Small Metallacarborane *closo*-$C_2B_4H_6Ru(PPh_3)_2HCl$ Formed from *nido*-5,6-$C_2B_8H_{12}$ by Ruthenium-Mediated Polyhedral Contraction

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$RuCl_2(PPh_3)_3$ (**1**), when heated with an equimolar amount of *nido*-5,6-$C_2B_8H_{12}$ (**2**) in toluene for a few hours, effected rather unexpected polyhedral contraction of **2** to give the new half-sandwich small ruthenacarborane *closo*-$C_2B_4H_6Ru(PPh_3)_2HCl$ (**3**) in moderate yield along with minor amounts of the two isomeric 11-vertex ruthenacarboranes [3-Cl-1-(η^6-C_6H_5Me)-1,2,4-$RuC_2B_8H_9$] (**4**) and [6-Cl-1-(η^6-C_6H_5Me)-1,2,4-$RuC_2B_8H_9$] (**5**) with open MC_2B_8 cluster structure. These new complexes were characterized by ^1H, ^{13}C, and ^{11}B NMR spectroscopy and, in the case of **3** and **5**, also by an X-ray crystal structure analysis.

Introduction

Polyhedral contraction, first introduced into metallacarborane chemistry by Hawthorne,[1] paved the way for the synthesis of a number of structurally novel metallacarborane clusters which, at least in some cases, are otherwise inaccessible.[2] Some limitations of this synthetic method, however, result from noticeable decomposition of starting metallacarboranes as well as side reactions which are frequently observed at conditions normally employed for their partial degradation (base or thermal).[3] It has also been demonstrated that some simple transition metal complexes when reacted thermally or at ambient temperature with anionic *arachno*-C_2B_7[4] or *nido*-C_2B_9[5] carboranes as well as certain 1,2-substituted derivatives of a neutral *closo*-1,2-C_2B_{10} carborane[6] were able to promote their partial degradation to give metallacarboranes with one boron vertex fewer than in the parent polyhedra. Previously,[7] we reported a rare example of an extensive polyhedral contraction reaction of a monocarbon *nido*-carborane $[nido\text{-}B_{10}H_{12}CH]^-Cs^+$ effected by $RuCl_2(PPh_3)_3$ (**1**), which resulted in electron-deficient *hyper-closo*-ruthenacarboranes of $RuCB_8$ and $RuCB_6$ cluster structure. We now wish to report a novel application of **1** as a promoter for degradative removal of four polyhedral {BH} vertexes from neutral *nido*-$C_2B_8H_{12}$ (**2**).

Results and Discussion

It was previously known that unsubstituted mono- and dimethylated dicarba derivatives of **2**, usually taken or in situ generated as anionic salts, react with either monomeric or dimeric ruthenium complexes such as $Ru(PPh_3)_3HCl$[8] or $[Ru(Ar)Cl_2]_2$ (Ar = C_6Me_6, MeC_6H_4-*i*-Pr),[9] yielding exclusively *isonido*-type RuC_2B_8 clusters with a quadrilateral open face. Contrary to these reactions, the treatment of a neutral *nido*-carborane **2** with $RuCl_2(PPh_3)_3$ under heating in toluene has been found to afford the half-sandwich small ruthenacarborane cluster *closo*-1,1-$(PPh_3)_2$-1-H-1-Cl-1,2,3-$RuC_2B_4H_6$ (**3**) in isolable yield of up to 16.8% (Scheme 1). In addition, two positional chloro-substituted isomers derived from the 11-vertex *isonido*-RuC_2B_8 cluster, [3-Cl-1-(η^6-C_6H_5Me)-1,2,4-$RuC_2B_8H_9$] (**4**) and [6-Cl-1-(η^6-C_6H_5Me)-1,2,4-$RuC_2B_8H_9$] (**5**), were isolated from the reaction as minor products in 7 and 4% yields, respectively.

