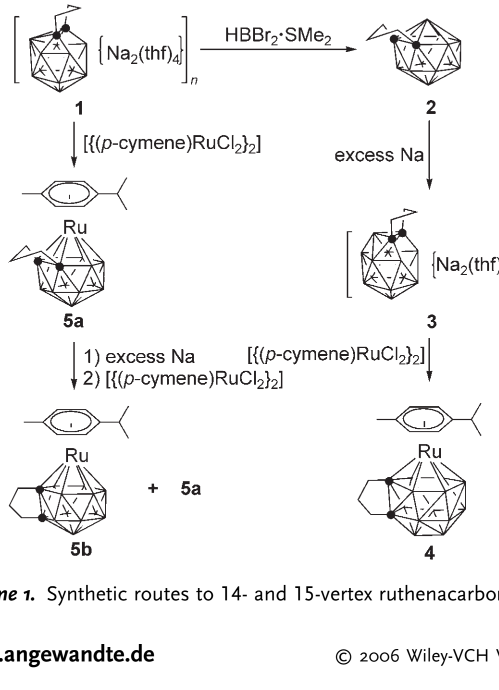


***Figure 1.*** Molecular structure of **2**. Selected bond lengths [Å]: C2–C3 1.608(4), B1–C2 1.907(5), B1–C3 1.917(4), B1–B4 1.881(5), B1–B5 1.864(5), B1–B6 1.866(5), B1–B7 1.886(5).



***Scheme 1.*** Synthetic routes to 14- and 15-vertex ruthenacarboranes.

The molecular structure of **3** was confirmed by single-crystal X-ray diffraction (Figure 2).[8] It is a coordination polymer in which $[Na(thf)_2]^+$ ions connect *nido*-carborane cages to form infinite one-dimensional zigzag chains. The 14-vertex *nido*-carborane dianion has an open bent pentagonal face with displacement of B9 by 0.55 Å out of the C1-C2-B5-B6 plane. This value is smaller than that of 0.68 Å in **1**.[4e] There are two seven-coordinate boron atoms (B7 and B8) in this cage. The average bond lengths between them and their neighboring vertices are 1.878(3) Å for B7 and 1.891(3) Å for B8, which are comparable to that of 1.902(3) Å in 2,13-$(CH_2)_3$-2,13-$C_2B_{12}H_{12}$.[6] Unlike 2,13-$(CH_2)_3$-2,13-$C_2B_{12}H_{12}$, the two hexagonal planes in **3** are not parallel; rather, they share the B4–B10 bond as common edge.[6]

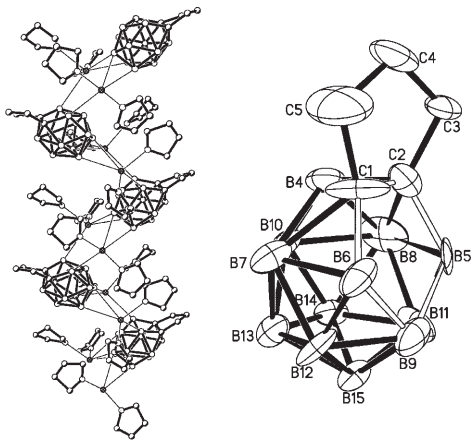


***Figure 2.*** Left: a portion of the infinite polymeric chains in **3**. Right: structure of the anion in **3**. Selected bond lengths [Å]: C1–C2 1.404(3), C1–B6 1.696(2), C2–B5 1.605(3), B5–B9 1.684(3), B6–B9 1.840(3).

Reaction of **3** with 0.5 equivalents of $[\{(p\text{-cymene})RuCl_2\}_2]$ in THF afforded 15-vertex ruthenacarborane 1,4-$(CH_2)_3$-7-(*p*-cymene)-7,1,4-$RuC_2B_{12}H_{12}$ (**4**) in 62% yield after column chromatographic separation (Scheme 1). To our knowledge compound **4** is one of the largest metallacarboranes known.[9,14] It is noteworthy that the reaction of **3** with $HBBr_2{\cdot}SMe_2$, $[NiCl_2(dppe)]$ (dppe = 1,2-bis(diphenylphosphanyl)ethane), or $[RuCl_2(PPh_3)_3]$ under various reaction conditions gave either the 14-vertex carborane 2,13-$(CH_2)_3$-2,13-$C_2B_{12}H_{12}$ or a mixture of inseparable products, and this indicates that the $\{(p\text{-cymene})Ru\}$ fragment is crucial for the formation of the 15-vertex species. Complex **4** is quite stable in air and soluble in polar organic solvents such as $CH_2Cl_2$, $CHCl_3$, and THF. It was fully characterized by $^1H$, $^{13}C$, and $^{11}B$ NMR spectroscopy, as well as high-resolution mass spectrometry. Its $^{11}B\{^1H\}$ NMR spectrum displayed a 1:2:1:2:1:1:1:1:1:1 pattern in the range 14.8 to −31.1 ppm, indicative of a species of low symmetry.

