FACILE PREPARATION OF CHLORO-CAGE-SUBSTITUTED 11-VERTEX 1-(η^6-ARENE)-*isonido*-1,2,4-RUTHENACARBORANES FROM $[RuCl_2(PPh_3)_3]$ AND *nido*-5,6-$C_2B_8H_{12}$ IN ARENE SOLVENTS

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Dedicated to Professor Jaromír Plešek on the occasion of his 75th birthday in recognition of his outstanding contribution to chemistry and stereochemistry of transition-metal boron clusters and carboranes.

A series of arene-ruthenium 11-vertex complexes 3-Cl-1-(η^6-arene)-*isonido*-1,2,4-$RuC_2B_8H_9$ (**4a**–**4h**) and 6-Cl-1-(η^6-arene)-*isonido*-1,2,4-$RuC_2B_8H_9$ (**5a**, **5b**, **5f**, **5g**) (arene = *p*-xylene (**a**), mesitylene (**b**), *p*-cymene (**c**), benzene (**d**), toluene (**e**), hexamethylbenzene (**f**), 1,2,4,5-tetramethylbenzene (**g**), 1,2,4-trimethylbenzene (**h**)) have been obtained as isomeric mixtures **4a**, **4b**, **4f**, **4g** and **5a**, **5b**, **5f**, **5g** or, predominantly, as single isomers **4c**–**4e**, **4h** by the treatment of *nido*-5,6-$C_2B_8H_{12}$ (**1**) with $[RuCl_2(PPh_3)_3]$ (**2**), either in the corresponding arene solvents at 80–85 °C (in the case of **4a**–**4e** and **5a**, **5b**) or in the arene/1,2-dichloroethane solution under reflux (in the case of **4f**–**4h** and **5f**, **5g**) in the presence of *N*,*N*,*N*′,*N*′-tetramethylnaphthalene-1,8-diamine. The compounds prepared were characterized by combination of analytical, IR and multinuclear NMR data, including a crystallographic study of **4b**. A possible pathway for the formation of isomeric complexes **4** and **5** is discussed.

Keywords: Ruthenium; Middle carboranes; Boranes; Metallaboranes; Metallacarboranes; *isonido*-Ruthenacarboranes; NMR spectroscopy, ^1H, ^{11}B, ^{13}C, [^{11}B-^{11}B]-COSY; X-Ray diffraction; Arene complexes.

Transition-metal 16-electron complexes of the $[MCl_n(PPh_3)_m]$ type in which phosphine groups can be replaced by arenes or other planar carbocyclic ligands in the course of their thermal displacement reactions with neutral or anionic *nido*-carborane substrates have been rarely explored as the reagents

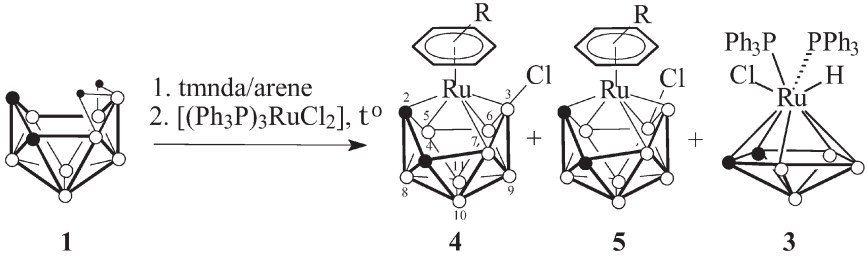
for the syntheses of (η-L)-*closo*-metallacarborane (L = carbocycle)[1] and, in particular, have never been used for the preparative syntheses of 11-vertex 1-(η^6-arene)-*isonido*-1,2,4-ruthenacarboranes. Such *isonido*-metallacarboranes with η^6-arene, η^5-Cp or η^5-Cp* ligands which adopt an open-face cluster structure are usually prepared either by the traditional ligand-exchange method using the reaction between *nido*-5,6-$C_2B_8H_{12}$ (**1**) or its alkyl-substituted derivatives and dimeric arene-metal μ-halide complexes $[MCl_2(\eta\text{-L})]_2$ (L = Ar, M = Ru, Os [2–4]; L = Cp*, M = Rh [4]) in the presence of a base or, in some cases, by polyhedral contraction of highest (η-L)-*closo*-metallacarborane precursors[5,6]. Recently, we have found[7] that the reaction of *nido*-carborane **1** with $[RuCl_2(PPh_3)_3]$ (**2**) under heating in toluene solution, produced, along with 7-vertex *closo*-$C_2B_4H_6Ru(PPh_3)_2HCl$ (**3**), a minor amount of isomeric 11-vertex clusters 3-Cl-1-(η^6-C_6H_5Me)-*isonido*-1,2,4-$RuC_2B_8H_9$ (**4e**) and 6-Cl-1-(η^6-C_6H_5Me)-*isonido*-1,2,4-$RuC_2B_8H_9$ (**5e**). An investigation, therefore, has been undertaken in an effort to develop a more powerful synthetic route to *isonido*-ruthenacarboranes which, in particular, would not require the preliminary preparation of arene-ruthenium dimeric precursors $[RuCl_2(\eta\text{-L})]_2$[8]. We report here the result of this study, including the facile synthesis of a series of isomeric 3-Cl-1-(η^6-arene)-*isonido*-1,2,4-$RuC_2B_8H_9$ and 6-Cl-1-(η^6-arene)-*isonido*-1,2,4-$RuC_2B_8H_9$ with a wide variety of arene ligands which are formed in good to moderate yields, primarily from **1** and **2** in the corresponding arene solvents or in a mixed solution of arene/1,2-dichloroethane in the presence of *N*,*N*,*N*′,*N*′-tetramethylnaphthalene-1,8-diamine (tmnda).

RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization of (η^6-Arene)-isonido-1,2,4-$RuC_2B_8H_9Cl$ Isomers

It has been found that heating to 80–85 °C of equimolar amounts of **1** and **2** in solution of the corresponding arenes in the presence of twofold excess of tmnda for a few hours readily afforded either a mixture of isomeric complexes 3-Cl-1-(η^6-arene)-*isonido*-1,2,4-$RuC_2B_8H_9$ (**4a**, **4b**) and 6-Cl-1-(η^6-arene)-*isonido*-1,2,4-$RuC_2B_8H_9$ (**5a**, **5b**), where arenes are *p*-xylene (**a**), mesitylene, (**b**) or, predominantly, single isomers **4c**–**4e**, where arenes are *p*-cymene (**c**), benzene (**d**), and toluene (**e**), respectively (Scheme 1). We have succeeded in separation of mixtures of **4a**, **4b** and **5a**, **5b** into individual isomeric compounds by column chromatography on 5–40 mesh silica gel. The yields of the principal isomeric products varied from 55% for **4e** to

17% for the *p*-cymene complex **4c**. No evidence of cluster isomerization of the type *isonido*-1,2,4-RuC_2B_8 → *closo*-1,2,3-RuC_2B_8 [3,4] has been observed under thermal conditions used in the reactions. However, in most of these reactions leading to **4** and **5**, complex **3** [7] was also formed (from trace to minor amounts) as a side product which could be easily separated from the major 11-vertex *isonido*-clusters in the course of their purification by column chromatography.



SCHEME 1

In the course of our studies the above mentioned synthetic procedure was slightly modified for those arenes which are solids, *e.g.*, hexamethylbenzene (**f**) and 1,2,3,4-tetramethylbenzene (**g**). Specifically, this involved the reaction of starting reagent **1** with a twofold amount of tmnda in 1,2-dichloroethane solution followed by treatment of the deprotonated *nido*-carborane species with **2** and the corresponding benzene derivatives at elevated temperature. However, the yields of compounds **4f**, **4g** and **5f**, **5g** obtained as mixtures of isomers proved to be lower than those of the related complexes prepared from liquid arenes and did not exceed 20%. When the same reagents **1**, tmnda and **2** were heated in a 2 : 1 mixture of 1,2-dichloroethane and 1,2,4-trimethylbenzene (**h**), under reflux, a mixture of diastereomeric complexes **4h′** and **4h″** in 1 : 1 ratio was obtained in 26% yield. Both mixtures of **4g** and **5g** and **4h′** and **4h″** were inseparable, either by column or thin-layer chromatography on silica gel or fractional crystallization, while separation of a mixture of complexes **4f** and **5f** into individual isomers was achieved by the same chromatographic procedure as for **4a**, **4b** and **5a**, **5b**.

All individual complexes or mixtures of isomeric complexes thus obtained after recrystallization from appropriate solvents were characterized by IR, ^1H and $^{11}B/^{11}B\{^1H\}$ NMR spectroscopy as well as by microanalysis performed for the selected compounds mostly with those isomers which were obtained in higher yields (see Experimental). The IR spectra of complexes

showed strong bands in the 2 514–2 540 cm^{-1} region assignable to ν_{B-H} as well as a set of stretching bands of middle intensity in the 1 070–1 460 cm^{-1} region compatible with $\nu_{C=C}$ of coordinating η^6-arenes in the related (π-arene)-*closo*-metallacarboranes[9]. In the ^1H NMR spectra of all isomeric complexes the resonances of η^6-arene moieties were shifted *ca* 2–2.5 ppm upfield compared with the free arene ligands. In accord with the asymmetric 1,2,4-RuC_2B_8 cluster structure of **4** and **5**, the corresponding carbon-cage protons revealed in the ^1H NMR spectra of complexes as somewhat broadened singlets in separate regions, usually near 4.1 and 3.5 ppm. The $^{11}B/^{11}B\{^1H\}$ NMR spectra of complexes **4** and **5** consisted of a set of eight distinct resonances in the range –40 to +70 ppm with one of the signals at an extremely low field, confirming the presence of at least one boron atom with low cluster connectivity. A very similar boron nuclear shielding behavior was observed in the ^{11}B NMR spectra of the recently reported isomeric complexes 3-Br-1-Cp-1,2,4-$CoC_2B_8H_9$ and 6-Br-1-Cp-1,2,4-$CoC_2B_8H_9$ [10] as well as the related 5-Br-1-(η^6-C_6Me_6)-1,2,4-$RuC_2B_8H_9$ and 7-Br-1-(η^6-C_6Me_6)-1,2,4-$RuC_2B_8H_9$ [4]. In this work one pair of individual isomeric complexes **4b** and **5b** has been examined by [^{11}B-^{11}B]-COSY spectroscopy which, coupled with $^1H\{^{11}B$(selective and broad-band)$\}$ experiments, permitted complete assignment of cluster ^{11}B and ^1H chemical shifts. In the [^{11}B-^{11}B]-COSY spectra of the crystallographically established **4b** (*vide infra*) and its isomeric complex **5b** there exists a correlation between most of the signals from the adjacent boron atoms with a short B–B bond. However, several theoretical cross-peaks were not observed in the [^{11}B-^{11}B]-COSY spectra of both **4b** and **5b**. In particular, these were not found for those boron atoms which are connected to skeletal carbons, *i.e.* between B(5) and B(8), B(7) and B(10), B(8) and B(10) in the case of **4b**, or B(5) and B(8), B(5) and B(11), B(7) and B(10), and B(8) and B(10) in the case of **5b**. In [^{11}B-^{11}B]-COSY spectra of known *isonido*-[2–4] and/or *closo*-metallacarboranes[11] the observed cross-peaks for such boron atoms flanking the more electronegative heteroatoms are known to appear weaker than those for other pairs of the adjacent boron atoms. The $^{13}C\{^1H,^{11}B\}$ NMR spectra of **4b** and **5b** both displayed two well defined sharp singlets for the non-equivalent cage carbon atoms at 34.8 and 54.9 ppm (**4b**) and at 32.3 and 48.0 ppm (**5b**) along with a set of characteristic resonances, which is consistent with the presence of an η^6-mesitylene ring in these molecules.

