Inorg. Chem. **2005**, *44*, 1655–1659

Inorganic Chemistry

Article

Synthesis and Rearrangements of Aminosubstituted Ferra- and Ruthenatricarbaboranes

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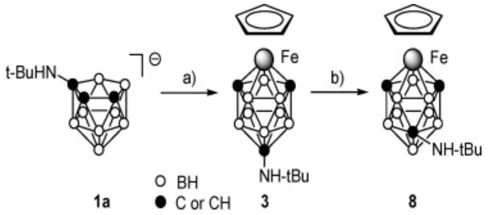
Received November 18, 2004

A room-temperature reaction between the [7-^{t}BuNH-*nido*-7,8,9-$C_3B_8H_{10}$]$^-$ anion (**1a**) and [Cp*RuCl]$_4$ leads to the ruthenatricarbollide [1-Cp*-12-^{t}BuNH-1,2,4,12-$RuC_3B_8H_{10}$] (**2**) (yield 85%). Analogously, the room-temperature photochemical reaction of **1a** with [CpFe(C_6H_6)]PF_6 gives the previously reported iron complex [1-Cp-12-^{t}BuNH-1,2,4,12-$FeC_3B_8H_{10}$] (**3**) (yield 82%). Both reactions are associated with extensive polyhedral rearrangement, which occurs under very mild conditions and brings the carbon atoms to positions of maximum separation within the framework. Compounds **2** and **3** were also surprisingly obtained via complexation of the isomeric [8-^{t}BuNH-*nido*-7,8,9-$C_3B_8H_{10}$]$^-$ (**1b**) anion. Complex **2** rearranges further to [1-Cp*-10-^{t}BuNH-1,2,4,10-$RuC_3B_8H_{10}$] (**4**) upon refluxing in xylene (145 °C). Density functional theory calculations at the B3LYP/SDD level were used to estimate relative stabilities of these metallacarborane isomers. Compounds **2** and **4**, along with the 11-vertex closo compounds [1-Cp*-1,2,3,10-$RuC_3B_7H_{10}$] (**5**) and [1-Cp*-10-^{t}BuNH-1,2,3,10-$RuC_3B_7H_9$] (**6**), were also isolated from the reaction between [Cp*$RuCl_2$]$_2$ and **1a** in boiling xylene. The structure of **2** was established by an X-ray diffraction study, and the constitution of all compounds was determined unambiguously by multinuclear NMR spectroscopy, mass spectrometry, and elemental analyses.

Introduction

It was reported[1] that the reaction between [CpFe$(CO)_2$I] and [7,8,9-$C_3B_8H_{11}$]$^-$ in refluxing toluene results in the formation of [1-Cp-1,2,4,10-$FeC_3B_8H_{11}$] (**7**) as the main reaction product. In contrast, a similar reaction of the aminosubstituted analogue, [7-^{t}BuNH-7,8,9-$C_3B_8H_{10}$]$^-$ (**1a**), gives the cage-isomeric ferratricarbollide [1-Cp-12-^{t}BuNH-1,2,4,12-$FeC_3B_8H_{10}$] (**3**) (see path a of Scheme 1).[2] The formation of **3** is associated with an extensive rearrangement that moves the cluster carbons into positions of maximum space separation within the 12-vertex *closo*-FeC_3B_8 cage. Complex **3**, containing the substituted cage carbon atom in the para position with respect to the Fe center, can be converted into the thermodynamically more stable meta isomer, [1-Cp-10-^{t}BuNH-1,2,4,10-$FeC_3B_8H_{10}$] (**8**) (derivative of the unsubstituted compound **7**), via thermal rearrangement at high temperatures (path b of Scheme 1).[3] A general feature of the rearrangement−complexation reactions outlined above is that they must be thermally induced, which applies to most

Scheme 1. Formation of Isomeric Ferratricarbollides via Rearrangement−Complexation and Thermal Isomerization[a]



[a] Key: (a) [CpFe(C_6H_6)]PF_6, CH_2Cl_2, visible light irradiation, room temperature (this work) or CpFe$(CO)_2$I, xylene reflux, see ref 2. (b) Mesitylene, reflux, see ref 3.