An X-ray analysis revealed that **4** adopts a *closo* structure with 26 triangular faces and has approximate $D_{3h}$ symmetry with a $C_3$ axis passing through the centers of the C1-B2-B3 and B13-B14-B15 planes if the tethering group is omitted and the differences among the Ru, B, and C atoms are ignored.[8] This geometry is very similar to that predicted for $[B_{15}H_{15}]^{2-}$ by theoretical calculations.[10] In this sandwich-type molecule (Figure 3), the arene ring is parallel to the hexagonal bonding face (C4-B2-B5-B10-B12-B15) of the carborane ligand with an Ru−Ar(cent) distance of 1.78 Å and Ru−$CB_5$(cent) distance of 1.41 Å, which are comparable to the corresponding values of 1.73 and 1.46 Å in 14-vertex (*p*-cymene)$_2Ru_2C_2B_{10}H_{12}$.[9e] The average Ru–cage atom distance of 2.247(3) Å and average Ru−C(Ar) distance of 2.272(3) Å are very close to those of 2.249(3) and 2.225(3) Å in (*p*-cymene)$_2Ru_2C_2B_{10}H_{12}$.[9e] Examination of the structures of **3** and **4** shows that significant cage rearrangement occurred during the reaction. High-temperature $^{11}$B NMR experiments suggested that **4** is a thermodynamically stable product.

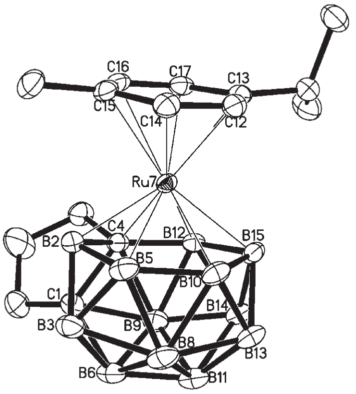


*Figure 3.* Molecular structure of **4**. Selected bond lengths [Å]: C1−C4 1.641(4), Ru7−C4 2.234(3), Ru7−B2 2.190(3), Ru7−B5 2.263(3), Ru7−B10 2.269(3), Ru7−B12 2.262(3), Ru7−B15 2.265(3).

After the successful preparation of **4**, we wondered if it could be synthesized by the capitation reaction of $Na_2$-*nido*-[(*p*-cymene)Ru{$(CH_2)_3C_2B_{12}H_{12}$}] with $HBBr_2{\cdot}SMe_2$. The new 14-vertex metallacarborane 2,3-$(CH_2)_3$-1-(*p*-cymene)-1,2,3-$RuC_2B_{11}H_{11}$ (**5a**) was readily isolated in 72% yield from the reaction of 13-vertex *nido*-carborane salt [{$(CH_2)_3C_2B_{11}H_{11}$}{$Na_2(thf)_4$}]$_n$ (**1**) with 0.5 equivalents of [{(*p*-cymene)$RuCl_2$}$_2$] in THF. Complex **5a** was treated with an excess of sodium metal in THF to produce a new species with an $^{11}B\{^1H\}$ NMR spectroscopic signature ($\delta = -11.50$ (1B), −14.88 (2B), and −32.81 ppm (8B)) distinct from those of **1** and **5a**, which was presumed to be $Na_2$-**5a**. This salt reacted with 2 equivalents of $HBBr_2{\cdot}SMe_2$ in toluene to give **5a** and 2,13-$(CH_2)_3$-1-(*p*-cymene)-1,2,13-$RuC_2B_{11}H_{11}$ (**5b**) in 80 and 5% yield of isolated product, respectively, after column chromatographic separation (Scheme 1). This reaction was monitored by $^{11}$B NMR spectroscopy, and no **4** was detected. In view of the successful preparation of 13- and 14-vertex bimetallic metallacarboranes $(C_5H_5)_2Fe_2C_3B_8H_{11}$,[11] $(C_5H_5)_2Co_2C_2B_{10}H_{12}$,[9d] and (*p*-cymene)$_2Ru_2C_2B_{10}H_{12}$,[9e] the reaction of $Na_2$-**5a** with 0.5 equivalents of [{(*p*-cymene)$RuCl_2$}$_2$] in THF was then examined. Again, a redox reaction lead to **5a** and **5b** in a ratio similar to that mentioned above after column chromatographic separation. These results indicate that the reducing power of the 14-vertex *nido*-metallacarborane is much higher than those of 12- and 13-vertex *nido*-metallacarboranes.

