

Synthesis of Monocarbollide Complexes of Rhodium[†]

John C. Jeffery,[‡] Vyacheslav N. Lebedev,^{§,||} and F. Gordon A. Stone^{*,§}

Department of Chemistry, Baylor University, Waco, Texas 76798-7348, and
School of Chemistry, The University, Bristol BS8 1TS, U.K.

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The compounds $[\text{RhX}(\text{PPh}_3)_3]$ react with *nido*-7- NH_2Bu^t -7- $\text{CB}_{10}\text{H}_{12}$ in toluene to give the 16-electron complexes $[\text{RhX}(\text{PPh}_3)(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}\text{H}_{10})]$ (**1a**, X = Br; **1b**, X = Cl). The structure of the zwitterionic molecule **1a** was determined by X-ray crystallography. Crystals are monoclinic, space group $P2_1/c$, with $a = 12.937(3)$ Å, $b = 18.101(4)$ Å, $c = 14.695(4)$ Å, $\beta = 104.21(2)^\circ$, and $Z = 4$. The metal atom is coordinated on one side by Br and PPh_3 groups and on the other in the pentahapto manner by the open CBBBB face of the cage system. Reactions of the complexes with several donor molecules have been investigated. With CNBu^t , by changing the stoichiometry or work-up procedures either the 18-electron complexes $[\text{RhX}(\text{CNBu}^t)(\text{PPh}_3)(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}\text{H}_{10})]$ (**2a**, X = Br; **2b**, X = Cl) or $[\text{Rh}(\text{CNBu}^t)_2(\text{PPh}_3)(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}\text{H}_{10})]$ (**3**) are obtained, or the 16-electron complex $[\text{Rh}(\text{CNBu}^t)(\text{PPh}_3)(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}\text{H}_{10})]$ (**4**) is formed. Formation of **3** and **4**, in which the rhodium atoms are ligated by a *nido*-7- NH_2Bu^t -7- $\text{CB}_{10}\text{H}_{10}$ cage, formally a 3π -electron donor, is unusual and results from loss of HX from the precursors **1**. To establish firmly the nature of these species, their molecular structures were determined by X-ray crystallography. Crystals of **3** are monoclinic, space group $P2_1/c$, with $a = 10.533(2)$ Å, $b = 19.110(4)$ Å, $c = 19.707(4)$ Å, $\beta = 105.413(9)^\circ$, and $Z = 4$, while those of **4** are triclinic, space group $P1$, with $a = 9.840(3)$ Å, $b = 10.809(3)$ Å, $c = 17.287(3)$ Å, $\alpha = 88.49(2)^\circ$, $\beta = 84.57(2)^\circ$, $\gamma = 69.809(14)^\circ$, and $Z = 2$. The two molecular structures are very similar: the rhodium atom is attached on one side via an η^5 -bonding mode to the open face of the 7- NH_2Bu^t -7- $\text{CB}_{10}\text{H}_{10}$ cage and on the other by the PPh_3 ligand and one or two CNBu^t molecules, respectively. The reactions between the compounds **1** and PET_3 , PMe_3 , $\text{NC}_5\text{H}_4\text{Me-4}$, and tetrahydrofuran (thf) give the complexes $[\text{RhBr}(\text{PET}_3)(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}\text{H}_{10})]$ (**5**), $[\text{RhCl}(\text{PMe}_3)_2(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}\text{H}_{10})]$ (**6**), and $[\text{RhBr}(\text{L})(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}\text{H}_{10})]$ (**7a**, L = $\text{NC}_5\text{H}_4\text{Me-4}$; **7b**, L = thf), respectively. Prolonged refluxing of mixtures of $[\text{CoCl}(\text{PPh}_3)_3]$ and *nido*-7- NH_2Bu^t -7- $\text{CB}_{10}\text{H}_{12}$ in toluene gives the arene-(carborane)-cobalt complex $[\text{Co}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}\text{H}_{10})]$ (**8**), the structure of which was determined by X-ray diffraction. Crystals are monoclinic, space group $P2_1/c$, with $a = 16.332(5)$ Å, $b = 10.397(2)$ Å, $c = 22.186(6)$ Å, $\beta = 102.94(2)^\circ$, and $Z = 8$. NMR data for the new compounds are reported and discussed in relation to their structures.