Complex **3** was obtained as an air-stable light yellow crystalline solid, and its solid state structure was determined by an X-ray diffraction study, which proved this species to be a small 7-vertex *closo*-ruthenacarborane (Figure 1), in agreement with NMR spectroscopic

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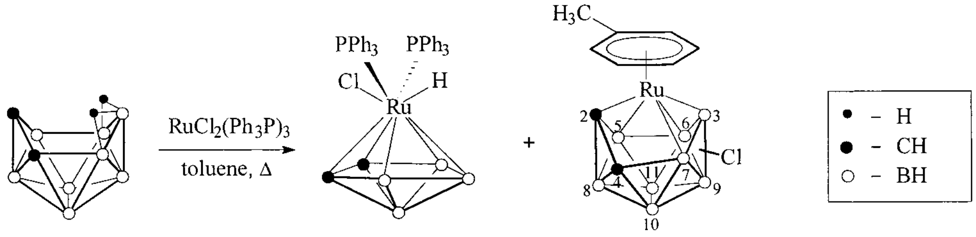
Scheme 1



(**2**) (**3**) 3-Cl (**4**); 6-Cl (**5**)

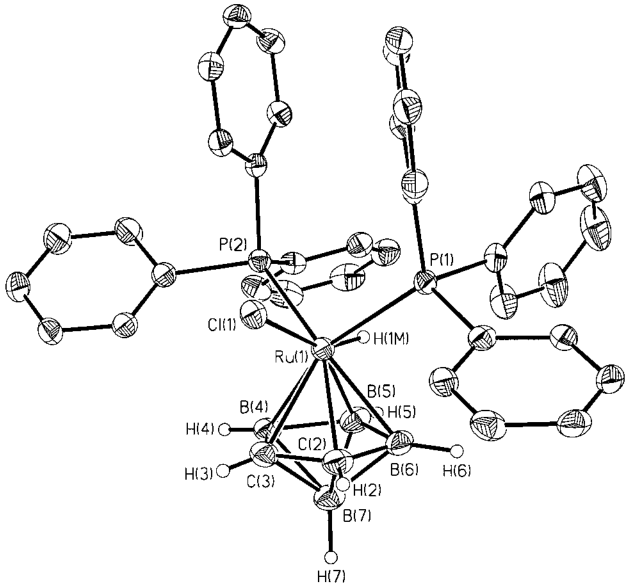


Figure 1. ORTEP drawing of the molecular structure of **3**, showing 50% probability ellipsoids for the non-hydrogen atoms. Hydrogen atoms of the Ph groups have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−C(2), 2.176(3); Ru(1)−C(3), 2.196(3); Ru(1)−B(4), 2.303(3); Ru(1)−B(5), 2.283(3); Ru(1)−B(6), 2.246(3); Ru(1)−P(1), 2.3653(6); Ru(1)−P(2), 2.3773(6); Ru(1)−Cl(1), 2.4311(5); Ru(1)−H(1M), 1.41(3); C(2)−C(3), 1.474(3); C(2)−B(6), 1.530(4); C(2)−B(7), 1.740(4); C(3)−B(7), 1.744(4); C(3)−B(4), 1.537(4); B(4)−B(5), 1.713(4); B(5)−B(6), 1.732(4); P(1)−Ru(1)−Cl(1), 86.89(2); P(2)−Ru(1)−Cl(1), 90.36(2); Cl(1)−Ru(1)−H(1M), 156.5(12); P(1)−Ru(1)−P(2), 103.42(2); P(1)−Ru(1)−H(1M), 79.0(12); P(2)−Ru(1)−H(1M), 75.0(12).

and analytical data. Although, this particular type of mononuclear *closo*-(phosphine)$_n$chlorohydrido species is well-documented among icosahedral platinum metal metallacarboranes,[10] to our best knowledge, no complexes belonging to the family of transition metal small metallacarboranes of the *closo*-1,2,3-$L_nM(R^1R^2C_2B_4H_4)$ type bearing simultaneously phosphines, hydride, and/or chloro ligands at the metal vertex have, as yet, been reported.[11]