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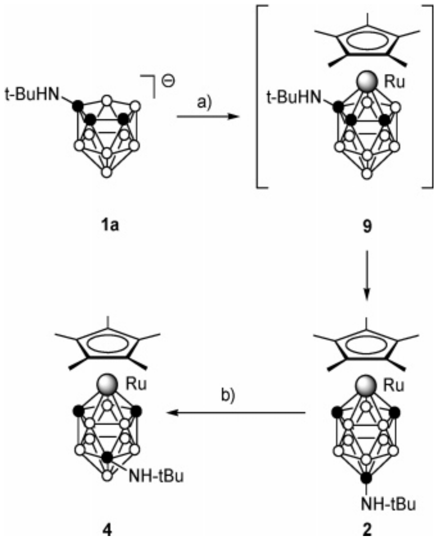
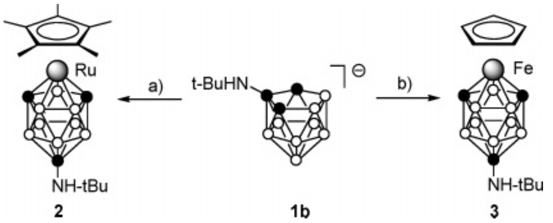
10.1021/ic0483702 CCC: $30.25

Scheme 2. Schematic Representation of Ru-complexation Reactions[a]



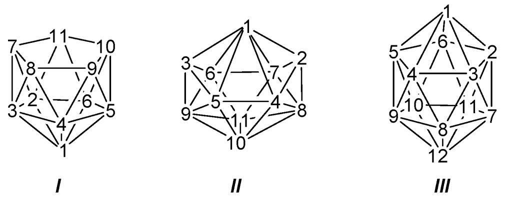
[a] Key: (a) $[Cp^*RuCl]_4$, THF, room temperature. (b) *m*-Xylene, reflux.

Scheme 3. Schematic Representation of the Reactions of the **1b**$^-$ Anion[a]



[a] Key: (a) $[Cp^*RuCl]_4$, THF, room temperature. (b) $[CpFe(C_6H_6)]PF_6$, CH_2Cl_2, visible light rrradiation, room temperature.

of the metal-complexation reactions in the 11-vertex carborane series.[4,5] Nevertheless, there are a few examples of low-temperature isomerizations, facilitated by bulky substituents on the cage carbon atoms.[6] Herein, we report *room-temperature* Fe and Ru rearrangement−complexation reactions that involve the isomeric anions **1a** and $[8\text{-}^t\text{BuNH-7,8,9-}C_3B_8H_{10}]^-$ (**1b**). The work is also complemented by the characterization of two 11-vertex ruthenatricarbaboranes of a new 1,2,3,10-MC_3B_7 cluster configuration. The numbering system for the 11-vertex nido and closo and 12-vertex closo tricarbaborane cages discussed in this work is in general structures ***I***, ***II***, and ***III***, respectively.



Results and Discussion

Syntheses. As shown in Scheme 2, a room-temperature reaction between $[Cp^*RuCl]_4$ and Tl**1a** in THF, reasonably supposed to proceed via a nonisolable $[1\text{-Cp}^*\text{-2-}^t\text{BuNH-}$*closo*-1,2,3,4-$RuC_3B_8H_{10}]$ intermediate (**9**) (path a), leads in high yield (85%) to a single isomer of constitution $[1\text{-Cp}^*\text{-12-}^t\text{BuNH-}$*closo*-1,2,4,12-$RuC_3B_8H_{10}]$ (**2**). It should be noted that the reaction is extremely clean and no other metallacarborane products were detected in the reaction mixture. It is readily seen that the formation of **2** is associated with an extensive polyhedral rearrangement of high regioselectivity, in which the substituted carbon vertex is moved into the para position with respect to the Ru vertex. Analogous to the previously reported iron complex **3**, heating of ruthenatricarbollidecarborane **2** in refluxing xylene (145 °C) for 6 h leads to further rearrangement to give $[1\text{-Cp}^*\text{-10-}^t\text{BuNH-}$*closo*-1,2,4,10-$RuC_3B_8H_{10}]$ (**4**) (yield 72%, path b).