Introduction

We have recently shown that the *nido*-carboranes 7,8- $\text{C}_2\text{B}_9\text{H}_{13}$ and 7- NR_3 -7- $\text{CB}_{10}\text{H}_{12}$ ($\text{NR}_3 = \text{NMe}_3$, NH_2Bu^t , NMe_2Bu^t) react with $[\text{Ru}_3(\text{CO})_{12}]$ to afford, respectively, the mononuclear ruthenium complex $[\text{Ru}(\text{CO})_3(\eta^5\text{-7,8-C}_2\text{B}_9\text{H}_{11})]$ and the triruthenium complexes $[\text{Ru}_3(\text{CO})_8(\eta^5\text{-7-NR}_3\text{-7-CB}_{10}\text{H}_{10})]$.¹ Formation of *closo*-metallacarboranes from reactions between 11-vertex *nido*-carboranes and low-valent metal complexes would appear to be a promising preparative route to species having either MC_2B_9 or MCB_{10} 12-vertex cage frameworks. In order to extend the scope of this methodology we have investigated the reaction between the *nido*-carborane 7- NH_2Bu^t -7- $\text{CB}_{10}\text{H}_{12}$ and the compounds $[\text{RhX}(\text{PPh}_3)_3]$ (X = Cl or Br) as a possible direct route to species with *closo*-RhCB₁₀ structures, and report herein the results of this study. At the present time relatively

few icosahedral monocarbon metallacarboranes are known, in contrast with the numerous dicarbon 12-vertex MC_2B_9 polyhedra which have been characterized.² A few mono- and binuclear rhodium monocarbon carborane complexes, however, are well established in the literature,^{3,4} and some of these species are discussed further below since they are relevant to the present work.

Results and Discussion

In toluene at reflux temperature the compounds $[\text{RhX}(\text{PPh}_3)_3]$ (X = Cl or Br) and *nido*-7- NH_2Bu^t -7- $\text{CB}_{10}\text{H}_{12}$ afford the mononuclear *closo*-rhodacarboranes $[\text{RhX}(\text{PPh}_3)(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}\text{H}_{10})]$ (**1a**, X = Br; **1b**, X = Cl), isolated by column chromatography and characterized by the data summarized in Tables 1–3. These species are zwitterionic 16-electron Rh^{III} complexes in which the metal is ligated by an $\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}\text{H}_{10}$ group. They are closely related to the previously reported compounds $[\text{RhBr}(\text{PPh}_3)(\eta^5\text{-7-NH}_2(\text{CH}_2\text{CH}=\text{CHMe})\text{-7-CB}_{10}\text{H}_{10})]$ and $[\text{RhBr}(\text{PPh}_3)(\eta^5\text{-7-NH}(\text{CH}_2\text{CH}=\text{CHMe})_2\text{-7-CB}_{10}\text{H}_{10})]$, which were obtained by N-quaternization of the

[†] The compounds described in this paper have a rhodium atom incorporated into a *closo*-1-carba-2-rhodadodecaborane structure. However, to avoid a complicated nomenclature for the complexes reported, and to relate them to the many known rhodium species with η^2 -coordinated cyclopentadienyl ligands, we treat the cages as *nido*-11-vertex ligands with numbering as for an icosahedron from which the twelfth vertex has been removed.

[‡] University of Bristol.

[§] Baylor University.

^{||} Permanent address: A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov St. 28, Moscow 117813, Russia.