The ruthenium atom in **3** is coordinated by two PPh_3 groups [2.3643(6) and 2.3773(6) Å], a terminal hydrogen [1.41(3) Å], and a chlorine [2.4311(5) Å] ligand. It is also essentially symmetrically η^5-coordinated by the C_2B_3 open face of the carborane cage (see caption to Figure 1 for the ruthenium-to-cage-atom distances). Taking into account that the C_2B_3 face is generally considered to cover three coordination sites, the formal coordination number of the Ru(IV) atom in **3** should thus be calculated as seven. The separation between C(2) and C(3) found in **3** is, in fact, the shortest cage distance [1.474(3) Å], which provides convincing evidence for the adjacent positions of the carbon atoms in the cluster. Additional arguments for such assignment are given by the fact that the C(2)−B(6) [1.530(4) Å] and C(3)−B(4) [1.537(4) Å] bond lengths are indeed very close to each other and have intermediate values as compared with the shortest C−C [1.474(3) Å] and the longest B−B [1.713(4)−1.794(4) Å] cage distances, the tendency commonly observed for unsubstituted metallacarboranes with a symmetrically coordinating C_2B_3 open face.[12,13] The overall geometry of the $Ru(PPh_3)_2HCl$ moiety in **3** proved to be very close to that found in the known icosahedral *closo*-metallacarboranes belonging to a group of neutral seven-coordinate M(IV) complexes *closo*-3,3-$(PPh_3)_2$-3-H-3-Cl-3,1,2-$MC_2B_9H_{11}$ (**6**, M = Ru,[10b] and **7**, M = Os[10d]). In each species **3**, **6**, and **7** the Cl−M−H plane bisects the corresponding C−C bonds, and the Cl···H vector is approximately perpendicular to these bonds. Consequently, the M−H bond in **3**, **6**, and **7** adopts an almost eclipsed position with respect to the B−H bond located *trans* to the C−C bond in the C_2B_3 open face. Remarkably, the B−H···H−Ru distances in complexes **3** and **6** [2.12(4) and 2.11(8) Å, respectively] are almost equal, however, each of which is significantly shorter than that found in **7** [2.42(7) Å]. This difference was found to be in good correlation with the ^{31}P decoupled ^1H NMR spectra of both **3** and **6**, wherein, in contrast to the spectra of **7**,[10d] we have observed the unique $H_{Ru}\cdots H_{B(5)}$ coupling with $J(H,H) = 9.6$ and 10.3 Hz, respectively. Such values of long-range coupling $J(H,H)$ observed for **3** and **6**, as far as we are aware, did not have any precedent for metallacarborane or metallaborane clusters of similar structure and might be attributed to $H_{Ru}\cdots H_{B(5)}$ through-space spin−spin interaction. For instance, the long-range coupling $^3J(H_{Ru},H_{B(6)})$ has not been found in the ^1H NMR spectrum of the related *closo*-ruthenaborane cluster

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(13) Although, isomeric *closo*-MC_2B_4 complexes having nonadjacent (2, 4) carbons are known,[14] neither metal-promoted nor thermal isomerization of contracted product **3** leading to separation of {CH} vertexes occurred under the reaction conditions.

1,1,1-$(PPh_3)HCl$-3,5-$(PPh_3)_2$-1-RuB_9H_7 (**8**),[15] wherein the Ru−H bond is also located *cis* to the B(6)−H bond (the dihedral angle H_{Ru}−Ru−B_6−$H_{B(6)}$ is equel 4.1°), but the $H_{Ru}\cdots H_{B(6)}$ distance is somewhat longer [2.23 Å] than those observed in **3** and **6**.