Complexes **5a** and **5b** are air- and moisture-stable and soluble in polar organic solvents such as $CH_2Cl_2$, $CHCl_3$, and THF. They were fully characterized by various spectroscopic techniques. The $^{11}B\{^1H\}$ NMR spectrum of **5a** displayed a 3:3:3:2 pattern in the range $\delta = -3.8$ to −18.8 ppm, whereas that of **5b** showed a 1:1:2:1:1:1:1:2:1 pattern in the range 1.9 to −27.3 ppm, which indicates that **5a** has higher symmetry. The $^1$H and $^{13}$C NMR spectra also exhibited consistent symmetry patterns. Variable-temperature $^{11}$B NMR experiments in $n$Bu$_2$O (20–140 °C) showed that both **5a** and **5b** are thermally stable and **5a** can not be transformed into **5b** under these conditions. Hence, **5b** must be formed in a redox reaction.

Single-crystal X-ray analyses revealed that **5a** and **5b** are isomers with a bicapped hexagonal antiprism geometry,[8] similar to that of 14-vertex carboranes.[6] The Ru atom occupies one of the apical vertices and the two cage carbon atoms are located in the 2,3- and 2,13-positions, respectively, as shown in Figures 4 and 5. The Ru−$C_2B_4$(cent) distance of 1.46 Å in **5a** and Ru−$CB_5$(cent) distance of 1.40 Å in **5b** are close to that of 1.41 Å in **4** and 1.46 Å in (*p*-cymene)$_2Ru_2C_2B_{10}H_{12}$.[9e] Examination of the structures of **1**[6] and

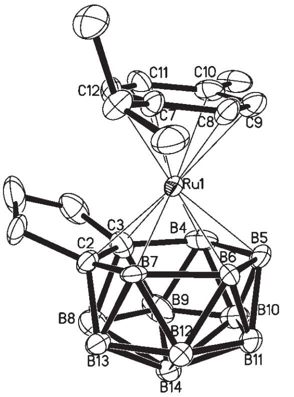


*Figure 4.* Molecular structure of **5a**. Selected bond lengths [Å]: C2−C3 1.644(12), Ru1−C2 2.268(8), Ru1−C3 2.251(9), Ru1−B4 2.258(11), Ru1−B5 2.288(10), Ru1−B6 2.280(9), Ru1−B7 2.252(8).

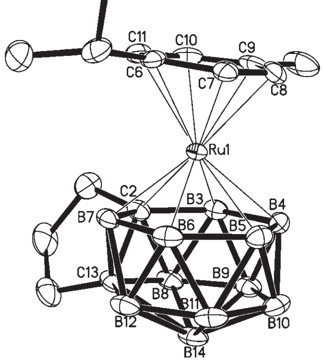


*Figure 5.* Molecular structure of **5b**. Selected bond lengths [Å]: C2−C13 1.631(5), Ru1−C2 2.192(3), Ru1−B3 2.231(4), Ru1−B4 2.275(4), Ru1−B5 2.290(4), Ru1−B6 2.276(4), Ru1−B7 2.199(4).

**5a**,**b** indicates that significant cage rearrangement took place in the reaction of **1** with [{(*p*-cymene)$RuCl_2$}$_2$]. A similar phenomenon was also observed in the formation of **4**.