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Chart 1

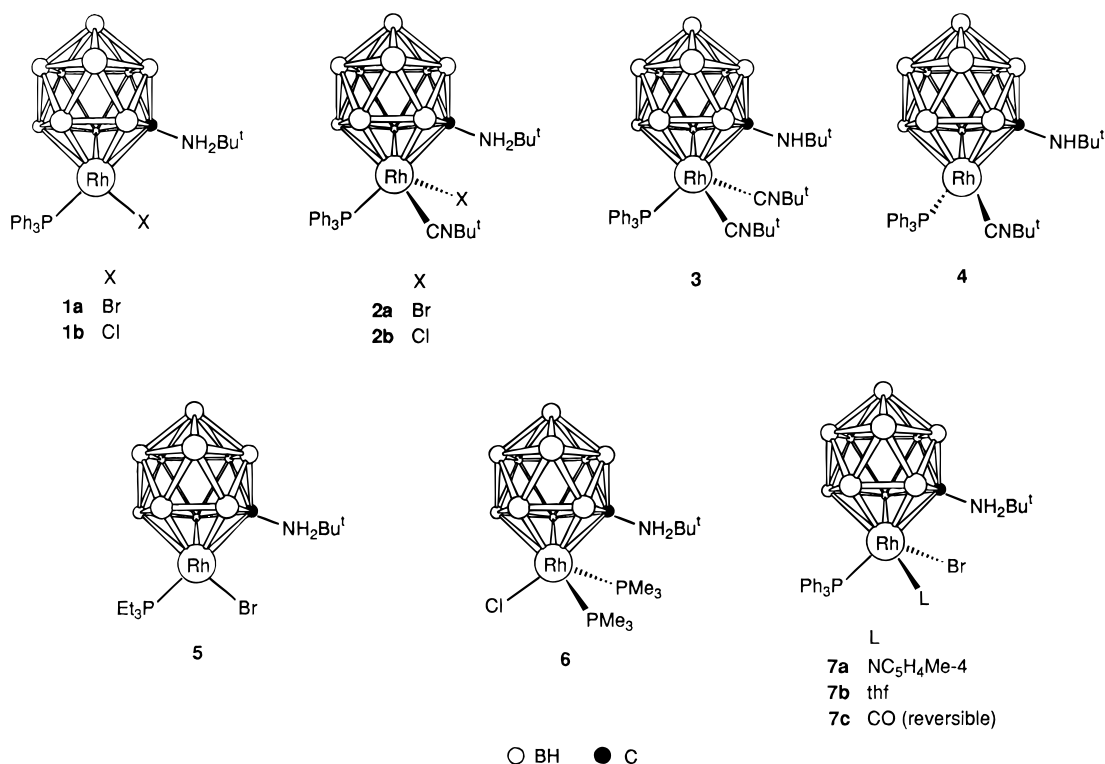


Table 1. Analytical and Physical Data

	compd ^a	color	yield/%	anal. ^b /%		
				C	H	N
1a	[RhBr(PPh ₃)(η^5 -7-NH ₂ Bu ^t -7-CB ₁₀ H ₁₀)]	red	56	42.2 (42.6)	5.5 (5.6)	2.1 (2.2)
1b	[RhCl(PPh ₃)(η^5 -7-NH ₂ Bu ^t -7-CB ₁₀ H ₁₀)]	red	62	42.5 (41.8)	5.6 (5.5)	2.2 (2.0) ^c
2a	[RhBr(CNBu ^t)(PPh ₃)(η^5 -7-NH ₂ Bu ^t -7-CB ₁₀ H ₁₀)]	orange	86	42.7 (42.6)	5.7 (5.8)	3.9 (3.4) ^c
2b	[RhCl(CNBu ^t)(PPh ₃)(η^5 -7-NH ₂ Bu ^t -7-CB ₁₀ H ₁₀)]	orange	85	45.2 (45.1)	6.4 (6.1)	3.6 (3.6) ^c
3	[Rh(CNBu ^t) ₂ (PPh ₃)(η^5 -7-NHBu ^t -7-CB ₁₀ H ₁₀)]	yellow	61 ^d	53.9 (53.4)	7.9 (7.4)	5.6 (5.7)
4	[Rh(CNBu ^t)(PPh ₃)(η^5 -7-NHBu ^t -7-CB ₁₀ H ₁₀)]	red	80 ^e	51.8 (51.6)	6.8 (6.9)	4.3 (4.3)
5	[RhBr(PEt ₃)(η^5 -7-NH ₂ Bu ^t -7-CB ₁₀ H ₁₀)]	red	90	31.1 (31.1)	8.3 (8.5)	3.1 (3.3)
6	[RhCl(PMe ₃) ₂ (η^5 -7-NH ₂ Bu ^t -7-CB ₁₀ H ₁₀)]	red-orange	82	26.4 (25.8)	8.1 (7.4)	2.8 (2.5)
7a	[RhBr(NC ₅ H ₅ Me-4)(PPh ₃)(η^5 -7-NH ₂ Bu ^t -7-CB ₁₀ H ₁₀)]	red	90	48.5 (49.9)	5.8 (5.9)	3.8 (3.6) ^f
7b	[RhBr(thf)(PPh ₃)(η^5 -7-NH ₂ Bu ^t -7-CB ₁₀ H ₁₀)]	red	82	44.3 (45.0)	6.1 (6.1)	1.8 (1.9)
8	[Co(η^6 -C ₆ H ₅ Me)(η^5 -7-NHBu ^t -7-CB ₁₀ H ₁₀)]	red	15	40.3 (40.6)	8.1 (8.2)	3.9 (3.9)

