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Synthesis and X-ray Structure of the Monocarbon Rhodacarborane Complex $[RhBr(PPh_3)(\eta^5\text{-7-}NH_2Bu^t\text{-8-}CH_2CO_2Et\text{-7-}CB_{10}H_9)]$[†]

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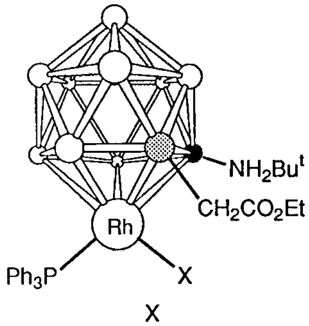
Introduction

The selective introduction of functional groups on the carbon and boron vertices of the polyhedral carboranes and metallacarboranes is a topic of continued interest. Although attachment of functional groups to the carbon vertices is well developed, our knowledge of species where substitution has occurred at the BH vertices is much more limited.[1,2] We recently reported the synthesis and some reactions of the charge-compensated 16-electron rhodacarboranes $[RhX(PPh_3)(\eta^5\text{-7-}NH_2Bu^t\text{-7-}CB_{10}H_{10})]$ (X = Br (**1a**) or Cl (**1b**)).[3] Conceivably the electronically unsaturated metal centers in these complexes might provide a pathway for substitution at the BH vertices through initial coordination of a reactive organic fragment in a preliminary step.

Results and Discussion

The reagents **1** readily react with one mol equiv. of the diazoalkane $N_2C(H)CO_2Et$ in CH_2Cl_2 to afford the complexes $[RhX(PPh_3)(\eta^5\text{-7-}NH_2Bu^t\text{-8-}CH_2CO_2Et\text{-7-}CB_{10}H_9)]$ (X = Br (**2a**), or Cl (**2b**)) in good yield. These products arise from insertion of a $C(H)CO_2Et$ moiety into a BH bond of the cage. As far as we are aware, these are the first examples of insertion of an organic fragment into a BH bond of a monocarbon carborane.



	X
2a	Br
2b	Cl

○ BH ▨ B ● C

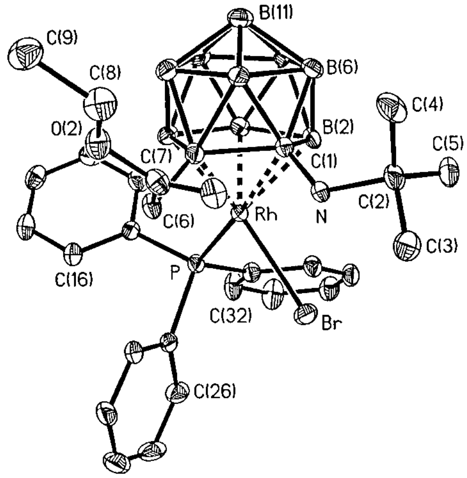


Figure 1. Molecular structure of $[RhBr(PPh_3)(\eta^5\text{-7-}NH_2Bu^t\text{-8-}CH_2CO_2Et\text{-7-}CB_{10}H_9)]$ (**2a**) showing the crystallographic labeling scheme. Hydrogen atoms have been omitted for clarity, and thermal ellipsoids are at the 50% probability level.