In conclusion, we have prepared several new 14- and 15-vertex ruthenacarboranes. These supermetallacarboranes are air-, moisture-, and heat-stable. They are best described as 18$e^-$ metal species in which the 13- and 14-vertex *nido*-carboranes act as 6$e^-$ $\pi$ ligands. This work clearly indicates that the reducing power of *nido*-carborane dianions increases with increasing cluster size and the *nido*-metallacarborane dianion is a very strong reductant, which limits success in the preparation of supercarboranes. Prevention of redox reactions is the key to obtaining successively larger clusters.[14]

## Experimental Section

**3**: Finely cut sodium metal (100 mg, 4.35 mmol) was added to a solution of **2** (208 mg, 1.00 mmol) in THF (10 mL), and the mixture was stirred at room temperature for one week to give a clear yellow solution. After removal of excess sodium metal, the resulting yellow solution was concentrated to about 5 mL, and 4 mL of toluene was added. Complex **3** was obtained as colorless crystals after this solution was kept at room temperature for one week (434 mg, 80 %). $^1$H NMR (300 MHz, [D$_5$]pyridine): $\delta = 3.65$ (m, 16 H), 1.60 (m, 16 H; THF), 2.95 (m, 2 H; $CH_2CH_2CH_2$), 2.55 ppm (m, 4 H; $CH_2CH_2CH_2$); $^{13}C\{^1H\}$ NMR (100 MHz, [D$_5$]pyridine): $\delta = 67.84$, 25.47 (THF), 37.81 ($CH_2CH_2CH_2$), 31.70 ppm ($CH_2CH_2CH_2$), signals for the cage carbon atoms were not observed; $^{11}B\{^1H\}$ NMR (128 MHz, THF): $\delta = 0.21$ (1), −4.62 (2), −15.91 (2), −32.39 (3), −36.01 (2), −44.32 (1), −50.56 ppm (1); IR (KBr): $\tilde{\nu} = 2455$ cm$^{-1}$ (vs; BH); C,H analysis (%) calcd for $C_{19}H_{46}B_{12}Na_2O_{3.5}$ (**3**−0.5 THF): C 45.08, H 9.16; found: C 44.74, H 9.02.

**4**: A solution of **3** (542 mg, 1.00 mmol) in THF (10 mL) was slowly added to a suspension of [{(*p*-cymene)$RuCl_2$}$_2$] (306 mg, 0.50 mmol) in THF (10 mL) at −78 °C, and the mixture was then stirred at room temperature for 12 h to give a deep brown solution. Removal of the precipitate and solvents gave a brown sticky solid. Chromatographic separation ($SiO_2$, 300–400 mesh, *n*-hexane/$CH_2Cl_2$ (1:4) as eluent) afforded **4** as a pale orange solid (275 mg, 62 %). Single crystals suitable for X-ray analysis were grown from a THF solution. $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 5.89$ (d, $J = 6.6$ Hz, 1 H), 5.81 (d, $J = 6.6$ Hz, 1 H), 5.51 (d, $J = 6.3$ Hz, 1 H), 5.35 (d, $J = 6.3$ Hz, 1 H; $CH_3C_6H_4CH(CH_3)_2$), 3.27 (m, 1 H; $CH_2$), 3.05 (m, 1 H; CH), 2.72 (m, 1 H; $CH_2$), 2.31 (s, 3 H; $CH_3C_6H_4CH(CH_3)_2$), 2.09 (m, 4 H; $CH_2$), 1.30 (d, $J = 6.6$ Hz, 3 H), 1.26 ppm (d, $J = 6.6$ Hz, 3 H; $CH_3C_6H_4CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 122.9$, 112.9, 100.0, 97.13, 96.01, 92.79 ($CH_3C_6H_4CH(CH_3)_2$), 46.99, 36.53, 29.93, 28.14, 23.13, 22.13, 17.89 ppm, signals for the cage carbon atoms were not observed; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): $\delta = 14.83$ (1), 2.46 (2), −0.45 (1), −6.17 (2), −9.87 (1), −12.99 (1), −17.78 (1), −19.81 (1), −26.83 (1), −31.12 ppm (1); IR (KBr): $\tilde{\nu} = 2506$ (vs), 2450 cm$^{-1}$ (s; BH); HRMS calcd for $[C_{15}H_{32}B_{12}Ru]^+$: *m*/*z* 444.2731; found: 444.2735.