^a All compounds show broad medium-intensity bands in their infra-red spectra, measured in CH₂Cl₂, at ca. 2550 cm⁻¹ due to B-H absorptions. There are also medium-intensity $\nu_{\max}(\text{NC})$ bands observed for compounds **2a** (2190 cm⁻¹), **2b** (2190 cm⁻¹), **3** (2192, 2174 cm⁻¹), and **4** (2180 cm⁻¹). ^b Calculated values are given in parentheses. ^c Crystallizes with 1 molecule of CH₂Cl₂. ^d Also synthesized from compound **1b** and from compound **4** (see Experimental Section). ^e Also prepared from compound **1b** (see Experimental Section). ^f Crystallizes with 0.5 molecule of C₆H₆.

dimeric anion present in [N(PPh₃)₂][Rh₂(μ -H)(PPh₃)₂(η^5 -7-NH₂-7-CB₁₀H₁₀)₂] with crotyl bromide.^{3b} In order to establish firmly the molecular structures of the compounds **1**, a single-crystal X-ray diffraction study was carried out on **1a**. Selected interatomic distances and angles are listed in Table 4, and the molecule is shown in Figure 1.

On one side the rhodium atom is coordinated by PPh₃ [Rh-P 2.334(2) Å] and by Br [Rh-Br 2.5165(9) Å] groups. On the other it is bonded to the *nido*-7-NH₂Bu^t-7-CB₁₀H₁₀ cage in the pentahapto manner [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) 2.131(6) Å]. In these respects the structure is very similar to that determined for [RhBr(PPh₃)(η^5 -7-NH(CH₂CH=CHMe)₂-7-CB₁₀H₁₀)]. In the latter the Rh-P distance is 2.354(1) Å, the Rh-C(1) connectivity is 2.243(5) Å, and the Rh-B separations are 2.127(5)-2.174(5) Å.^{3b} However, this study revealed a somewhat shorter than expected Rh-Br distance [2.488(1) Å], attributable to some Br sites in the crystal being occupied by Cl atoms due to halide exchange. In contrast, in **1a** the Rh-Br bond length

is similar to that found (average 2.530 Å) in several other mononuclear rhodium complexes containing this group,⁵ and may be compared with the similar distances in the salt [PPh₃][RhBr₂(PPh₃)(η^5 -7,8-C₂B₉H₁₁)] [2.520(2) and 2.598(1) Å].⁶

An intramolecular N-H...Br hydrogen bond is present in [RhBr(PPh₃)(η^5 -7-NH(CH₂CH=CHMe)₂-7-CB₁₀H₁₀)], a structural feature revealed by N...Br and Br...H distances of 3.074(6) and 1.92(7) Å, respectively.^{3b} In our study of **1a** the NH₂ protons were not located, but their inclusion in sensible calculated positions gives the shortest distance between the NH₂ hydrogens and the Br atom as 2.31 Å, from which we infer the absence of any N-H...Br bonding.