The molecular structure of **2a** was established by X-ray diffraction. The molecule is shown in Figure 1, and selected bond distances and angles are listed in Table 1. The rhodium atom is coordinated by the Br [Rh−Br 2.5116(5) Å] and PPh_3 [Rh−P 2.3492(8) Å] groups, with bond lengths similar to those found for these ligands in **1a** [Rh−Br 2.5165(9), Rh−P 2.334(2) Å].[3] Interest centers on the carborane cage system coordinated in the η^5-bonding mode to the rhodium. As expected the carbon atom of the $\overline{CBBBB}$ ring carries the NH_2Bu^t group [C(1)−N 1.501(3) Å], as it does in the precursor **1a** [C(1)−N 1.488(7) Å]. However, significantly the CH_2CO_2Et substituent [B(5)−C(6) 1.643(4) Å] is attached to one of the two boron atoms adjacent to the carbon in the $\overline{CBBBB}$ ring, so that evidently insertion of the $C(H)CO_2Et$ unit occurs preferentially at one or other of the CB_α sites, either of which would yield enantiomers of the same product. Presumably the pathway for the reaction involves formation of a coordinatively and electronically saturated intermediate complex $[RhX\{C(H)CO_2Et\}(PPh_3)(\eta^5\text{-7-}NH_2Bu^t\text{-7-}CB_{10}H_{10})]$, followed by insertion of the alkylidene ligand into an adjacent BH bond of the 2,1-$RhCB_{10}$ framework. There is ample precedent for such a process from earlier work.[4] The distances between the rhodium atom in **2a** and the atoms of the CB_4 ring [Rh−C(1) 2.243(2), Rh−B(2) 2.142(3), Rh−B(3) 2.156(3), Rh−B(4) 2.191(3), Rh−B(5) 2.135(3) Å] differ insignificantly from the analogous parameters for **1a** [Rh−C(1) 2.240(5), Rh−B(2) 2.129(6), Rh−B(3) 2.182(6), Rh−B(4) 2.179(6), Rh−B(5) 2.129(6) Å].[3]

The NMR data for **2a** are in accord with the results of the crystal structure study. The ^1H NMR spectrum displays diagnostic peaks for the various groups present, including the diastereotopic protons of the BCH_2 group at δ 2.50 and 2.85 [J(AB) = 15 Hz] and those of the NH_2 group at δ 9.67 and 10.08 [J(HH) = 12 Hz]. The $^{13}C\{^1H\}$ NMR spectrum shows characteristic peaks for the C=O (δ 177.9), cage carbon (δ 75.2), and BCH_2 (δ 31.0) groups, with the last signal broad as is usual.[4] In the $^{11}B\{^1H\}$ NMR spectrum, the resonance for the

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[†] This complex has a rhodium atom incorporated into a *closo*-1-carba-2-rhodadodecaborane structure. In order to relate the compound to the many known rhodium species with η^5-coordinated cyclopentadienyl ligands, following precedent (Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A.; Woollam, S. F. *Organometallics* **1994**, *13*, 157), we treat the cage as a *nido* 11-vertex ligand with numbering as for an icosahedron from which the 12th vertex has been removed.

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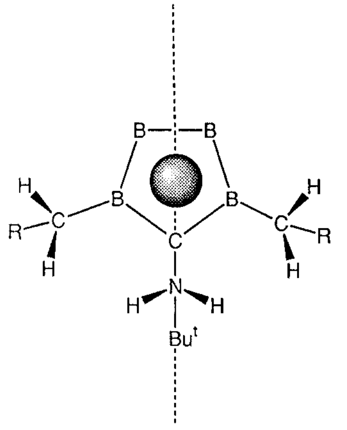
Table 1. Selected Internuclear Distances (Å) and Angles (deg) for [RhBr(PPh$_3$)(η^5-7-NH$_2$Bu^t-8-CH$_2$CO$_2$Et-7-CB$_{10}$H$_9$)] (**2a**) with Estimated Standard Deviations in Parentheses

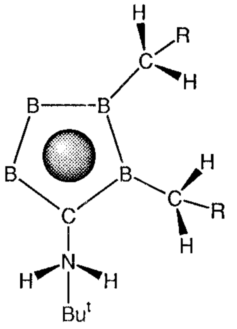
Rh−B(5)	2.135(3)	Rh−B(2)	2.142(3)	Rh−B(3)	2.156(3)	Rh−B(4)	2.191(3)
Rh−C(1)	2.243(2)	Rh−P	2.3492(8)	Rh−Br	2.5116(5)	P−C(21)	1.826(3)
P−C(31)	1.827(3)	P−C(11)	1.832(3)	N−C(1)	1.501(3)	N−C(2)	1.546(3)
C(2)−C(5)	1.519(4)	C(2)−C(3)	1.523(4)	C(2)−C(4)	1.526(4)	C(6)−C(7)	1.490(4)
B(5)−C(6)	1.643(4)	C(7)−O(1)	1.228(3)	C(7)−O(2)	1.320(3)	C(8)−O(2)	1.475(3)
C(8)−C(9)	1.496(4)						