**5a**: A solution of **1** (531 mg, 1.00 mmol) in THF (10 mL) was slowly added to a suspension of [{(*p*-cymene)$RuCl_2$}$_2$] (306 mg, 0.50 mmol) in THF (10 mL) at −78 °C, and the mixture was then stirred at room temperature for 12 h to give a deep brown solution. Removal of the precipitate and solvents gave a brown sticky solid. Chromatographic separation ($SiO_2$, 300–400 mesh, *n*-hexane/$CH_2Cl_2$ (1:4) as eluent) afforded **5a** as a yellow solid (310 mg, 72 %). Single crystals of **5a**·THF suitable for X-ray analysis were grown from a THF solution. $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 5.51$ (d, $J = 6.6$ Hz, 2 H), 5.41 (d, $J = 6.6$ Hz, 2 H; $CH_3C_6H_4CH(CH_3)_2$), 3.76 (m, 4 H), 1.85 (m, 4 H; THF), 3.13 (m, 2 H; $CH_2$), 2.95 (m, 1 H; $CH_3C_6H_4CH(CH_3)_2$), 2.47 (m, 4 H; $CH_2$), 2.29 (s, 3 H; $CH_3C_6H_4CH(CH_3)_2$), 1.31 ppm (d, $J = 6.9$ Hz, 6 H; $CH_3C_6H_4CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 117.4$, 108.1, 94.87, 92.03 ($CH_3C_6H_4CH(CH_3)_2$), 67.96, 25.59 (THF), 42.38, 27.86 ($CH_2$), 30.20 (CH), 29.93, 22.43 ppm ($CH_3$), signals for the cage carbon atoms were not observed; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): $\delta = -3.84$ (3), −12.17 (3), −15.22 (3), −18.82 ppm (2); IR (KBr): $\tilde{\nu} = 2512$ cm$^{-1}$ (vs; BH); HRMS calcd for $[C_{15}H_{31}B_{11}Ru]^+$: *m*/*z* 432.2560; found: 432.2550.

**5b**: Finely cut sodium metal (69 mg, 3.00 mmol) was added to a solution of **5a** (432 mg, 1.00 mmol) and naphthalene (13 mg, 0.10 mmol) in THF (10 mL), and the mixture was stirred at room temperature for two days to give a deep green solution. After removal of excess sodium metal, [{(*p*-cymene)$RuCl_2$}$_2$] (367 mg, 0.60 mmol) was added to the solution at −30 °C in one portion, and the mixture was stirred at room temperature for 6 h. Chromatographic separation ($SiO_2$, 300–400 mesh, *n*-hexane/$CH_2Cl_2$ (1:2) as eluent) afforded **5a** (346 mg, 80 %) and **5b** (22 mg, 5 %), both as yellow solids. Single crystals of **5b** suitable for X-ray analysis were grown from a THF solution. $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 5.51$ (m, 4 H; $CH_3C_6H_4CH(CH_3)_2$), 2.69 (m, 6 H; $CH_2$), 2.28 (m, 4 H; $CH_3C_6H_4CH(CH_3)_2$), 1.11 ppm (s, 6 H; $CH_3C_6H_4CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 118.7$, 108.8, 95.16, 94.26, 91.88, 91.61 ($CH_3C_6H_4CH(CH_3)_2$), 42.82, 41.40, 30.24, 29.69, 22.99, 22.35, 18.37 ppm, signals for the cage carbon atoms were not observed; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): $\delta = 1.89$ (1), −1.67 (1), −6.62 (2), −9.23 (1), −11.01 (1), −20.39 (1), −23.62 (1), −24.81 (2), −27.28 ppm (1); IR (KBr): $\tilde{\nu} = 2517$ cm$^{-1}$ (vs; BH); HRMS calcd for $[C_{15}H_{31}B_{11}Ru]^+$: *m*/*z* 432.2560; found: 432.2550.

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**Keywords:** boron · cage compounds · carboranes · cluster compounds · ruthenium