Two minor products, **4** and **5**, were isolated from the reaction mixture in essentially pure crystalline form using silica gel column chromatography. Although these complexes were not available for complete analytical characterization, their open RuC_2B_8 cluster structure has been successfully deduced from a combination of multinuclear NMR spectroscopic data. The ^{11}B and ^{1}H NMR spectra of both **4** and **5** exhibited extreme similarity in nuclear shielding behavior with those of typical 11-vertex *isonido*-MC_2B_8 clusters.[9,16] Their 128.33 MHz $^{11}B\{^{1}H\}$ NMR spectra revealed eight distinct resonances in the range −40 to +71 ppm with one of the signals at extremely low field indicating the presence of at least one boron atom with low cluster connectivity.[17] In the ^{11}B NMR spectra of both **4** and **5** among a set of doublets there is just one singlet at +70.6 (in the case of **4**) and 14.6 ppm (in the case of **5**). This fact coupled with the positive elemental analyses on chlorine obtained for each of **4** and **5** suggested that these represented isomers chlorinated at different cage boron atoms. By comparison of the ^{1}H and $^{11}B/^{11}B\{^{1}H\}$ NMR spectra of **4** and **5** with those previously reported for *closo*-1-(η^6-C_6Me_6)-3-Cl-4-Me-1,2,4-$RuC_2B_8H_8$ and other related analogues,[9b] and on the basis of an X-ray diffraction study of **5** which unambiguously positioned the chloro substituent at the B(6) atom of the carborane cage (Figure 2), these complexes were finally formulated as 1-(η^6-C_6H_5Me)-3-Cl-1,2,4-$RuC_2B_8H_9$ (**4**) and 1-(η^6-C_6H_5Me)-6-Cl-1,2,4-$RuC_2B_8H_9$ (**5**), respectively.

The crystal structure of **5** shows considerable distortion of the cluster geometry as compared to the canonical 11-vertex closed octadecahedron. This is most prominently manifested in the drastic lengthening of the Ru···C(4) distance (up to 2.658(9) Å), which is no longer regarded as a bonding interaction, thus giving rise to a tetragonal open-face Ru(1)C(2)C(4)B(7). The values of Ru−C(2) [2.103(9) Å] and Ru−B(3) [2.082(11) Å] bond lengths in **5** reflect quite well the tendency in shortening of the distance between a metal atom and the cage low-connectivity vertexes upon bonding.[9,16b] Thus, the separation between Ru and C(2) in **5** proved to be very similar to those found in *isonido*-1,2,4-RuC_2B_8 [2.124(6) Å] and *closo*-1,2,3-RuC_2B_8 [2.107(9) and 2.101(9) Å] clusters both having carbon atoms of cluster connectivity of four.[9b] The shortest cage distance found in **5** is C(2)−C(4) [1.495(13) Å], confirming the adjacency of carbon atoms in the polyhedral cage.

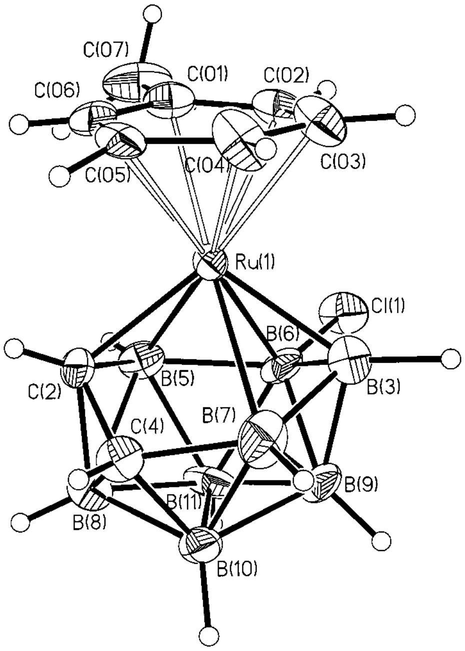

Figure 2. ORTEP drawing of the molecular structure of **5**, showing 50% probability ellipsoids for the non-hydrogen atoms. Hydrogen atoms of the Ph groups have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−C(Ar), 2.156(9)−2.269(9); C(01)−C(07), 1.506(14); Ru(1)−C(2), 2.103(9); Ru(1)−B(3), 2.082(11); Ru(1)−B(5), 2.281(11); Ru(1)−B(6), 2.263(10); Ru(1)−B(7), 2.363(13); Ru(1)···C(4), 2.658(9); Cl(1)−B(6), 1.864(10); C(2)−C(4)−B(7), 110.9(8); C(4)−C(2)−B(5), 112.5(8); B(3)−B(7)−C(4), 127.7(8); C(4)−B(7)−Ru(1), 79.4(5); C(4)−C(2)−Ru(1), 93.7(6).