B(5)−Rh−B(2)	83.44(11)	B(5)−Rh−B(3)	84.90(11)	B(2)−Rh−B(3)	51.90(11)
B(5)−Rh−B(4)	50.22(11)	B(2)−Rh−B(4)	86.32(11)	B(3)−Rh−B(4)	49.00(11)
B(5)−Rh−C(1)	47.39(9)	B(2)−Rh−C(1)	46.23(9)	B(3)−Rh−C(1)	82.87(10)
B(4)−Rh−C(1)	83.04(9)	B(5)−Rh−P	131.31(8)	B(2)−Rh−P	128.96(8)
B(3)−Rh−P	90.15(8)	B(4)−Rh−P	91.73(8)	C(1)−Rh−P	172.96(6)
B(5)−Rh−Br	119.00(8)	B(2)−Rh−Br	102.89(8)	B(3)−Rh−Br	145.22(8)
B(4)−Rh−Br	165.50(8)	C(1)−Rh−Br	95.18(6)	P−Rh−Br	91.05(2)
C(21)−P−C(31)	107.21(12)	C(21)−P−C(11)	103.21(11)	C(31)−P−C(11)	104.65(12)
C(21)−P−Rh	109.86(9)	C(31)−P−Rh	111.50(8)	C(11)−P−Rh	119.52(8)
C(1)−N−C(2)	127.0(2)	C(5)−C(2)−C(3)	110.7(3)	C(5)−C(2)−C(4)	114.1(2)
C(3)−C(2)−C(4)	109.6(2)	C(5)−C(2)−N	109.9(2)	C(3)−C(2)−N	101.7(2)
C(4)−C(2)−N	110.1(2)	C(7)−C(6)−B(5)	109.6(2)	O(1)−C(7)−O(2)	123.6(2)
O(1)−C(7)−C(6)	123.3(2)	O(2)−C(7)−C(6)	113.1(2)	O(2)−C(8)−C(9)	106.4(3)
C(7)−O(2)−C(8)	116.5(2)				

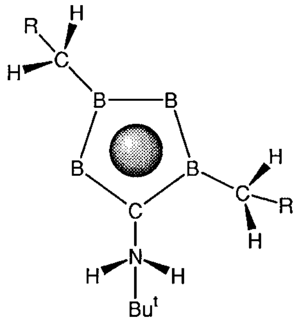
Chart 1



3a



3b



3c

● = RhCl(PPh$_3$)

R = CO$_2$Et

upper part of cages omitted for clarity

BCH$_2$ group is at δ 14.2 and remains a singlet in a fully coupled ^{11}B spectrum. The NMR data for **2b** are similar.

Formation of complexes **2** raised the possibility of whether reactions employing an excess of the reagent N$_2$C(H)CO$_2$Et would result in insertion of more than one C(H)CO$_2$Et fragment into the cage system of **1**. It is noteworthy that, under appropriate conditions, up to three alkyne molecules RC≡CH can be inserted into the BH bonds of the pentagonal ligating CCBBB ring of an Ru(η^5-7,8-C$_2$B$_9$H$_{11}$) system.[5] Accordingly, **1b** was treated with a 2-fold excess of the diazo compound and the mixture chromatographed. Again, complex **2b** was the major product, but a further species was isolated. Microanalytical data for the latter accorded with a formulation [RhCl(PPh$_3$)(η^5-7-NH$_2$Bu^t-7-CB$_{10}$H$_8$(CH$_2$CO$_2$Et)$_2$)] (**3**) corresponding to incorporation of two C(H)CO$_2$Et units from the diazoalkane. The ^{31}P{^{1}H} NMR spectrum of **3** would be expected to display a doublet resonance like that of the precursor **2b**. However, examination of the spectrum revealed that it was formed as a mixture of two isomers since there were doublet signals at δ 28.3 [J(RhP) =159 Hz] and 21.2 [J(RhP) = 131 Hz] of relative intensity ca. 3:1, respectively. Thus one isomer was predominant in the mixture.