The likely pathway for the formation of isomeric arene-ruthenium *isonido* complexes **4** and **5** may involve the triphenylphosphine-arene thermal displacement reaction with concomitant intermolecular chlorination at boron

atoms of the initially formed 16-electron species – 1,1-$(PPh_3)_2$-*closo*-1,2,4-$RuC_2B_8H_{10}$ (**7**). Earlier, the same complex **7** has been considered to be an apparent intermediate in the reaction of $[RuHCl(PPh_3)_3]$ with $[nido\text{-}5,6\text{-}C_2B_8H_{11}]^-Na^+$ where the final product obtained was formulated as 1,1,3-$(PPh_3)_3$-1-H-*closo*-1,2,4-$RuC_2B_8H_9$ (**8**)[12]. We have found that complex **8** as the only metallacarborane product is also formed in the reaction of **1**, tmnda and **2** in benzene solution at room temperature (see Experimental). Comparison of its ^1H, ^{31}P and $^{11}B/^{11}B\{^1H\}$ spectra with those reported earlier for **8** [12] showed full structural and composition identity of these two species. However, these spectroscopic data alone without an X-ray diffraction study of **8** appear to be insufficient for unambiguous assignment of the detailed cluster structure of this complex and, in particular, to resolve the question whether complex **8** adopts classical *closo* or *isonido* cage geometry. It is interesting that **8** turned out to be thermally unstable in solution undergoing an extensive decomposition when heated in benzene under reflux temperature in the presence of tmnda.

Thus, depending on the temperature conditions, intermediate **7**, if formed, either gets attacked by free PPh_3 at a boron atom to give complex **8** or becomes involved in the phosphine-arene displacement and then chlorination reaction at higher temperature yielding finally η^6-arene-ruthenium isomeric complexes **4** and **5**. Both these processes, in fact, result in structural and electronic stabilization of the initially formed 16-electron complex **7**, since the metal atom in the final compounds adopts an 18-electron configuration in the valence shell.

*Crystal Structure of Complex **4b***

Eleven-vertex metallacarboranes of general formula $[1\text{-}L_n\text{-}1,2,4\text{-}MC_2B_8H_{10}]$ (L = carbocycle as well as phosphine and hydrido ligands) have long been recognized as having completely closed deltahedral geometry[6,12], because they are presumed to have a formal *closo* $(2n + 2)$ electron count. Compounds of this type isolated so far and crystallographically studied[2–4,7,10,13] exhibited, however, dramatic distortion of their cage geometry away from the C_{2v} symmetry of the idealized *closo*-MC_2B_8 cluster structure. This is manifested mostly in the lengthening of one of their M–C distances to such an extent that quadrilateral open-face M(1)C(2)C(4)B(7) is generated in cluster systems and, therefore, transition-metal metallacarboranes obtained by metallation of the neutral *nido*-carborane **1** and/or its deprotonated anion $[nido\text{-}5,6\text{-}C_2B_8H_{11}]^-$ have been regarded as *isonido*-type clusters[13a].

The structure of isomer **4b** determined by a single-crystal X-ray diffraction study has also revealed common geometric features of *isonido*-type clusters. The molecular structure of **4b** is represented in Fig. 1 and the principal geometric characteristics (selected bond lengths and angles) are given in Table I. As can be seen from Fig. 1, a considerable cage distortion in **4b** led to the formation of well defined tetragonal open-face Ru(1)C(2)C(4)B(7) with an essentially non-bonding Ru(1)···C(4) distance of 2.695(2) Å. In **4b** the separation between the metal and the cage C(2) and B(3) atoms resided at low-connectivity positions proved to be significantly shorter (Ru–C(2), 2.095(2) Å; Ru–B(3), 2.049(2) Å) than that between the metal and those atoms with higher cluster connectivity involved in metal-to-cluster bonding interaction (Ru–B(5), 2.293(2) Å; Ru–B(6), 2.303(2) Å; Ru–B(7), 2.383(2) Å). The shortest cage distance found in **4b** is C(2)–C(4) (1.472(3) Å), supporting the adjacency of the carbon atoms in the polyhedral cage. Moreover, both distances, C(2)–B(5) (1.613(3) Å) and C(4)–B(7) (1.718(3) Å), have intermediate values as compared with the shortest C–C and longest B–B bond lengths observed in the structure (Table I), a feature which is commonly observed for the structurally related *isonido*-clusters and consistent with the above positioning of the cage-carbon atoms. In addition, the crystal structure of **4b** has unambiguously positioned the chloro substituent at the B(3) atom of the carborane cage. The bond lengths and angles involving carbon atoms of the η^6-coordinating mesitylene ligand in **4b** are unexceptional

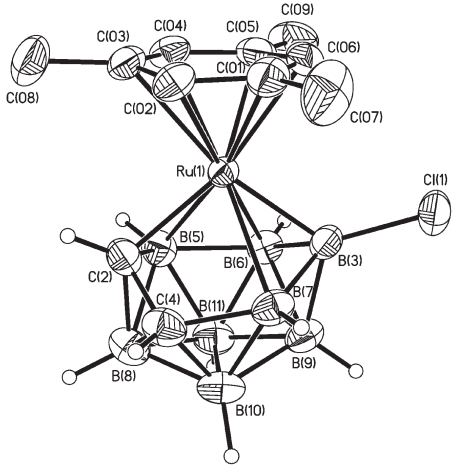


FIG. 1

Molecular structure of compound **4b** (thermal ellipsoids are drawn at the 50% probability level); the arene group hydrogen atoms are omitted for clarity