The mechanism of transformation of **2** to **3** is fairly complex and undoubtedly involves at least several reaction steps. In the known polyhedral contraction reaction of *closo*-1-Cp-1,2,4-$CoC_2B_8H_{10}$ to its next lowest homologue *closo*-1-Cp-1,2,9-$CoC_2B_7H_9$ the monometallic intermediate has been successfully isolated and crystallographically established as having an open-cage cluster structure, *nido*-8-Cp-8,6,7-$CoC_2B_7H_{11}$ (**9**).[2e] On the basis of electronic similarity with complex **9**, one may suggest 18-electron *nido* 10-vertex ruthenacarborane with one of the polyhedral vertexes occupied by a $Ru(PPh_3)_2ClH$ unit as one of the possible candidates for the key intermediate species on the way to small *closo*-ruthenacarborane **3**. However, such a cluster, if indeed formed, should readily lose one of the PPh_3 groups under thermal conditions due to the steric bulk of the Ru-$(PPh_3)_2ClH$ moiety; the presence of a free PPh_3 ligand in the reaction system after approximately 2 h of heating of **1** and **2** in toluene solution is indeed observed by TLC. The resulting 16-electron *nido*-Ru((PPh_3)-$ClHC_2B_7$ species would be expected to undergo substantial degradation, presumably due to its low thermal stability in solution to produce a C_2B_4 cluster, which could then be “trapped” by the remaining ruthenium complex **1** in solution, thus affording final product **3**.

According to the above hypothetical reaction pathway leading to the formation of **3**, ruthenium complex **1** could serve in the reaction as both degrading and coordinating agent. It should also be taken into consideration that some part of **1** is consumed as a Ru(II) source for the formation of the 11-vertex clusters **4** and **5**. On the assumption that **4** and **5** are formed via a series of reaction steps starting from the [*nido*-$C_2B_8H_{10}$]$^{2-}$ anion,

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1, and toluene, followed by chlorinating at the cage boron atoms, we may consider complex **1** as a reagent promoting loss of bridging hydrogens from neutral *nido*-carborane **2**. The elimination of dihydrogen is indeed accompanying the formation of certain types of *closo*-metallacarborane clusters. This was observed, for instance, when **8**[15] was prepared from **1** and *arachno*-$[B_9H_{14}]^-$ as well as in the reaction of electron-rich $Co(PEt_3)_4$ with **2** to form 1,1-$(Et_3P)_2$-1,2,4-$CoC_2B_8H_{10}$.[18] All these considerations taken together coupled with possible decomposition of **1** during the reaction of **1** and **2** may account for a rather low isolable yield of **3** obtained by this method.

Conclusion. This work demonstrates that simple 16-e transition metal complexes such as **1** can be used as promoters for rather extensive polyhedral contraction of a neutral *nido*-$C_2B_8H_{12}$ carborane to give smaller metallacarborane *closo*-RuC_2B_4 cluster structure. Potential applications of this method for transformations of other polyhedral *nido*- and *closo*-carboranes effected either by **1** or its osmium congener are currently under investigation.

Experimental Section

General Procedures. The reaction was carried out under argon atmosphere using standard Schlenk techniques. Toluene and those solvents used for the purification of the products, as well as for the recording of IR spectra, were dried under appropriate drying agents and distilled under argon prior to use. The ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and other NMR spectra were recorded with a Bruker AMX-400 spectrometer using TMS as an internal reference and 85% H_3PO_4 as an external reference. IR spectra were obtained on a Specord M-82. Microanalyses were performed at the Analytical Laboratory of the Institute of Organoelement Compounds of the RAS. Starting materials, *nido*-5,6-$C_2B_8H_{12}$[19] and $RuCl_2(PPh_3)_3$,[20] were prepared by methods published elsewhere.