The NMR data for the species **1** are given in Tables 2 and 3. The ¹H NMR spectra show broad signals for the NH₂ groups at δ 9.80 (**1a**) and δ 8.30 (**1b**), corresponding in intensity to two

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Table 2. Hydrogen-1 and Carbon-13 NMR Data^a

compd	¹ H/δ ^b	¹³ C/δ ^{c,d}
1a	1.65 (s, 9 H, CMe ₃), 7.46–7.57 (m, 15 H, Ph), 9.80 (br s, 2 H, NH ₂)	ε135.6–129.1 (Ph), 76.5 (CB ₁₀ H ₁₀), 66.0 (NCMe ₃), 27.0 (CMe ₃)
1b	1.61 (s, 9 H, CMe ₃), 7.43–7.54 (m, 15 H, Ph), 8.30 (br s, 2 H, NH ₂)	134.9–128.6 (Ph), 75.8 (CB ₁₀ H ₁₀), 66.3 (NCMe ₃), 27.2 (CMe ₃)
2a	1.28, 1.51 (s × 2, 18 H, CMe ₃), 6.75 [d, 1 H, NH ₂ , <i>J</i> (HH) = 13], 7.36–7.77 (m, 15 H, Ph), 7.95 [d, 1 H, NH ₂ , <i>J</i> (HH) = 13]	135.5–127.8 (Ph), 82.3 [d of d, CB ₁₀ H ₁₀ , <i>J</i> (PC) = 39, <i>J</i> (RhC) = 10], 66.6 (NCMe ₃), 58.3 (CMe ₃), 29.7, 27.6 (CMe ₃)
2b	1.27, 1.50 (s × 2, 18 H, CMe ₃), 6.85 [d, 1 H, NH ₂ , <i>J</i> (HH) = 13], 7.40–7.80 (m, 15 H, Ph), 8.32 [d, 1 H, NH ₂ , <i>J</i> (HH) = 13]	135.2–127.9 (Ph), 83.7 [d of d, CB ₁₀ H ₁₀ , <i>J</i> (PC) = 40, <i>J</i> (RhC) = 10], 65.9 (NCMe ₃), 58.1 (CMe ₃), 29.7, 27.6 (CMe ₃)
3	1.26 (s, 18 H, CNCMe ₃), 1.17 (s, 9 H, NHCMe ₃), 3.50 (br s, 1 H, NH), 7.43–7.50 (m, 15 H, Ph)	134.7–128.1 (Ph), 106.5 (br, CB ₁₀ H ₁₀), 58.1, 54.4 (CMe ₃), 30.8, 29.6 (CMe ₃)
4	1.14, 1.20 (s × 2, 18 H, CMe ₃), 3.15 (br s, 1 H, NH), 7.43–7.51 (m, 15 H, Ph)	134.7–128.6 (Ph), 118.7 (br, CB ₁₀ H ₁₀), 58.1, 57.7 (CMe ₃), 31.3, 29.7 (CMe ₃)
5	1.13 (m, 9 H, CH ₂ Me), 1.63 (s, 9 H, CMe ₃), 2.15 (m, 6 H, PCH ₂), 8.20 (br s, 2 H, NH ₂)	73.1 (CB ₁₀ H ₁₀), 54.0 (CMe ₃), 27.1 (CMe ₃), 17.5 [d, PCH ₂ , <i>J</i> (PC) = 30], 8.2 (CH ₂ Me)
6	1.38 (s, 9 H, CMe ₃), 1.69 (m, 18 H, PMe), 7.25 (br s, 2 H, NH ₂)	65.5 (CMe ₃), 27.1 (CMe ₃), 19.2 [d, PMe, <i>J</i> (PC) = 33]
7a	1.57 (s, 9 H, CMe ₃), 2.35 (s, 3 H, NC ₅ H ₄ Me-4), 7.06–7.51 (m, 19 H, Ph and NC ₅ H ₄ Me-4), 8.55 (br s, 2 H, NH ₂)	150.2–125.4 (Ph and NC ₅ H ₄ Me-4), 78.2 (CB ₁₀ H ₁₀), 65.3 (CMe ₃), 27.3 (CMe ₃), 20.2 (NC ₅ H ₄ Me-4)
7b^f	1.63 (s, 9 H, CMe ₃), 1.84 (m, 4 H, CH ₂), 3.69 (m, 4 H, CH ₂ O), 7.39–7.55 (m, 15 H, Ph), 8.51 (br s, 2 H, NH ₂)	
8	1.52 (s, 9 H, CMe ₃), 2.58 (br s, 1 H, NH), 2.67 (s, 3 H, Me), 6.28–6.92 (m, 5 H, Ph)	121.6 (vbr, CB ₁₀ H ₁₀), 119.7 (C ¹ , C ₆ H ₅ Me), 109.5, 108.8 (C ² , C ³ , C ₆ H ₅ Me), 107.7 (C ⁴ , C ₆ H ₅ Me), 56.5 (CMe ₃), 30.4 (CMe ₃), 20.7 (C ₆ H ₅ Me)