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[8] Crystal data for **2**·$C_{10}H_8$: $C_{15}H_{26}B_{12}$, $M_r = 336.1$, monoclinic, space group $P2_1/c$, $a = 7.836(4)$, $b = 16.662(8)$, $c = 15.795(8)$ Å, $\beta = 100.69(1)°$, $V = 2027(2)$ Å$^3$, $T = 293$ K, $Z = 4$, $\rho_{calcd} = 1.102$ g cm$^{-3}$, $2\theta_{max} = 50°$, $\mu(Mo_{K\alpha}) = 0.71073$ Å, absorption corrections applied by using SADABS,[12] relative transmission factors in the range 0.984–1.000. A total of 10927 reflections were collected and led to 3571 unique reflections, 3571 of which with $I > 2\sigma(I)$ were considered as observed, $R_1 = 0.0774$, $wR_2(F^2) = 0.2060$. Crystal data for **3**: $C_{21}H_{50}B_{12}Na_2O_4$, $M_r = 542.3$,

orthorhombic, space group $Pna2_1$, $a=11.441(1)$, $b=16.692(2)$, $c=17.224(2)$ Å, $V=3289(1)$ Å$^3$, $T=293$ K, $Z=4$, $\rho_{\text{calcd}}=1.095$ g cm$^{-3}$, $2\theta_{\max}=50°$, $\mu(\text{Mo}_{K\alpha})=0.71073$ Å, absorption corrections applied by using SADABS,[12] relative transmission factors in the range 0.566–1.000. A total of 14726 reflections were collected and led to 4965 unique reflections, 4965 of which with $I>2\sigma(I)$ were considered as observed, $R_1=0.0797$, $wR_2(F^2)=0.1940$. Crystal data for **4**: $C_{15}H_{32}B_{12}Ru$, $M_r=443.2$, monoclinic, space group $P2_1/c$, $a=8.426(1)$, $b=15.911(2)$, $c=15.977(2)$ Å, $\beta=101.63(1)°$, $V=2098(1)$ Å$^3$, $T=293$ K, $Z=4$, $\rho_{\text{calcd}}=1.403$ g cm$^{-3}$, $2\theta_{\max}=50°$, $\mu(\text{Mo}_{K\alpha})=0.71073$ Å, absorption corrections applied by using SADABS,[12] relative transmission factors in the range 0.794–1.000. A total of 11266 reflections were collected and led to 3695 unique reflections, 3695 of which with $I>2\sigma(I)$ were considered as observed, $R_1=0.0266$, $wR_2(F^2)=0.0646$. Crystal data for **5a**·THF: $C_{19}H_{39}B_{11}ORu$, $M_r=503.5$, monoclinic, space group $P2_1/c$, $a=15.893(5)$, $b=10.347(3)$, $c=16.159(5)$ Å, $\beta=106.01(1)°$, $V=2554(1)$ Å$^3$, $T=293$ K, $Z=4$, $\rho_{\text{calcd}}=1.309$ g cm$^{-3}$, $2\theta_{\max}=50°$, $\mu(\text{Mo}_{K\alpha})=0.71073$ Å, absorption corrections applied by using SADABS,[12] relative transmission factors in the range 0.508–1.000. A total of 13305 reflections were collected and led to 4501 unique reflections, 4501 of which with $I>2\sigma(I)$ were considered as observed, $R_1=0.0671$, $wR_2(F^2)=0.1637$. Crystal data for **5b**: $C_{15}H_{31}B_{11}Ru$, $M_r=431.4$, monoclinic, space group $P2_1/c$, $a=14.427(2)$, $b=8.281(1)$, $c=17.514(3)$ Å, $\beta=104.17(1)°$, $V=2029(1)$ Å$^3$, $T=293$ K, $Z=4$, $\rho_{\text{calcd}}=1.412$ g cm$^{-3}$, $2\theta_{\max}=50°$, $\mu(\text{Mo}_{K\alpha})=0.71073$ Å, absorption corrections applied by using SADABS,[12] relative transmission factors in the range 0.738–1.000. A total of 10671 reflections were collected and led to 3574 unique reflections, 3574 of which with $I>2\sigma(I)$ were considered as observed, $R_1=0.0303$, $wR_2(F^2)=0.0655$. These structures were solved by direct methods and refined by full-matrix least-squares techniques on $F^2$ by using the SHELXTL/PC package.[13] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were geometrically fixed by using the riding model. CCDC 600498–600502 (**2**·$C_{10}H_8$, **3**, **4**, **5a**·THF, **5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[14] Note added in proof: While this manuscript was in press we have learnt of the synthesis of another 15-vertex metallacarborane by a different group: R. D. McIntosh, D. Ellis, G. M. Rosair, A. J. Welch *Angew. Chem.* **2006**, *118*, 4419–4424; *Angew. Chem. Int. Ed.* **2006**, *45*, 4313–4316, next Communication in this issue.