Reaction of *nido*-5,6-$C_2B_8H_{12}$ (2) with $RuCl_2(PPh_3)_3$ (1). To a stirred solution of **2** (24 mg, 0.2 mmol) in 15 mL of absolute toluene under argon was added **1** (190 mg, 0.2 mmol) as solid; the mixture was then gently heated at approximately 95 °C for 15 h. The reaction mixture was filtered off from brown intractable materials, and after removal of the solvent, the resulting semisolid residue was treated by column chromatography on 70-230 mesh silica gel using a CH_2Cl_2/*n*-hexane (2:1) mixture as eluent. The yellow band, which eluted first, was collected and evaporated to dryness. Recrystallization of the crude solid from a benzene/*n*-hexane mixture afforded yellow crystals of **3** (24.5 mg, 16.8% yield): IR (CH_2Cl_2) ν_{BH} 2581 cm^{-1}, ν_{RuH} 1964 cm^{-1}; ^1H NMR (400.13 MHz, C_6D_6, J(Hz)) 7.81 (t br, 12H, H_{Ph-m}, $J_t = 8.4$), 7.05 (m, 18H, $H_{Ph-o,p}$), 6.09 (s br, 2H, CH_{Cb}), −13.04 (m br, 1H, H_{Ru}, $^2J(H,P) = 20.0$, $J(H_{Ru}\cdots H_{B(5)}) = 9.6$) (the values of ^2J and J were obtained from broad triplet and doublet signals observed in the broad band (δ 0.8−1.8 ppm) proton decoupled ^1H and $^1H\{^{31}P\}$ NMR spectra of **3**, respectively); $^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6) 29.0 (s); $^{13}C\{^1H\}$ NMR (100.51 MHz, C_6D_6) 137.0 (d, C-*k*, $J(C,P) = 45$ Hz), 135.1−135.0 (m, C-*o*,*m*), 130.1 (s, C-*p*), 84.9 (q br, C_{Cb}); ^{11}B NMR (128.33 MHz, 20 °C, C_6D_6; J(B,H) were not observed) +16.0 (s br, 1B), +6.7 (s br, 2B), −11.9 (s br, 1B). Anal. Calcd for $C_{38}H_{37}B_4ClP_2Ru\cdot 0.5CH_2Cl_2$: C, 59.45; H, 4.92; B, 5.56; Cl, 9.12. Found: C, 59.58; H, 5.12; B, 5.70; 8.33. All other fractions from the silica gel column were combined, concentrated in vacuo, and then separated by repeated column chromatography on 5-40 mesh silica gel into two purple fractions, which after evaporation to dryness resulted in pure crystalline **4** (5 mg, 7% yield) and **5** (2.8 mg, 4% yield). Characterization data for **4** and **5** are as follows. **4**: IR (Nujol mull) ν_{BH} 2528 cm^{-1}, ν_{BCl} 383 cm^{-1}; ^1H NMR (400.13 MHz, C_6D_6, J(Hz)) 5.05, (t d, 1H, H_{Ph-p}, $J_t = 5.6$, $J_d = 1.2$), 4.92, 4.88 (t d, 1H+1H, H_{Ph-m}, $J_t = 5.6$, $J_d = 1.2$), 4.75, 4.59 (d, 1H+1H, H_{Ph-o}, $J_d = 5.6$), 4.03 (s br, 1H, CH_{Cb}), 3.60 (s br, 1H, CH_{Cb}), 1.62 (s, 3H, Me); $^{13}C\{^1H\}$ NMR (100.51 MHz, C_6D_6) 110.3 (s, C_{Ar-k}), 95.7, 95.4, 95.3, 94.8, 93.4 (s, $C_{Ar-o,m,p}$), 55.8, 31.7 (s br, C_{Cb}), 18.6 (s, C_{Me}); ^{11}B NMR (128.33 MHz, C_6D_6, J(B,H) (Hz)) +70.6 (s, 1B, B3−Cl), +14.1 (d, 1B, 154.2), +0.6 (d, 1B, 137.9), −0.2 (d, 1B, 141.1), −12.3 (d, 1B, 147.1), −22.6 (d, 1B, 167.8), −26.1 (d, 1B, 149.3), −40.7 (d, 1B, 151.0). Anal. Calcd for $C_9H_{17}B_8ClRu$: Cl, 10.20. Found: Cl, 10.26. **5**: ^1H NMR (400.13 MHz, C_6D_6, J(Hz)) 4.90 (t, 1H, H_{Ph-p}, $J_t = 5.6$), 4.84, 4.72 (t br, 1H+1H, H_{Ph-m}, $J_t = 6.0$), 4.70, 4.65 (d, 1H+1H, H_{Ph-o}, $J_d = 5.6$), 4.15 (s br, 1H, CH_{Cb}), 3.72 (s br, 1H, CH_{Cb}), 1.71 (s, 3H, Me); ^{11}B NMR (128.33 MHz, C_6D_6, J(B,H) (Hz); $\delta(^1H)$ assigned by ^1H-(^{11}B-selective) experiment are in square brackets) +66.6 (d, 1B, B3, 154; [8.63]), +17.8 (d, 1B, 142.8; [5.52]), +14.4 (s, 1B, B6-Cl, −), +4.2 (d, 1B, 153; [3.27]), −10.9 (d, 1B, 157; [?]), −17,8 (d, 1B, 176; [2.50]), −21.0 (d, 1B, 153; [2.01]), −40.94 (d, 1B, 153; [−1.49]). Anal. Calcd for $C_9H_{17}B_8ClRu$: Cl, 10.20. Found: Cl, 10.37.