TABLE I
Selected bond lengths (in Å) and angles (in °) for compound **4b**

Ru1–C2	2.095(2)	B3–B7	1.737(3)
Ru1···C4	2.695(2)	B3–B9	1.713(3)
Ru1–B3	2.049(2)	C4–B7	1.718(3)
Ru1–B5	2.293(2)	C4–B8	1.710(4)
Ru1–B6	2.303(2)	C4–B10	1.642(4)
Ru1–B7	2.383(2)	B5–B6	1.815(3)
Ru1–C01	2.245(2)	B5–B8	1.825(4)
Ru1–C02	2.246(2)	B5–B11	1.809(4)
Ru1–C03	2.3349(19)	B6–B9	1.786(3)
Ru1–C04	2.257(2)	B6–B11	1.786(3)
Ru1–C05	2.1837(19)	B7–B9	1.900(3)
Ru1–C06	2.224(2)	B7–B10	1.834(4)
Cl1–B3	1.807(2)	B8–B10	1.747(4)
C2–C4	1.472(3)	B8–B11	1.723(4)
C2–B5	1.613(3)	B9–B10	1.764(4)
C2–B8	1.691(3)	B9–B11	1.753(4)
B3–B6	1.733(3)	B10–B11	1.791(4)
C4–C2–B5	112.73(18)	C2–B5–B6	115.40(16)
C4–C2–Ru1	96.63(14)	C2–B5–Ru1	62.00(10)
B5–C2–Ru1	75.17(11)	B6–B5–Ru1	67.03(10)
B6–B3–B7	101.88(16)	B3–B6–B5	116.36(16)
B6–B3–Cl1	129.62(17)	B3–B6–Ru1	59.02(10)
B7–B3–Cl1	125.23(15)	B5–B6–Ru1	66.46(10)
B6–B3–Ru1	74.50(11)	C4–B7–B3	126.64(16)
B7–B3–Ru1	77.54(12)	C4–B7–Ru1	80.39(12)
Cl1–B3–Ru1	127.91(12)	B3–B7–Ru1	57.09(9)
C2–C4–B7	109.34(17)		

and close to those found in a number of transition-metal metallacarborane complexes with planar π-arene ligands[9,14].

Summarising, we have developed an efficient and versatile preparative method for the synthesis of chloro-cage-substituted 11-vertex 1-(η^6-arene)-*isonido*-1,2,4-ruthenacarboranes from easily available starting materials.

EXPERIMENTAL

All reactions were performed under argon using the standard Schlenk technique with manipulation in air during purification of products. All solvents including those used in the reactions and for purification of products as well as some arenes (benzene, toluene, mesitylene) were distilled with appropriate drying agents (CaH_2 or Na) before use. Other arenes were used in reactions as received (Aldrich). Starting carborane **1** was prepared by the procedure first introduced by Plešek *et al.*[15] Reagent **2** was obtained by the method published elsewhere[16]. The ^1H, ^{31}P, $^{11}B/^{11}B\{^1H\}$ and $^{13}C\{^1H,^{11}B\}$ NMR spectra were obtained with Bruker AMX-400 (^1H, 400.13 MHz; ^{11}B, 128.33 MHz; ^{31}P, 161.98 MHz) and Bruker DRX-500 (^{13}C, 125.76 MHz) spectrometers. Chemical shifts (δ, ppm) are given relative to TMS as an internal reference and $BF_3{\cdot}Et_2O$ as external reference; for high-field resonances they are negative. Coupling constants (*J*) are given in Hz. The correlation [^{11}B-^{11}B]-COSY and $^1H\{^{11}B$(selective and broad-band)} spectra of **4b** and **5b** were recorded in CD_2Cl_2 on a Bruker ARX-250 spectrometer using a COSY 45 pulse program slightly modified to allow the ^1H decoupling during acquisition. All IR spectra (wavenumbers in cm^{-1}) were obtained on an instrument Specord M82 in KBr pellets. Elemental analyses were performed by the Analytical Laboratory of the Institute.

General Preparation of Isomeric Complexes 3-Chloro-1-(η^6-arene)-*isonido*-1,2,4-ruthenadicarbaundecaborane (**4a**–**4e**) and 6-Chloro-1-(η^6-arene)-*isonido*-1,2,4-ruthenadicarbaundecaborane (**5a**, **5b**) Using Liquid Arenes

To a solution of **1** (0.013 g, 0.106 mmol) and tmnda (0.045 g, 0.21 mmol) in *ca* 10 ml of arene, after 10-min stirring, was added solid complex **2** (0.1 g, 0.104 mmol) and the mixture was gently heated at 85 °C for *ca* 1 h until starting **2** dissolved and a colored precipitate appeared on the walls of the flask. After distilling off the arene from the reaction mixture under vacuum into a trap cooled with dry ice, the crude solid was applied onto a short silica gel column eluting **3** [7] (yellow band) and a mixture of **4** and **5** (orange band) with $CHCl_3$. The yields of **3** in most of these reactions were not as high as *ca* 2–4% based on the starting reagent **2**. Repeated column chromatography (5–40 mesh silica gel) of the solid obtained from the orange fraction using a 1 : 1 mixture of CH_2Cl_2/hexane as eluent afforded isomeric complexes **4** and **5** or only isomers of **4**, which were then recrystallized from a CH_2Cl_2/hexane mixture resulting in pure crystalline compounds.

3-Chloro-1-(η^6-1,4-dimethylbenzene)-isonido-1,2,4-ruthenadicarbaundecaborane (**4a**). Yield 15 mg, 40%. IR: ν(BH) 2 528; $\nu(CH_{Ar})$ 3 056; $\nu(C{=}C_{Ar})$ 1 448, 1 086. ^1H NMR (400.13 MHz, C_6D_6): 4.94 br m, 2 H (Ar, H-2,3 (or 5,6)); 4.90 br m, 2 H (Ar, H-5,6 (or 2,3)); 4.20 br s, 1 H (carborane CH); 3.57 br s, 1 H (carborane CH); 1.47 s, 6 H (CH_3). ^{11}B NMR (128.33 MHz, C_6D_6): 69.1 s, 1 B (B-3); 13.2 d, 1 B, ^1J(B,H) = 146.6 (B-9); 0.2 d, 2 B, ^1J(B,H) = 143.2 (B-5,6);

–13.4 d, 1 B, ^1J(B,H) = 129.6 (B-10); –22.7 d, 1 B, ^1J(B,H) = 163.4 (B-8); –26.7 d, 1 B, ^1J(B,H) = 143.0 (B-11); –40.5 d, 1 B, ^1J(B,H) = 168.4 (B-7). For $C_{10}H_{19}B_8ClRu$ (362.3) calculated: 33.16% C, 5.29% H, 23.87% B, 9.79% Cl; found: 32.94% C, 5.20% H, 23.67% B, 10.11% Cl.