^a Chemical shifts (δ) in ppm, coupling constants (*J*) in Hz, measurements at room temperature in CD₂Cl₂ unless otherwise stated. ^b Resonances for terminal BH protons occur as broad unresolved signals in the range δ ca. –1 to 2.5. ^c Hydrogen-1 decoupled; chemical shifts are positive to high frequency of SiMe₄. ^d Signals for CNBu^t nuclei not observed in spectra of compounds **2**, **3**, and **4**. ^e Measured in (CD₃)₂CO. ^f ¹³C{¹H} not measured due to dissociation of thf ligand.

Table 3. Boron-11 and Phosphorus-31 NMR Data^a

compd	¹¹ B/δ ^b	³¹ P/δ ^c
1a	9.9 (3 B), 5.4 (2 B), –6.9 (1 B), –14.8 (4 B)	34.1 [d, <i>J</i> (RhP) = 160]
1b	9.1 (3 B), 5.9 (2 B), –6.5 (1 B), –15.1 (4 B)	33.8 [d, <i>J</i> (RhP) = 160]
2a	10.9 (1 B), 4.9 (1 B), 0.2 (3 B), –7.7 (1 B), –10.9 (2 B), –14.4 (1 B), –18.6 (1 B)	36.4 [d, <i>J</i> (RhP) = 123]
2b	10.2 (1 B), 5.2 (1 B), 1.1 (1 B), –1.1 (2 B), –7.7 (1 B), –11.0 (2 B), –14.8 (1 B), –19.2 (1 B)	36.8 [d, <i>J</i> (RhP) = 125]
3	13.4 (1 B), 1.6 (4 B), –9.2 (3 B), –13.6 (2 B)	39.2 [d, <i>J</i> (RhP) = 108]
4	17.5 (1 B), 6.1 (2 B), –0.6 (2 B), –6.9 (1 B), –13.4 (4 B)	33.7 [d, <i>J</i> (RhP) = 133]
5	7.9 (3 B), 3.8 (2 B), –7.4 (1 B), –15.5 (4 B)	38.1 [d, <i>J</i> (RhP) = 150]
6	7.3 (1 B), 0.3 (2 B), –5.2 (2 B), –10.7 (3 B), –17.4 (2 B)	–6.3 [d, <i>J</i> (RhP) = 124]
7a	9.6 (1 B), 4.9 (4 B), –7.7 (1 B), –13.7 (3 B), –15.1 (1 B)	34.0 [d, <i>J</i> (RhP) = 137]
8	14.8 (1 B), 11.3 (2 B), 4.2 (2 B), –5.0 (1 B), –6.5 (2 B), –9.7 (2 B)	

^a Chemical shifts (δ) in ppm, coupling constants (*J*) in Hz, measurements in CD₂Cl₂, and at room temperature. ^b Hydrogen-1 decoupled; chemical shifts are positive to high frequency of BF₃·Et₂O (external). ^c Hydrogen-1 decoupled; chemical shifts are positive to high frequency of 85% H₃PO₄ (external).