This reaction sequence thus exactly copies that established for the analogous iron complexes **3** and **8**,[2] except that the first rearrangement−complexation step proceeds spontaneously at *room temperature*. The main reason for this difference is that, in the case of iron complexation, the reaction must be thermally induced to eliminate CO from the starting $[CpFe(CO)_2I]$ in the reactions with **1a**.[2] By use of photochemical generation of the $[CpFe]^+$ fragment from the benzene complex $[CpFe(C_6H_6)]PF_6$, we were able to obtain **3** in 82% yield at room temperature (see Scheme 1, path a). As compound **3** is now becoming one of essential synthons of metallatricarbollide chemistry,[7] this method therefore represents a significant improvement in this area.

To get further insights into the mechanisms of the rearrangement−complexation processes, we have also examined the reactions of $[Cp^*RuCl]_4$ and $[CpFe(C_6H_6)]PF_6$ with the isomeric 8-aminosubstituted anion **1b**.[8] (see Scheme 3). Surprisingly, in both cases, the corresponding compounds **2** and **3** were obtained, the same as in the reactions of **1a**. The rearrangement is again very clean, and no other metallacarborane isomers were detected in the reaction mixture. Although these results do not allow us to elucidate the mechanism of the rearrangement process, they unambiguously confirm a greater preference for the formation of the 1,2,4,12-MC_3B_8 cluster isomer. This is also rather surprising as this isomer is not the most thermodynamically stable.[3]

To estimate the relative stabilities of the isomers with different positions of carbon atoms, we carried out density functional theory calculations at the B3LYP/SDD level on the parent ruthenatricarbollides of general formula $CpRuC_3B_8H_{11}$. The 1,2,4,10-isomer (analogue of **4**) was shown to be 6.27 kcal·mol^{-1} more stable than the 1,2,4,12-isomer (analogue of **2**) and 31.16 kcal·mol^{-1} more stable than the carbon-adjacent 1,2,3,4-isomer (analogue of **9**). The results correlate

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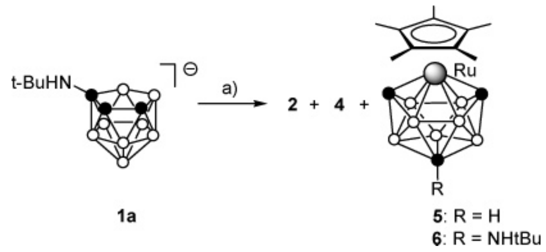
Scheme 4. Schematic Representation of Complexation via $[Cp^*RuCl_2]_2$[a]



[a] Key: (a) $[Cp^*RuCl_2]_2$, xylene, reflux.

nicely with the observed isomerization sequence of Scheme 2. The instability of **9** is easily explained by Coulomb repulsion among negatively charged carbon atoms, which is apparently the main driving force of the polyhedral rearrangement.

The reaction of Tl**1a** with $[Cp^*RuCl_2]_2$ in refluxing xylene also gives both compounds **2** and **4** in 3 and 10% yields, respectively (Scheme 4). However, this reaction in addition generates the two 11-vertex closo complexes [1-Cp*-1,2,3,-10-$RuC_3B_7H_{10}$] (**5**) (yield 3%) and [1-Cp*-10-^{t}BuNH−1,2,3,10-$RuC_3B_7H_9$] (**6**) (yield 4%). The formation of complexes **5** and **6** seems to be a consequence of B3 removal in structure **4**, followed by oxidative closure of the open pentagonal face thus generated by excess of $[Cp^*RuCl_2]_2$. It should be noted that 1,2,3,4-cage isomers of the Ru compounds **5** and **6** have also been prepared.[9]

Structural Studies. The structures of compound **2** was determined by single-crystal X-ray diffraction analysis, and all compounds isolated were characterized by ^{1}H and ^{11}B NMR spectroscopy, mass spectrometry, and elemental analysis. The structure of **2**, shown in Figure 1, confirms cluster constitution that is entirely analogous to that reported earlier[2] for the Fe analogue **3**.