6-Chloro-1-(η^6*-1,4-dimethylbenzene)-isonido-1,2,4-ruthenadicarbaundecaborane* (**5a**). Yield 5 mg, 13%. IR: ν(BH) 2 519; ν(CH_{Ar}) 3 065; ν(C=C_{Ar}) 1 449, 1 078. ^{1}H NMR (400.13 MHz, C_6D_6): 4.96 dd, 2 H, ^3J(AB) = 6.0, ^4J(2,6) = ^4J(3,5) = 1.3 (Ar, H-2,3 (or 5,6)); 4.77 dd, 2 H, ^3J(AB) = 6.0, ^4J(5,3) = ^4J(6,2) = 1.3 (Ar, H-5,6 (or 2,3)); 4.12 br s, 1 H (carborane CH); 3.43 br s, 1 H (carborane CH); 1.58 s, 6 H (CH_3). ^{11}B NMR (128.33 MHz, CD_2Cl_2): 62.5 d, 1 B, ^1J(B,H) = 156.0 (B-3); 13.7 d, 1 B, ^1J(B,H) = 147.1 (B-9); 10.5 s, 1 B (B-6); 1.0 d, 1 B, ^1J(B,H) = 144.4 (B-5); –15.1 d, 1 B, ^1J(B,H) = 157.8 (B-10); –21.5 d, 1 B, ^1J(B,H) = 164.3 (B-8); –24.9 d, 1 B, ^1J(B,H) = 142.4 (B-11); –43.8 d, 1 B, ^1J(B,H) = 146.3 (B-7). For $C_{10}H_{19}B_8ClRu$ (362.3) calculated: 9.79% Cl; found: 9.42% Cl.

3-Chloro-1-(η^6*-1,3,5-trimethylbenzene)-isonido-1,2,4-ruthenadicarbaundecaborane* (**4b**). Yield 16 mg, 40%. IR: ν(BH) 2 514; ν(CH_{Ar}) 3 046; ν(C=C_{Ar}) 1 450, 1 082. ^{1}H{^{11}B} NMR (250.13 MHz, CD_2Cl_2; assignments were made by ^{1}H{^{11}B(selective)} NMR experiments): 5.49 s, 3 H (Ar, H-2,4,6); 4.17 br s, 1 H (carborane CH); 3.95 br s, 1 H (carborane CH); 3.72 s, 1 H (H-9); 2.40 s, 1 H (H-5); 2.22 s, 9 H (CH_3); 1.70 s, 2 H (H-6,8); 1.03 s, 1 H (H-10); 0.41 s, 1 H (H-11); –1.76 br s, 1 H (H-7). ^{11}B NMR (80.25 MHz, CD_2Cl_2): 68.3 s, 1 B (B-3); 12.0 d, 1 B, ^1J(B,H) = 151.3 (B-9); 1.2 d, 1 B, ^1J(B,H) = 170.4 (B-6); –1.2 d, 1 B, ^1J(B,H) = 157.7 (B-5); –12.8 d, 1 B, ^1J(B,H) = 155.1 (B-10); –22.3 d, 1 B, ^1J(B,H) = 172.9 (B-8); –27.1 d, 1 B, ^1J(B,H) = 143.7 (B-11); –40.8 d, 1 B, ^1J(B,H) = 145.0 (B-7). ^{13}C{^{1}H,^{11}B} NMR (125.77 MHz, CD_2Cl_2): 111.3 (Ar, C_{ipso}); 95.8 (Ar, CH); 54.9 (carborane CH); 34.8 (carborane CH); 19.0 (CH_3). For $C_{11}H_{21}B_8ClRu$ (376.3) calculated: 35.11% C, 5.63% H, 22.98% B, 9.42% Cl; found: 34.84% C, 5.61% H, 22.98% B, 9.78% Cl.

6-Chloro-1-(η^6*-1,3,5-trimethylbenzene)-isonido-1,2,4-ruthenadicarbaundecaborane* (**5b**). Yield 5 mg, 13%. IR: ν(BH) 2 519; ν(CH_{Ar}) 3 070; ν(C=C_{Ar}) 1 454, 1 073. ^{1}H{^{11}B} NMR (250.13 MHz, CD_2Cl_2; assignments were made by ^{1}H{^{11}B(selective)} NMR experiments): 7.76 s, 1 H (H-3); 5.60 s, 3 H (Ar, H-2,4,6); 4.29 br s, 1 H (carborane CH); 4.11 s, 1 H (H-9); 3.66 br s, 1 H (carborane CH); 2.60 s, 1 H (H-5); 2.18 s, 9 H (CH_3); 1.92 s, 1 H (H-8); 0.71 s, 2 H (H-10,11); –2.33 s, 1 H (H-7). ^{11}B NMR (80.25 MHz, CD_2Cl_2): 61.1 d, 1 B, ^1J(B,H) = 160.0 (B-3); 12.3 d, 1 B, ^1J(B,H) = 145.0 (B-9); 9.6 s, 1 B (B-6); 0.3 d, 1 B, ^1J(B,H) = 145.0 (B-5); –15.5 d, 1 B, ^1J(B,H) = 153.9 (B-10); –21.7 d, 1 B, ^1J(B,H) = 183.1 (B-8); –24.8 d, 1 B, ^1J(B,H) = 147.5 (B-11); –44.1 d, 1 B, ^1J(B,H) = 148.8 (B-7). ^{13}C{^{1}H,^{11}B} NMR (125.77 MHz, CD_2Cl_2): 110.2 (Ar, C_{ipso}); 93.5 (Ar, CH); 48.0 (carborane CH); 32.3 (carborane CH); 19.3 (CH_3). For $C_{11}H_{21}B_8ClRu$ (376.3) calculated: 9.42% Cl; found: 9.80% Cl.