Although the ^{31}P{^{1}H} NMR data revealed the formation of two isomers of **3**, there are three possible isomeric forms **3a**−**c** on the reasonable assumption that the two C(H)CO$_2$Et fragments insert into BH groups in the open face of the CBBBB ring (see Chart 1). Each isomer would be expected to reveal a doublet resonance in the ^{31}P{^{1}H} NMR spectrum. The ^{1}H, ^{13}C{^{1}H}, and ^{11}B{^{1}H} NMR spectra of the inseparable mixture were complex, resulting from overlapping peaks and the dominance of one isomer masking signals due to the other. The ^{1}H and ^{11}B{^{1}H} NMR spectra of the isomeric mixture did clearly show some peaks due to a major isomer, which is symmetrical, having a mirror plane bisecting the cage. This plane includes the cage carbon, the nitrogen, the rhodium, the chlorine, and the phosphorus atoms. Of the three possibilities **3a**−**c**, only **3a** displays this symmetry, and we therefore designate **3a** as the major isomer [RhCl(PPh$_3$)(η^5-7-NH$_2$Bu^t-8,11-(CH$_2$CO$_2$Et)$_2$-7-CB$_{10}$H$_8$)]. In particular in the ^{1}H NMR spectrum, the region containing resonances due to BCH$_2$ protons is relatively clean

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(5) Anderson, S.; Mullica, D. F.; Sappenfield, E. L; Stone, F. G. A. *Organometallics* **1996**, *15*, 1676.

Table 2. Crystallographic Data for **2a**

formula	$C_{27}H_{42}B_{10}BrNO_2PRh$	μ(Mo Kα) (mm^{-1})	1.724
M_r	734.51	F(000) (e)	1488
T (K)	173	crystal dimensions (mm)	0.30 × 0.30 × 0.15
crystal system	monoclinic	crystal color, shape	red plate
space group	$P2_1/c$	reflcns measd	15 356
a (Å)	11.116(2)	no. of independent reflcns	6060
b (Å)	17.329(4)	2θ range (deg)	5.0−50.0
c (Å)	18.017(3)	refinement method	full-matrix least-squares on all F^2 data
β (deg)	95.49(1)	final residuals	$wR_2 = 0.066^a$ ($R_1 = 0.027$)^b
V (Å^3)	3455(1)	weighting factors	$d = 0.0213$; $e = 3.100^a$
Z	4	goodness of fit on F^2	1.114
d_{calcd} (g cm^{-3})	1.412	final electron density diff features (max/min) (e Å^{-3})	0.41, −0.49

[a] Structure was refined on F_o^2 using all data: $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$ where $w^{-1} = [\sigma^2(F_o^2) + (dP)^2 + eP]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$. [b] The value in parentheses is given for comparison with refinements based on F_o with a typical threshold of $F \geq 4\sigma(F)$ and $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $w^{-1} = [\sigma^2(F_o) + gF_o^2]$.

and devoid of other complicated, overlapping signals. As expected for **3a**, only two AB signals are seen for the four BCH_2 protons at δ 2.87 and 3.09 [J(AB) = 13 Hz] as a result of the effect of the mirror plane. Other notable signals for **3a** include the NH_2 doublet resonances at δ 9.70 and 10.43 [J(HH) = 14 Hz]. Peaks corresponding to the NH_2 protons in the minor isomer were not discernible; however, the BCH_2 protons did give rise to four sets of weak AB signals as expected for a nonsymmetrical system (**3b** or **3c**). The $^{11}B\{^1H\}$ NMR spectrum for **3** shows a set of six signals of relative intensity 2:2:2:2:1:1, consistent with a symmetrical cage system in **3a**, in addition to other weaker signals for the minor isomer, which were not logged.