The substituted carbon atom C12 is situated in the para position with respect to the metal center while the cage carbon atoms, C2 and C4, lie in the metal-bonded C_2B_3 face. The Cp* and C_2B_3 ligand planes are essentially parallel (dihedral angle 3.0°), adopting a semi-staggered conformation (torsion angle 21°). The Ru···C_2B_3(centroid) distance (1.58 Å) is slightly shorter than that in the related dicarbollide complex $[3\text{-}Cp^*\text{-}3,1,2\text{-}RuC_2B_9H_{11}]^-$ (1.60 Å),[10] while the Ru···Cp*(centroid) distance (1.82 Å) is the same.

The NMR spectra of all compounds isolated in this study were completely assigned using [^{11}B−^{11}B] correlation spectroscopy (COSY)[11] and ^{1}H−{^{11}B(selective)}[12] NMR techniques and are entirely in agreement with the structures proposed. Simplified stick diagrams in Figure 2 show graphical intercomparison between the ^{11}B NMR shifts for the previously reported ferratricarbollides **3** and **8** and those for the structurally related ruthenatricarbollides **2** and **4** prepared in this work. It is clearly seen that the ^{11}B NMR spectra of the compounds **2** and **3** (cluster constitution *closo*-1,2,4,12-MC_3B_8) exhibit very similar 2:1:2:1:2 patterns, in comparison to the spectra of the cage isomeric compounds **4** and **8** (cluster constitution *closo*-1,2,4,10-MC_3B_8) that display 2:1:1:2:2 behavior.

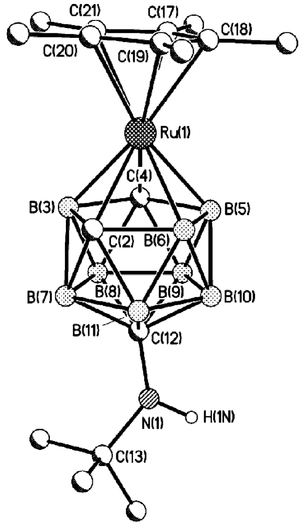


Figure 1. The molecular structure of **2**. Selected interatomic distances (Å): Ru1−C2, 2.177(5); Ru1−C4, 2.147(5); Ru1−B3, 2.168(6); Ru1−B5, 2.1535; Ru1−B6, 2.160(6); C12−N1, 1.439(5); C13−N1, 1.455(6).

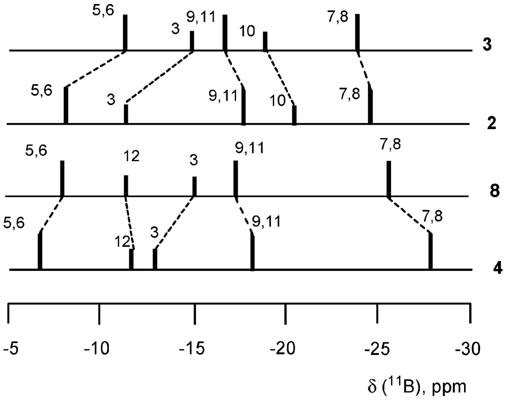


Figure 2. Simplified stick representation of the ^{11}B NMR shifts and NMR comparisons between Fe and Ru metallatricarbollides of closo configurations 1,2,4,12-MC_3B_8 (compounds **2** and **3**) and 1,2,4,10-MC_3B_8 (compounds **4** and **8**).