3-Chloro-1-(η^6*-1,4-isopropylmethylbenzene)-isonido-1,2,4-ruthenadicarbaundecaborane* (**4c**). Yield 7 mg, 17%. IR: ν(BH) 2 514; ν(CH_{Ar}) 3 059; ν(C=C_{Ar}) 1 460, 1 084. ^{1}H NMR (400.13 MHz, C_6D_6): 5.51 dd, 1 H, ^3J(AB) = 6.0, ^4J(H,H) = 1.6 (Ar, CH); 5.16 dd, 1 H, ^3J(AB) = 6.0, ^4J(H,H) = 1.4 (Ar, CH); 5.05 dd, 1 H, ^3J(AB) = 6.0, ^4J(H,H) = 1.6 (Ar, CH); 4.70 dd, 1 H, ^3J(AB) = 6.0, ^4J(H,H) = 1.4 (Ar, CH); 4.31 br s, 1 H (carborane CH); 3.61 br s, 1 H (carborane CH); 2.13 septet, 1 H, ^3J(H,H) = 7.0 (iPr, CH); 1.51 s, 3 H (Ar, CH_3); 0.87 d, 3 H, ^3J(H,H) = 7.0 (iPr, CH_3); 0.81 d, 3 H, ^3J(H,H) = 7.0 (iPr, CH_3). ^{11}B NMR (128.33 MHz, C_6D_6): 69.2 s, 1 B (B-3); 13.1 d, 1 B, ^1J(B,H) = 143.3 (B-9); 0.1 d, 2 B, ^1J(B,H) = 143.2 (B-5,6); –13.5 d, 1 B, ^1J(B,H) = 153.7 (B-10); –22.8 d, 1 B, ^1J(B,H) = 167.1 (B-8); –26.8 d, 1 B, ^1J(B,H) = 144.2 (B-11); –41.0 d, 1 B, ^1J(B,H) = 141.3 (B-7). For $C_{12}H_{23}B_8ClRu$ (390.3) calculated: 36.93% C, 5.94% H, 22.16% B, 9.08% Cl; found: 36.60% C, 5.86% H, 22.03% B, 9.13% Cl.

3-Chloro-1-(η^6-benzene)-isonido-1,2,4-ruthenadicarbaundecaborane (**4d**). Yield 18 mg, 51%. IR: ν(BH) 2 524; ν(CH_{Ar}) 3 085; ν($C{=}C_{Ar}$) 1 449, 1 089. ^{1}H NMR (400.13 MHz, C_6D_6): 4.79 s, 6 H (C_6H_6); 4.08 br s, 1 H (carborane CH); 3.56 br s, 1 H (carborane CH). ^{11}B NMR (128.33 MHz, C_6D_6): 70.7 s, 1 B (B-3); 14.2 d, 1 B, ^1J(B,H) = 134.7 (B-9); –0.3 d, 1 B, ^1J(B,H) ≈ 135 (B-6); –0.7 d, 1 B, ^1J(B,H) ≈ 140 (B-5); –12.4 d, 1 B, ^1J(B,H) = 150.0 (B-10); –22.8 d, 1 B, ^1J(B,H) = 164.3 (B-8); –26.2 d, 1 B, ^1J(B,H) = 136.0 (B-11); –41.3 d, 1 B, ^1J(B,H) = 157.3 (B-7). For $C_8H_{15}B_8ClRu$ (334.2) calculated: 28.75% C, 4.52% H, 25.88% B, 10.61% Cl; found: 28.89% C, 4.39% H, 25.67% B, 10.32% Cl.

3-Chloro-1-(η^6-toluene)-isonido-1,2,4-ruthenadicarbaundecaborane (**4e**). Yield 20 mg, 55%. IR: ν(BH) 2 530; ν(CH_{Ar}) 3 080; ν($C{=}C_{Ar}$) 1 459, 1 089. ^{1}H NMR (400.13 MHz, C_6D_6): 5.15 t, 1 H, ^3J(H,H) = 5.8 (Ar, H-4); 5.02 apparently quintet, 2 H, ^3J(H,H) = 5.3 (Ar, H-3,5); 4.84 d, 1 H, ^3J(H,H) = 5.9 (Ar, H-2); 4.68 d, 1 H, ^3J(H,H) = 5.6 (Ar, H-6); 4.14 br s, 1 H (carborane CH); 3.70 br s, 1 H (carborane CH); 1.47 s, 3 H (CH_3). ^{11}B NMR (128.33 MHz, C_6D_6): 69.7 s, 1 B (B-3); 13.5 d, 1 B, ^1J(B,H) = 144.1 (B-9); –0.4 br d, 2 B, ^1J(B,H) = 140.4 (B-5,6); –12.9 d, 1 B, ^1J(B,H) = 156.9 (B-10); –22.8 d, 1 B, ^1J(B,H) = 168.1 (B-8); –26.5 d, 1 B, ^1J(B,H) = 145.7 (B-11); –41.3 d, 1 B, ^1J(B,H) = 137.8 (B-7). For $C_9H_{17}B_8ClRu$ (348.2) calculated: 31.04% C, 4.92% H, 24.83% B, 10.18% Cl; found: 30.78% C, 4.61% H, 24.95% B, 10.33% Cl.

Preparation of Complexes 3-Chloro-1-(η^6-1,2,4,5-tetramethylbenzene)-*isonido*-1,2,4-ruthenadicarbaundecaborane (**4g**) and 6-Chloro-1-(η^6-1,2,4,5-tetramethylbenzene)-*isonido*-1,2,4-ruthenadicarbaundecaborane (**5g**)