Table 4. Selected Internuclear Distances (Å) and Angles (deg) for [RhBr(PPh₃)(η⁵-7-NH₂Bu^t-7-CB₁₀H₁₀)]·CH₂Cl₂ (**1a**) with Estimated Standard Deviations in Parentheses

Rh–B(2)	2.129(6)	Rh–B(5)	2.131(6)	Rh–B(4)	2.179(6)	Rh–B(3)	2.182(6)
Rh–C(1)	2.240(5)	Rh–P	2.334(2)	Rh–Br	2.5165(9)	C(1)–N(1)	1.488(7)
C(1)–B(10)	1.687(8)	C(1)–B(9)	1.695(8)	C(1)–B(2)	1.727(8)	C(1)–B(5)	1.740(8)
B(2)–B(6)	1.771(9)	B(2)–B(10)	1.805(9)	B(2)–B(3)	1.845(9)	B(3)–B(6)	1.770(9)
B(3)–B(7)	1.778(9)	B(3)–B(4)	1.800(9)	B(4)–B(7)	1.788(9)	B(4)–B(8)	1.789(10)
B(4)–B(5)	1.869(9)	B(5)–B(8)	1.760(9)	B(5)–B(9)	1.801(10)	B(6)–B(10)	1.776(10)
B(6)–B(7)	1.786(10)	B(6)–B(11)	1.790(10)	B(7)–B(11)	1.773(10)	B(7)–B(8)	1.794(10)
B(8)–B(9)	1.761(10)	B(8)–B(11)	1.788(10)	B(9)–B(11)	1.770(10)	B(9)–B(10)	1.771(10)
B(10)–B(11)	1.767(10)	N(1)–C(2)	1.545(8)	C(2)–C(3)	1.521(10)	C(2)–C(5)	1.537(10)
C(2)–C(4)	1.570(11)						
B(2)–Rh–B(5)	83.0(3)	B(2)–Rh–B(4)	85.3(3)	B(5)–Rh–B(4)	51.4(3)		
B(2)–Rh–B(3)	50.7(2)	B(5)–Rh–B(3)	85.2(3)	B(4)–Rh–B(3)	48.8(2)		
B(2)–Rh–C(1)	46.5(2)	B(5)–Rh–C(1)	46.8(2)	B(4)–Rh–C(1)	83.3(2)		
B(3)–Rh–C(1)	82.5(2)	B(2)–Rh–P	129.2(2)	B(5)–Rh–P	132.7(2)		
B(4)–Rh–P	92.7(2)	B(3)–Rh–P	91.7(2)	C(1)–Rh–P	174.2(2)		
B(2)–Rh–Br	115.7(2)	B(5)–Rh–Br	106.4(2)	B(4)–Rh–Br	149.2(2)		
B(3)–Rh–Br	161.7(2)	C(1)–Rh–Br	95.10(14)	P–Rh–Br	90.50(4)		
C(1)–N(1)–C(2)	128.8(5)						

protons. In the ¹³C{¹H} NMR spectrum resonances at δ 76.5 (**1a**) and δ 75.8 (**1b**) are tentatively assigned to the carbon nuclei of the CB₁₀H₁₀ cages present in these molecules. At the present time there is a paucity of information on ¹³C chemical shifts for carbon atoms in monocarbaboranes,^{1b} the chemical shifts of which are likely to vary with the metal in the MCB₁₀ framework

and the character of any exo-polyhedral groups. The ³¹P{¹H} NMR spectra for **1** have diagnostic doublet signals for the PPh₃ ligands at δ 34.1 (**1a**) and δ 33.8 (**1b**), both with *J*(RhP) = 160 Hz.

The compounds **1** are 16-electron coordinatively unsaturated rhodium complexes, and as such relate in an isolobal manner

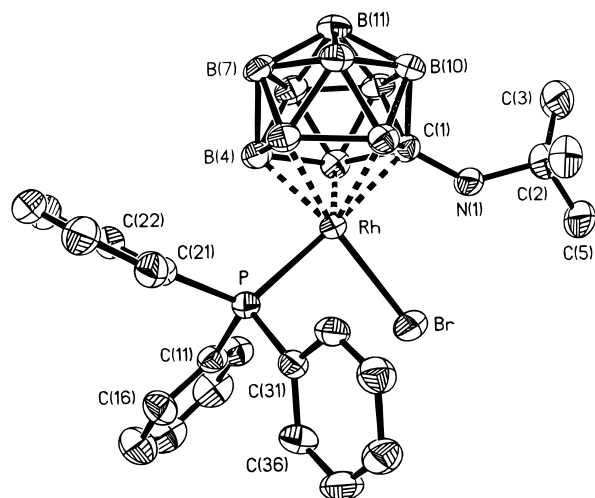


Figure 1. Molecular structure of $[\text{RhBr}(\text{PPh}_3)(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}\text{H}_{10})]$ (**1a**), showing the crystallographic labeling scheme. Thermal ellipsoids are at the 40% probability level, and hydrogen atoms are omitted for clarity.