Figure 3 shows a graphical correlation of the ^{11}B NMR shifts for the structurally characterized[7b] 11-vertex iron complex [1-Cp-*closo*-1,2,3,10-$FeC_3B_7H_{10}$] (**10**) (2:2 + 2:1 patterns) with those for the unsubstituted compound **5** and the aminoderivative **6** that exhibit a very similar 2:2:2:1 or 2:2 + 2:2:1 behavior. It is readily seen that the 10-^{t}BuNH substitution in **6** causes a downfield shift of the ^{11}B11 resonance by ca. 10 ppm. The spectra of compounds of type **5** are consistent with a new C_s symmetry *closo*-1,2,3,10-$MC_3B_7H_{10}$ cage, which is isomeric to that found for the parent 1-Cp-*closo*-1,2,3,4-$FeC_3B_7H_{10}$][1] and its 2-substituted derivatives.[13]

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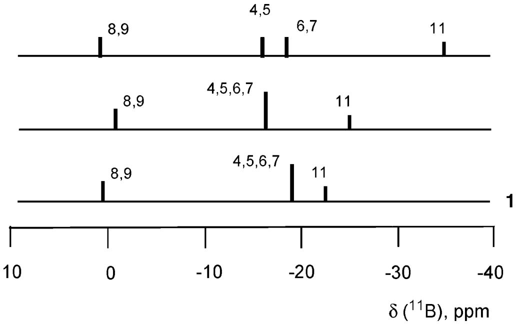

Figure 3. Simplified stick representation of the ^{11}B NMR shifts and NMR comparisons between **9** and its Ru analogues **5** and **6**. Data for compound **10** from ref 7b.

Because of the C_s symmetry, the ^{1}H NMR spectra of all compounds isolated show a single-intensity resonance assigned to the cage CH units. Accordingly, the ^{13}C NMR spectra of the 12-vertex ruthenatricarbollides **2** and **4** display 2:1 patterns, with a remarkable downfield shift of resonances due to substituted carbon vertexes. Mass spectra of all compounds display the expected molecular cutoffs in their parent envelops except for **6**, which shows fragmentation consistent with splitting off the ^{t}Bu group.

In summary, we have shown that the complexation of the [Cp*Ru]$^+$ fragment with the substituted tricarbollide anions **1a** and **1b** proceeds easily even at room temperature and shows close parallels to that of the [CpFe]$^+$ cation.[2] The complexation is evidently directed by the steric and electronic effects of the ^{t}BuNH substituent on the tricarbollide core and results in an extensive polyhedral rearrangement to give only a single para isomer **2**. As in the corresponding ferratricarbollide series,[3] this isomer can be smoothly rearranged to the more thermodynamically stable meta isomer **4**. In both isomers, **2** and **4**, the cage carbon atoms reside in mutual meta positions.

Experimental Section

Material and Methods. All the reactions were carried out under argon atmosphere, although the isolation of products was conducted in air. The starting materials [Cp*RuCl]$_4$,[14] [Cp*RuCl$_2$]$_2$,[15] Tl**1a**,[2] NBu$_4$**1a**,[2] and NBu$_4$**1b**[8] were prepared by literature procedures or slight modifications thereof. Proton (^{1}H), boron (^{11}B), and carbon (^{13}C) NMR spectroscopy was performed on Bruker AMX-400, Varian XL-500, and Varian MERCURY 400 instruments. The [^{11}B$-^{11}$B] COSY[11] and ^{1}H$-\{^{11}$B(selective)$\}$[12] NMR experiments were essentially as described in other related papers from our laboratories.[16] Chemical shifts are given in ppm to high frequency (low field) of $\Xi = 32.083\,971$ MHz (nominally F$_3$B·OEt$_2$ in CDCl$_3$) for ^{11}B (quoted ±0.5 ppm) and $\Xi = 100$ MHz (SiMe$_4$) for ^{1}H (quoted ±0.05 ppm), Ξ defined as in ref 17. It should be noted that compounds **2** and **4**, though stable in the solid state, are slightly air sensitive in solutions.