To a mixture of 1,2,4,5-tetramethylbenzene (0.5 g, 3.73 mmol), *nido*-carborane **1** (0.04 g, 0.33 mmol) and tmnda (0.14 g, 0.66 mmol) flushed with argon was added 5 ml of 1,2-dichloroethane under stirring and, after 10 min, was added solid **2** (0.32 g, 0.33 mmol) to the resulting solution. The reaction mixture was stirred at reflux for 2 h until the solution became reddish-brown. After cooling, the solvent was evaporated under reduced pressure and the residue was separated by column chromatography on silica gel (40–60 mesh). An orange band eluted from the column using a benzene/hexane (2 : 1) mixture consisted of isomers **4g** and **5g** in the 10 : 1 ratio; it could not be separated into pure isomers either by repeated column or thin-layer chromatography on silica gel of 5–40 mesh. The complexes after recrystallization from a CH_2Cl_2/hexane mixture were characterized as a mixture of isomers by elemental analysis, IR spectra, and multinuclear NMR spectroscopy. Mixture of isomers **4g** and **5g**. Yield 21 mg, 16%. IR: ν(BH) 2 526; ν(CH_{Ar}) 3 050; ν($C{=}C_{Ar}$) 1 440, 1 084. ^{1}H NMR (400.13 MHz, C_6D_6; throughout the data the asterisks indicate the non-overlapped resonances of the minor isomer **5g**): 5.06 s, 2 H (Ar, H-3,6); 4.82* s, 2 H (Ar, H-3,6); 3.96 br s, 1 H (carborane CH); 3.83* br s, 1 H (carborane CH); 3.56 br s, 1 H (carborane CH); 3.35* br s, 1 H (carborane CH); 1.64 s, 6 H (CH_3); 1.60* s, 6 H (CH_3); 1.56* s, 6 H (CH_3); 1.52 s, 6 H (CH_3). ^{11}B NMR (128.33 MHz, C_6D_6): 69.1 s, 1 B (B-3); 63.5* br d, 1 B, ^1J(B,H) = 147.4 (B-3); 12.5 d, 1 B, ^1J(B,H) = 142.4 (B-9); 10.3* s, 1 B (B-6); 1.8 d, 1 B, ^1J(B,H) ≈ 130 (B-6); 0.8 d, 1 B, ^1J(B,H) ≈ 130 (B-5); –12.8 d, 1 B, ^1J(B,H) = 157.6 (B-10); –15.4* br d, 1 B, ^1J(B,H) = 177.9; –22.5 d, 1 B, ^1J(B,H) = 167.8 (B-8); –24.6* d, 1 B; –26.4 d, 1 B, ^1J(B,H) = 142.4 (B-11); –40.4 d, 1 B, ^1J(B,H) = 142.4 (B-7); –43.7* d, 1 B, ^1J(B,H) = 129.4 (B-7). For $C_{12}H_{23}B_8ClRu$ (390.3) calculated: 36.93% C, 5.94% H, 9.08% Cl; found: 36.80% C, 6.07% H, 9.39% Cl.

Preparation of Isomeric Mixture of Complexes 3-Chloro-1-(η^6-hexamethylbenzene)-*isonido*-1,2,4-ruthenadicarbaundecaborane (**4f**) and 6-Chloro-1-(η^6-hexamethylbenzene)-*isonido*-1,2,4-ruthenadicarbaundecaborane (**5f**)

Similarly were reacted hexamethylbenzene (0.5 g, 3.3 mmol) in 8 ml of 1,2-dichloroethane, *nido*-carborane **1** (0.04 g, 0.33 mmol), tmnda (0.14 g, 0.66 mmol) and **2** (0.32 g, 0.33 mmol). The resulting crude mixture of isomers **4f** and **5f** was finally separated by repeated column chromatography on silica gel (5–40 mesh) using 2 : 1 CH_2Cl_2/hexane mixture as eluent. Complex **4f**. Yield 17 mg, 12%. IR: ν(BH) 2 518; ν(C=C_{Ar}) 1 448, 1 083. ^{1}H NMR (400.13 MHz, C_6D_6): 3.57 s, 1 H (carborane CH); 3.31 s, 1 H (carborane CH); 1.56 s, 18 H (CH_3). ^{11}B NMR (128.33 MHz, C_6D_6): 68.7 s, 1 B (B-3); 12.7 d, 1 B, ^1J(B,H) = 146.7 (B-9); 1.6 d, 1 B, ^1J(B,H) ≈ 154 (B-6); 1.1 d, 1 B, ^1J(B,H) ≈ 166.1 (B-5); –12.5 d, 1 B, ^1J(B,H) = 155.5 (B-10); –21.9 d, 1 B, ^1J(B,H) = 159.0 (B-8); –26.6 d, 1 B, ^1J(B,H) = 148.5 (B-11); –41.3 d, 1 B, ^1J(B,H) = 162.5 (B-7). For $C_{14}H_{27}B_8ClRu$ (418.4) calculated: 40.19% C, 6.50% H, 8.47% Cl; found: 40.37% C, 6.73% H, 8.62% Cl. Complex **5f**. Yield 5 mg, 4%. IR: ν(BH) 2 540; ν(C=C_{Ar}) 1 439, 1 073. ^{1}H NMR (400.13 MHz, $(CD_3)_2SO$): 4.10 s, 1 H (carborane CH); 3.71 s, 1 H (carborane CH); 2.09 s, 18 H (CH_3). ^{11}B NMR (128.33 MHz, $(CD_3)_2SO$): 60.5 d, 1 B, ^1J(B,H) = 139.8 (B-3); 11.4 d, 1 B, ^1J(B,H) = 135.3 (B-9); 8.6 s, 1 B (B-6); 1.0 d, 1 B, ^1J(B,H) = 146.0 (B-5); –17.2 d, 1 B, ^1J(B,H) = 144.5 (B-10); –21.2 d, 1 B, ^1J(B,H) = 143.2 (B-8); –25.0 d, 1 B, ^1J(B,H) = 138.1 (B-11); –43.6 d, 1 B, ^1J(B,H) = 132.2 (B-7). For $C_{14}H_{27}B_8ClRu$ (418.4) calculated: 8.47% Cl; found: 8.71% Cl.