Table 1. Crystal Data and Details of the X-ray Diffraction Experiments for 3 and 5

	3	5
formula	$C_{38}H_{37}B_4ClP_2Ru\cdot 0.5C_6H_6\ 0.5C_6H_{14}$	$C_9H_{17}B_8ClRu$
fw	817.52	348.23
cryst color, habit	yellow cubes	red prisms
cryst size, mm	0.15 × 0.20 × 0.25	0.10 × 0.20 × 0.20
symmetry, space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$
a, Å	10.6846(4)	7.023(2)
b, Å	21.1325(7)	5.186(7)
c, Å	17.9926(6)	13.637(5)
α, deg	90.0	90.0
β, deg	102.809(1)	99.60(3)
γ, deg	90.0	90.0
V, Å^3	3961.5(2)	1434.0(9)
Z	4	4
d_{calcd}, g/cm^3	1.371	1.613
λ(Mo Kα), Å	0.71073	0.71073
μ(Mo Kα), cm^{-1}	5.76	12.51
scan technique	ω/φ	$\theta/2\theta$
$2\theta_{max}$, deg	60	50
no. collected	43269	2735
no. of ind reflns (R_{int})	11 488 (0.0535)	2518 (0.0657)
no. obsd ($I > 2\sigma(I)$)	7766	1749
R_1[a]	0.0375	0.0615
wR_2[b]	0.0854	0.1525

[a] $R_1 = \sum|F_o - |F_c||/\sum(F_o)$ for observed reflections. [b] $wR_2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$ for all reflections.

Crystallographic Study of 3 and 5. Crystals of **3** and **5** suitable for an X-ray diffraction study were slowly grown from diluted solutions in C_6H_6/*n*-hexane and CH_2Cl_2/*n*-hexane mixtures, respectively. X-ray diffraction experiments were performed with a SMART CCD-1000 (in the case of **3**) and a Siemens P3/PC (in the case of **5**) diffractometers at 110.0(2) and 142.0(2) K, respectively. Details of the data collection and structure refinement of **3** and **5** are presented in Table 1. Data were corrected for Lorentz and polarization effects. The isometric shape and small size of single-crystal samples, the quality of obtained results, and the low absorption coefficient values justified no necessity for absorption corrections. Both structures have been solved by the direct methods and refined by the full-matrix least-squares procedure in anisotropic

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approximation for non-hydrogen atoms. All hydrogen atoms of both molecules including the hydride ligand in **3** were located in the difference Fourier maps and refined in the isotropic approximation; hydrogens in the disordered solvent molecules in the crystal of **3** were included in the refinement using riding approximation. The SHELXTL-97 program package[21] was used throughout the calculations, which were carried out on an IBM PC.

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Supporting Information Available: Tables of crystallographic data collection, parameters, atomic coordinates and *U* values, bond lenths and angles, and anisotropic parameters and ORTEP figures for **3** and **5**, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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