2: Method A. A mixture of [Cp*RuCl]$_4$ (82 mg, 0.075 mmol) and Tl**1a** (122 mg, 0.3 mmol) in THF (5 mL) was stirred overnight at room temperature. The resulting light-yellow solution was filtered and evaporated to dryness in vacuo at room temperature. The residue was dissolved in a CH$_2$Cl$_2$/petroleum ether (1:2) mixture and filtered through a thin layer (3 cm) of silica gel. The filtrate was evaporated to dryness to give small, light-yellow crystals of **2** (112 mg, 85%). Alternatively, [Cp*RuCl]$_4$ was generated in situ by reduction of [Cp*RuCl$_2$]$_2$ (92 mg, 0.15 mmol) with Zn dust (100 mg, excess) in THF for 1 h followed by addition of Tl**1a**. For **2**: R_f 0.34 (hexane$-$CH$_2$Cl$_2$ 3:1); ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) δ 2.71 (s, 1 H, H3), 2.38 (s, 2 H, H9,11), 2.20 (s, 2 H, H7,8), 1.86 (s, 1 H, H10), 1.83 (s, 15 H, Cp* methyls), 1.81 (br.s, 2 H, H2,4, cage CH), 1.25 (s, 9 H, ^{t}Bu), 2.27 (s, 1 H, NH); ^{11}B NMR (128 MHz, CDCl$_3$, 25 °C) δ -9.3 (d, ^1J(B,H) $= 149$ Hz, 2 B, B6,11), -12.9 (d, ^1J(B,H) $= 164$ Hz, 1 B, B3), -18.6 (d, ^1J(B,H) $= 171$ Hz, 2 B, B9,11), -21.8 (d, ^1J(B,H) $= 156$ Hz, 1 B, B10), -25.7 (d, ^1J(B,H) $= 171$ Hz, 2 B, B7,8); ^{13}C$\{^1$H$\}$NMR (100.6 MHz, CDCl$_3$, 25 °C) 92.0 (s, 5 C, Cp* ring), 62.3 (br.s, 1 C, C12), 54.6 (s, 1 C, ^{t}Bu), 40.8 (br.s, 2 C, C2,4), 30.7 (s, 3 C, ^{t}Bu), 10.4 (s, 5 C, Cp* methyls); MS (70 eV, EI), m/z (%) 442 (44) [M]$^+$, 441 (50) [M $-$ H]$^+$; C$_{17}$H$_{35}$B$_8$NRu calcd. C 46.30, H 8.00, B 19.61; found C 46.69, H 7.80, B 19.82.

2: Method B. Similar reaction of [Cp*RuCl]$_4$ (54 mg, 0.05 mmol) with NBu$_4$[8-^{t}BuNH-7,8,9-C$_3$B$_8$H$_{10}$] (89 mg, 0.2 mmol) in THF at room temperature followed by the isolation as described above gives **2**, as identified by its ^{1}H and ^{11}B NMR spectra (86 mg, 98%).

3: Method A. A mixture of NBu$_4$**1a** (67 mg, 0.15 mmol) and [CpFe(C$_6$H$_6$)]PF$_6$ (52 mg, 0.15 mmol) in 8 mL of CH$_2$Cl$_2$ was irradiated with stirring at room temperature for 4 h, resulting in color change from yellow to orange-red. The mixture was evaporated to dryness, and the residue was dissolved in CH$_2$Cl$_2$/petroleum ether (1:2) mixture and filtered through a thin layer (3 cm) of silica gel. The orange band was collected and evaporated to give 40 mg (82%) of **3** as orange-red crystals. ^{1}H$\{^{11}$B$\}$ NMR (400 MHz, CDCl$_3$, 25 °C) 1.15 (9H, ^{t}Bu), 1.24 (1H, NH) 2.03 (2H, CH-carb.), 4.52 (5H, Cp); ^{11}B$\{^1$H$\}$NMR (400 MHz, CDCl$_3$, 25 °C) -23.30, -18.45, -16.26, -14.67, -10.72 (2:1:2:1:2) (cf. ref 2).