Preparation of Diastereomers 3-Chloro-1-(η^6-1,2,4-trimethylbenzene)-*isonido*-1,2,4-ruthenadicarbaundecaborane (**4h′** and **4h″**)

A stirred solution of *nido*-carborane **1** (0.04 g, 0.33 mmol), tmnda (0.14 g, 0.66 mmol) and **2** (0.32 g, 0.33 mmol) in 15 ml of a 2 : 1 mixture of 1,2-dichloroethane and 1,2,4-trimethylbenzene was heated under reflux for 2 h. 1,2-Dichloroethane was evaporated under reduced pressure, and the resulting semisolid residue was twice chromatographed on a column of silica gel (5–40 mesh). The first band eluted from the column with CH_2Cl_2 contained a mixture of PPh_3 and 1,2,4-trimethylbenzene. The second orange band was then eluted with a CH_2Cl_2/hexane (1 : 1) mixture to give inseparable mixture of diastereomeric complexes **4h′** and **4h″** in the 1 : 1 ratio which, after one recrystallization from CH_2Cl_2/hexane, afforded a mixture of the complexes in the same ratio. Mixture of diastereomers **4h′** and **4h″**. Yield 32 mg, 26%. IR: ν(BH) 2 515; ν(CH_{Ar}) 3 066; ν(C=C_{Ar}) 1 435, 1 083. ^{1}H NMR (400.13 MHz, C_6D_6): 5.41 d, 1 H, ^3J(AB) = 5.8 (Ar, CH′); 5.21 d, 1 H, ^3J(AB) = 5.8 (Ar, CH″); 5.20 d, 1 H, ^3J(AB) = 5.8 (Ar, CH′); 5.12 d, 1 H, ^3J(AB) = 5.8 (Ar, CH″); 5.06 s, 1 H (Ar, CH′); 4.90 s, 1 H (Ar, CH″); 4.31 br s, 1 H (carborane CH′); 4.08 br s, 1 H (carborane CH″); 3.76 br s, 1 H (carborane CH′); 3.72 br s, 1 H (carborane CH″); 1.77 s, 3 H (CH_3'); 1.75 s, 3 H (CH_3'); 1.70 s, 3 H (CH_3'); 1.51 s, 3 H (CH_3''); 1.45 s, 3 H (CH_3''); 1.43 s, 3 H (CH_3''). ^{11}B NMR (128.33 MHz, C_6D_6): 68.6 s, 1 B (B-3); 12.7 d, 1 B, ^1J(B,H) = 142.4 (B-9); 0.3 d, 2 B, ^1J(B,H) = 137.3 (B-5,6); –13.2 d, 1 B, ^1J(B,H) = 152.5 (B-10); –22.7 d, 1 B, ^1J(B,H) = 167.8 (B-8); –26.7 d, 1 B, ^1J(B,H) = 129.4 (B-11); –40.8 d, 1 B, ^1J(B,H) = 147.4 (B-7). For $C_{11}H_{21}B_8ClRu$ (376.3) calculated: 35.11% C, 5.63% H, 22.98% B, 9.42% Cl; found: 35.19% C, 5.74% H, 23.18% B, 9.65% Cl.

Preparation of 1,1,3-$(PPh_3)_3$-1-H-1,2,4-$RuC_2B_8H_9$ (**8**)

To a stirred solution of **1** (0.013 g, 0.106 mmol) and tmnda (0.045 g, 0.21 mmol) in 10 ml benzene was added solid **2** (0.1 g, 0.104 mmol) in one portion. The resulting mixture was stirred at room temperature for 4 h, while the colour of the solution became purple. The solvent was removed, and the residue was chromatographed on silica gel (40–60 mesh). The purple band was eluted with $CHCl_3$, followed by recrystallization of the crude product from CH_2Cl_2/hexane, affording pure complex **8** as reddish-brown crystalline solid. Yield 90 mg, 86%. ^{1}H NMR (400.13 MHz, CD_2Cl_2): 7.89, 7.60, 7.42, 7.13, 7.02, 6.98–6.94, 6.88 set of br apparently t + m, 45 H (3 × Ph_3P); 2.96 br s, 1 H (carborane CH); 1.26 br s, 1 H (carborane CH); –3.45 apparent octet, 1 H (RuH). ^{31}P NMR (161.98 MHz, CD_2Cl_2): 57.9 d, 1 P, ^1J(P,P) = 22.9 (Ph_3P-Ru, P_1); 45.61 d, 1 P, ^1J(P,P) = 22.9 (Ph_3P-Ru, P_2); 14.6 q-like, 1 P, ^1J(P,B) = 137.4 (Ph_3P-B, P_3). ^{11}B NMR (128.33 MHz, CD_2Cl_2): 35.2 d, 1 B, ^1J(B,P) = 137.0; 6.05 d, 1 B, ^1J(B,H) = 142.5; 0.03 br d, 1 B, ^1J(B,H) ≈ 154; –5.4 d, 1 B, ^1J(B,H) = 129.4; –18.3 br d, 1 B, ^1J(B,H) ≈ 122; –22.9 br d, 1 B, ^1J(B,H) = 166.8; –27.5 d, 1 B, ^1J(B,H) = 142.5; –41.8 d, 1 B, ^1J(B,H) = 129.3. For $C_{56}H_{55}B_8P_3Ru$ (1 008.5) calculated: 66.69% C, 5.50% H, 8.57% B, 9.21% P; found: 66.56% C, 5.73% H, 8.58% B, 9.10% P.

Crystallographic Study of Complex **4b**

Single crystals of **4b** suitable for X-ray diffraction were slowly grown from the mixture of CH_2Cl_2/hexane. At 293 K crystal of **4b** ($C_{11}H_{21}B_8ClRu$) is orthorhombic, space group *Pbca*, a = 15.394(5) Å, b = 13.495(4) Å, c = 15.927(4) Å, V = 3 309(2) Å^3, Z = 8, M = 376.28, F(000) = 1 504, d_{calc} = 1.511 g/cm^3, μ(MoKα) = 10.91 cm^{-1}. Intensities of 5 235 independent reflections were measured on an Enraf Nonius CAD4 diffractometer at 293(2) K (λ(MoKα) = 0.71073 Å, θ–5/3θ scan technique, 2θ < 62°). The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were located based on the Fourier synthesis and refined in the isotropic approximation. The refinement converged to wR_2 = 0.0690 and GOF = 1.031 for all independent reflections (R_1 = 0.0244 was calculated against F for 3 876 observed reflections with $I > 2\sigma(I)$). Data reduction and further calculations were performed using the SHELXTL97 program package[17].

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