From this discussion we conclude that the major isomer formed is **3a** in which the two CH_2CO_2Et moieties are attached to borons α to the carbon vertex in the $\overline{\mathrm{CBBBB}}$ ring. The precise nature of the minor isomer is uncertain, as the limited NMR data available do not allow us to discriminate between **3b** and **3c**, both of which are nonsymmetrical.

Experimental Section

All experiments were conducted under an atmosphere of dry nitrogen using Schlenk tube techniques. Solvents were freshly distilled under nitrogen from appropriate drying agents before use. Petroleum ether refers to that fraction of bp 40−60 °C. Chromatography columns (ca. 60 cm long and 1 cm in diameter) were packed with silica gel (Aldrich, 70−230 mesh). The NMR measurements were recorded at ambient temperatures at the following frequencies: ^1H at 360.13, ^{13}C at 90.56, ^{11}B at 115.55, and ^{31}P at 145.78 MHz. Chemical shifts (δ) are in ppm, and coupling constants (J) are in Hz. For the $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ spectra, δ values are positive to high frequency of 85% H_3PO_4 (external) and $BF_3{\cdot}Et_2O$ (external), respectively. Peaks marked with an asterisk are due to a minor isomer. The complexes $[RhX(PPh_3)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**1**) were prepared as previously described.[3]

Synthesis of the Complexes $[RhX(PPh_3)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}8\text{-}CH_2CO_2Et\text{-}7\text{-}CB_{10}H_9)]$. A CH_2Cl_2 (20 mL) solution of **1a** (0.180 g, 0.28 mmol) was treated with $N_2C(H)CO_2Et$ (0.032 g, 29 μL, 0.28 mmol) and the mixture stirred for 2 h. Solvent was reduced in volume *in vacuo* to ca. 3 mL, and the mixture was chromatographed. Elution with CH_2Cl_2−petroleum ether (1:4) yielded an orange-yellow fraction which, after removal of solvent *in vacuo* and crystallization of the residue from CH_2Cl_2−petroleum ether (5 mL, 1:7), gave $[RhBr(PPh_3)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}8\text{-}CH_2CO_2Et\text{-}7\text{-}CB_{10}H_9)]$ (**2a**) (0.120 g, 60%). Anal. Calcd for $C_{27}H_{42}B_{10}BrNO_2PRh$: C, 44.1; H, 5.7; N, 1.9. Found: C, 44.2; H, 5.7; N, 1.9. NMR (CD_2Cl_2): ^1H, δ 1.32 [d of d, 3 H, CH_2*Me*, J(HH) = 7 and 7], 1.61 (s, 9 H, Bu^t), 2.50, 2.85 [AB, 2 H, BCH_2, J(AB) = 15], 4.16−4.27 (m, 2 H, OCH_2Me), 7.42−7.56 (m, 15 H, Ph), 9.67, 10.08 [d × 2, 2 H, NH_2, J(HH) = 12]; $^{13}C\{^1H\}$, δ 177.9 (C=O), 133.1−129.0 (Ph), 75.2 (br, CB_{10}), 65.2 (OCH_2), 62.6 (*C*Me_3), 31.0 (br, BCH_2), 26.9 (C*Me*$_3$), 14.2 (CH_2*Me*); $^{31}P\{^1H\}$, δ 33.5 [d, J(RhP) = 158]; $^{11}B\{^1H\}$, δ 14.2 (1 B, BCH_2), 9.6 (1 B), 6.7 (3 B), −5.4 (1 B), −12.9 (1 B), −14.3 (3 B).