3: Method B. A similar reaction between NBu$_4$**1b** (89 mg, 0.2 mmol) and [CpFe(C$_6$H$_6$)]PF$_6$ (69 mg, 0.2 mmol) carried out as in the preceding experiment gave 61 mg (90%) of **3**.

4: A solution of compound **2** (66 mg, 0.15 mmol) in *m*-xylene (5 mL) was heated at reflux for 6 h and then evaporated to dryness in vacuo. The residue was dissolved in a CH$_2$Cl$_2$/petroleum ether (1:2) mixture and eluted through a thin layer (3 cm) of silica gel. The filtrate was evaporated to give a light-yellow powder of pure **4** (48 mg, 72%). The analytically pure sample was obtained by crystallization from pentane at -78 °C. For **4**: R_f 0.25 (hexane$-$CH$_2$Cl$_2$ 3:1); ^{1}H$\{^{11}$B$\}$ NMR (400 MHz, CDCl$_3$, 25 °C) δ 3.41 (s, 1 H, H9), 2.62, (s, 1 H, H3), 2.43 s, 2 H, H9,11), 2.45 (s, 2 H, H6,11), 1.92 (s, 15 H, C$_5$Me$_5$), 1.82 (s, 2 H, cage CH), 1.42 (s, 2 H, H7,8), 1.13 (s, 9 H, ^{t}Bu); ^{11}B NMR (160 MHz, CDCl$_3$, 25 °C) δ -6.5 (d, ^1J(B,H) $= 162$ Hz, 2 B, B6,11), -11.6 (d, ^1J(B,H) $= \sim 170$ Hz, 1 B, B9), -12.8 (d, ^1J(B,H) $= \sim 160$ Hz, 1 B, B3), -18.3 (d, ^1J(B,H) $= 171$ Hz, 2 B, B9,11), -27.7 (d, ^1J(B,H) $= 156$ Hz, 2 B, B7,8); ^{13}C$\{^1$H$\}$ NMR (100.6 MHz, CDCl$_3$, 25 °C) 93.1 (s, 5 C, Cp* ring), 67.1 (br.s, 1 C, C10), 54.3 (s, 1 C, ^{t}Bu), 37.0 (br.s, 2 C, C2,4), 30.5 (s, 3 C, ^{t}Bu), 10.5 (s, 5 C, Cp* methyls); MS (70 eV, EI), m/z (%) 442 (45) [M]$^+$, 441 (50) [M $-$ H]$^+$; C$_{17}$H$_{35}$B$_8$NRu (441.09) calcd. C 46.28, H 8.00; found C 45.71, H 7.68.

6: To a suspension of Tl**1a** (300 mg, 0.73 mmol) in xylene (25 mL), [Cp*RuCl$_2$]$_2$ (225 mg, 73 mmol) was added, and the mixture