Table 3. Atomic Positional Parameters (Fractional Coordinates ×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for the Atoms of **2a**

atom	x	y	z	U(eq)^a
Rh	2522(1)	497(1)	2042(1)	24(1)
Br	1978(1)	378(1)	662(1)	39(1)
P	3646(1)	1620(1)	1871(1)	28(1)
N	747(2)	−836(1)	1678(1)	28(1)
C(1)	1601(2)	−599(1)	2334(1)	26(1)
B(2)	3153(3)	−637(2)	2350(2)	30(1)
B(3)	3794(3)	168(2)	2967(2)	30(1)
B(4)	2534(3)	720(2)	3240(2)	30(1)
B(5)	1181(3)	250(2)	2781(2)	28(1)
B(6)	2309(3)	−1247(2)	2922(2)	33(1)
B(7)	3655(3)	−796(2)	3298(2)	36(1)
B(8)	3254(3)	12(2)	3850(2)	36(1)
B(9)	1635(3)	81(2)	3736(2)	35(1)
B(10)	1072(3)	−706(2)	3178(2)	31(1)
B(11)	2365(3)	−840(2)	3820(2)	39(1)
C(2)	504(3)	−1665(1)	1382(2)	38(1)
C(3)	−380(3)	−1518(2)	698(2)	51(1)
C(4)	−113(3)	−2139(2)	1950(2)	49(1)
C(5)	1667(3)	−2019(2)	1159(2)	51(1)
C(6)	−49(2)	714(1)	2460(2)	32(1)
C(7)	−1130(2)	226(2)	2549(2)	36(1)
C(8)	−2679(2)	−102(2)	3317(2)	47(1)
C(9)	−3067(3)	172(2)	4044(2)	54(1)
O(1)	−1455(2)	−303(1)	2123(1)	41(1)
O(2)	−1682(2)	408(1)	3142(1)	41(1)
C(11)	4099(2)	2241(1)	2672(1)	31(1)
C(12)	4990(3)	2004(2)	3218(2)	42(1)
C(13)	5259(3)	2442(2)	3857(2)	46(1)
C(14)	4657(3)	3126(2)	3955(2)	46(1)
C(15)	3790(3)	3372(2)	3413(2)	47(1)
C(16)	3509(2)	2936(2)	2775(2)	38(1)
C(21)	2780(2)	2269(1)	1225(1)	32(1)
C(22)	1561(3)	2364(2)	1309(2)	37(1)
C(23)	856(3)	2877(2)	872(2)	48(1)
C(24)	1366(4)	3297(2)	336(2)	60(1)
C(25)	2562(4)	3202(2)	232(2)	59(1)
C(26)	3286(3)	2691(2)	675(2)	45(1)
C(31)	5056(2)	1400(1)	1470(1)	32(1)
C(32)	5967(3)	1947(2)	1474(2)	50(1)
C(33)	7010(3)	1788(2)	1141(2)	58(1)
C(34)	7163(3)	1079(2)	813(2)	47(1)
C(35)	6270(3)	532(2)	811(2)	42(1)
C(36)	5218(3)	686(2)	1138(2)	36(1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

A similar reaction between **1b** (0.160 g, 0.23 mmol) and $N_2C(H)CO_2Et$ (0.028 g, 26 μL, 0.23 mmol) in CH_2Cl_2 (15 mL) gave $[RhCl(PPh_3)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}8\text{-}CH_2CO_2Et\text{-}7\text{-}CB_{10}H_9)]$ (**2b**) (0.110 g, 70%). Anal. Calcd for $C_{27}H_{42}B_{10}ClNO_2PRh$: C, 47.0; H, 6.1; N, 2.0. Found: C, 46.9; H, 6.1; N, 1.9. NMR (CD_2Cl_2): ^1H, δ 1.35 [d of d, 3 H, CH_2*Me*, J(HH) = 9 and 9], 1.61 (s, 9 H, Bu^t), 2.61, 2.82 [AB, 2 H, BCH_2, J(AB) = 16], 4.20−4.26 (m, 2 H, OCH_2Me), 7.33−7.58 (m, 15 H, Ph), 9.66, 10.67 [d × 2, 2 H, NH_2, J(HH) = 13]; $^{13}C\{^1H\}$, δ 178.0 (C=O), 134.9−

127.0 (Ph), 75.8 [d of d, CB_{10}, J(RhC) = 45, J(PC) = 10], 64.7 (OCH_2), 62.6 (CMe$_3$), 31.2 (br, BCH_2), 27.0 (CMe_3), 14.1 (CH_2*Me*); $^{31}P\{^1H\}$, δ 33.2 [d, J(RhP) = 159]; $^{11}B\{^1H\}$, δ 14.2 (1 B, BCH_2), 9.4 (1 B), 6.6 (3 B), −5.1 (1 B), −13.1 (1 B), −14.7 (3 B).

Synthesis of the Isomers [RhCl(PPh$_3$)(η^5-7-NH$_2$Bu^t-7-CB$_{10}$H$_8$(CH$_2$CO$_2$Et)$_2$)]. A mixture of **1b** (0.160 g, 0.23 mmol) and $N_2C(H)CO_2Et$ (0.050 g, 55 μL, 0.49 mmol) was stirred in CH_2Cl_2 (20 mL) for 20 h. After solvent was removed *in vacuo*, the residue was treated with CH_2Cl_2 (5 mL) and the mixture added to silica gel (ca. 2 g) which was transferred to the top of a chromatography column. Elution with CH_2Cl_2 removed a fraction containing **2b** (0.07 g, 44%). Further elution with CH_2Cl_2−thf (9:1) removed a red eluate which, after removal of solvent *in vacuo*, gave red microcrystals of [RhCl(PPh$_3$)(η^5-7-NH$_2$Bu^t-7-CB$_{10}$H$_8$(CH$_2$CO$_2$Et)$_2$)] (**3**) (0.02 g, 11%). Anal. Calcd for $C_{31}H_{48}B_{10}ClNO_4PRh$: C, 47.9; H, 6.2; N, 1.8. Found: C, 47.5; H, 6.0; N, 1.8. NMR (CD_2Cl_2): ^1H, δ *1.17−1.37 (m, 6 H, CH_2*Me*), 1.33 [d of d, 6 H, CH_2*Me*, J(HH) = 9 and 9], 1.58 (s, 9 H, Bu^t), *1.62 (s, 9 H, Bu^t), *2.00, *2.31 [AB, 2 H, BCH_2, J(AB) = 14], *2.48 [AB, 1 H, BCH_2, J(AB) = 18], 2.87, 3.09 [AB, 2 H, BCH_2, J(AB) = 13], *3.18 [AB, 1 H, BCH_2, J(AB) = 18], 3.98−4.26 (m, 2 H, OCH_2Me), 7.42−7.58 (m, 15 H, Ph), 9.70, 10.43 [d × 2, 2 H, NH_2, J(HH) = 14]; $^{31}P\{^1H\}$, δ 28.3 [d, J(RhP) = 159] and *21.2 [d, J(RhP) = 131] with relative intensity 3:1; $^{11}B\{^1H\}$, δ 11.7 (2 B, BCH_2), 9.4 (2 B), −5.6 (1 B), −8.7 (1 B), −13.4 (2 B), −14.4 (2 B).

X-ray Structure Determination. A summary of the crystal data is given in Table 2. Crystals of **2a** were grown from CH_2Cl_2−petroleum ether (1:5), a suitable crystal was mounted on a glass fiber, and data were collected on a Siemens SMART CCD area-detector three-circle diffractometer using Mo Kα X-radiation. For three settings of ϕ, narrow data "frames" were collected for 0.3° increments in ω. A total of 1271 frames were collected, affording rather more than a hemisphere of data for the complex. After the data collection, the first 50 frames were recollected to establish that crystal decay had not taken place during measurements. The substantial redundancy in data allows empirical corrections to be applied using multiple measurements of equivalent reflections. Data frames were measured at 20 s per frame and integrated using SAINT.[6]

The structure was solved by conventional direct methods and was refined by full-matrix least-squares on all F^2 data using Siemens SHELTXL 5.03[6] with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were included in calculated positions with isotropic thermal parameters. Atomic Coordinates are listed in Table 3. All calculations were performed on Silicon Graphics Iris, Indigo, or Indy computers.

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Supporting Information Available: Complete tables of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters for **2a** (6 pages). Ordering information is given on any current masthead page.

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(6) Siemens X-ray Instruments, Madison, WI.