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was heated at reflux for 10 h. After the mixture was cooled to room temperature, the solvent was evaporated and the solid residue extracted by three 20-mL portions of CH_2Cl_2. The combined extracts were filtered, and the solvent was evaporated. The residue was dissolved in CH_2Cl_2 (3 mL) and placed onto a top of a silica gel column (1.5 × 15 cm), and the dark-yellow mixture of products was eluted under nitrogen using the same solvent. Preparative thin-later chromatography separation in hexane−CH_2Cl_2 (3:1) gave four yellow bands (R_f 0.75, 0.67, 0.34, and 0.25), which were mechanically separated, extracted with CH_2Cl_2, and evaporated to obtain yellow solids. Two compounds of highest R_f were characterized as the 11-vertex compounds **5** (8 mg, 3%) and **6** (12 mg, 4%). For **5**: R_f (C_6H_6−hexane 1:2) 0.57; ^{1}H{^{11}B} NMR (500 MHz, $CDCl_3$, 25 °C) δ 3.82 (s, 2H, H2,4, cage CH), 3.22 (H8,9), 1.79 (s, 15H, Cp* methyls), 1.64 (s, 1H, H10, cage CH), 1.09 and 1.06 (s, 2H, H4,5 and H6,7), 0.22 (s, H11); ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C) δ 1.16 (d, ^{1}J(B,H) = 165 Hz, 2B, B8,9), −17.2 (d, ^{1}J(B,H) = 146 Hz, 2B, B4,5), −19.6 (d, ^{1}J(B,H) = 158 Hz, 2B, B6,7), −35.1 (d, ^{1}J(B,H) = 156 Hz, 1B, B11); MS (70 eV, EI), m/z (%) 361 (42) $[M]^+$, 359 (100) $[M^+ - 2H]$. For **6**: R_f (C_6H_6−hexane 1:2) 0.52; ^{1}H{^{11}B} NMR (500 MHz, $CDCl_3$, 25 °C) δ 3.72 (s, 2H, H2,3, cage CH), 3.48 (s, 2H, H8,9), 1.78 (s, 15H, Cp* methyls), 1.45 and 1.28 (s, 2H, H4,5 and H6,7), 1.34 (s, H11), 1.06 (s, 9H, ^{t}Bu); ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C) δ −0.5 (d, ^{1}J(B,H) = 164 Hz, 2B, B8,9), −16.2 (d, ^{1}J(B,H) = 147 Hz, 4B, B4,5,6,7), −24.9 (d, ^{1}J(B,H) = 153 Hz, 1B, B11); MS (70 eV, EI), m/z (%) 377 (45) $[M^+ - {}^tBu + H]^+$, 374 (100) $[M^+ - {}^tBu - 2H]^+$, 359 (35) $[M^+ - {}^tBuNH]$. Other two compounds were identified as **2** (10 mg, 3%) and **4** (33 mg, 10%).

X-ray Crystallographic Studies. Crystals of **2** ($C_{17}H_{35}B_8NRu$, M = 441.01) are monoclinic, space group $P2_1/n$, at 120 K: a = 11.886(3) Å, b = 11.096(3) Å, c = 16.474(4) Å, β = 90.044(5)°, V = 2172.6(10) Å^3, Z = 4 (Z' = 1), d_{calcd} = 1.348 g cm^{-3}, μ(Mo Kα) = 7.24 cm^{-1}, F(000) = 912. Intensities of 13 850 reflections were measured with a Smart charge-coupled device diffractometer [λ(Mo Kα) = 0.710 72 Å, ω scans, $2\theta < 58°$] and 5 625 independent reflections [R_{int} = 0.0792] were used in further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic−isotropic approximation. Hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation. The analysis of systematic absences and the R_{int} value have revealed that, despite the fact that the β angle is close to 90°, the crystal of **2** is monoclinic. The account of twining law (TWIN 0 1 0 1 0 0 0 0 −1) lead to a significant decrease of the R factor (BASF parameter was equal to 0.433). Thus we can conclude that **2** is a twin of monoclinic crystals emulating the orthorhombic one. The refinement of **3** converged to wR2 = 0.0897 and GOF = 1.071 for all independent reflections (R1 = 0.0419 was calculated against F for 4190 observed reflections with $I > 2\sigma(I)$). All calculations were performed using SHELXTL PLUS 5.0 on IBM PC AT.[18] Atomic coordinates, bond lengths, angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center (CCDC). CCDC-245427 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax + 44-1223/336-033; e-mail deposit@ccdc.cam.ac.uk.

Calculation Details. All calculations were performed using Gaussian 98W (Revision A7) package.[19] The geometries were optimized at B3LYP/SDD level with C_s symmetry restriction. Frequency calculations were performed to confirm the global minimum. Single-point energies were calculated at B3LYP/SDD level including ZPE corrections.

Acknowledgment. This work was supported by the Grant Agency of the Czech Republic (Grant No. 203/05/2646) and by the program for fundamental research of the Division of General Chemistry and Material Sciences of the RAS (Grant No. 05-07). We thank Dr. M. G. S. Londesborough for helpful discussion and interest in this work.

Supporting Information Available: X-ray crystallographic file for the structure determination of **2** and Calculation details for three $[CpRuC_3B_8H_{11}]$ isomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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