with the previously reported dicarbon-rhodacarborane species $[\text{RhCl}(\text{PPh}_3)(\eta^5\text{-7,9-C}_2\text{B}_9\text{H}_{11})]$.⁷ In the complexes **1**, as in $[\text{RhCl}(\text{PPh}_3)(\eta^5\text{-7,9-C}_2\text{B}_9\text{H}_{11})]$, the electron deficiency is evidently metal centered since the cages are not distorted from a triangulated *closo*-icosahedral framework. The electronic and coordinate unsaturation of the species **1** prompted a study of their reactions with several simple electron pair donor groups. Studies commenced using the rodlike CNBu^t ligand in the expectation that this would minimize any steric effects.

Treatment of the compounds **1** in CH_2Cl_2 at -20°C with 1 mol equiv of CNBu^t gave the complexes $[\text{RhX}(\text{CNBu}^t)(\text{PPh}_3)(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}\text{H}_{10})]$ (**2a**, $\text{X} = \text{Br}$; **2b**, $\text{X} = \text{Cl}$). Data characterizing these products are summarized in Tables 1–3. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (Table 2) of these 18-electron complexes were informative. The chirality of the rhodium atoms in the complexes **2** results in the ^1H NMR spectra displaying two resonances for the diastereotopic protons of the NH_2 groups, and these occur as doublets [$J(\text{HH}) = 13\text{ Hz}$] at δ 6.75 and 7.95 for **2a** and at δ 6.85 and 8.32 for **2b**. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra revealed resonances at δ 82.3 (**2a**) and δ 83.7 (**2b**) which we assign to the cage-carbon nuclei. These appear as a doublet-of-doublets due to ^{31}P – ^{13}C and ^{103}Rh – ^{13}C coupling of ca. 40 and 10 Hz, respectively. No peaks were seen in either spectrum which could be attributed to the ligating carbon atoms of the CNBu^t ligand. These nuclei would be expected to resonate in the range δ ca. 130–180.^{8–10} In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the ruthenium cluster $[\text{Ru}_3(\text{CO})_7(\text{CNBu}^t)(\eta^5\text{-7-NMe}_3\text{-7-CB}_{10}\text{H}_{10})]$ the CNBu^t resonance is at δ 189.4.^{1b} Failure to observe peaks due to the CNBu^t nuclei in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **2** and other molecules containing this ligand, discussed below, is not surprising. Such signals are often weak and difficult to discern,¹⁰ and for **2** these peaks would be split by ^{103}Rh and ^{31}P coupling. Other resonances in the respective spectra were as expected.

In contrast with these results, the reaction between either of the complexes **1** with 2 mol equiv of CNBu^t in CH_2Cl_2 gave the bis(isocyanide)rhodium complex $[\text{Rh}(\text{CNBu}^t)_2(\text{PPh}_3)(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}\text{H}_{10})]$ (**3**) which was isolated by crystallization.

In this product the *nido*-cage system 7-NH Bu^t -7-CB $_{10}\text{H}_{10}$ is present. The latter formally donates three electrons to the rhodium atom rather than the four electrons donated to the metal by the charge compensated 7-NH $_{2\text{Bu}^t}$ -7-CB $_{10}\text{H}_{10}$ ligand in the species **1**. Evidently the reactions proceed with overall loss of HX via deprotonation of the CNH_2Bu^t group in the precursors **1**. Careful integration of the peaks in the ^1H NMR spectrum of **3** (Table 2) revealed that the resonance at δ 3.50 was due to an NH rather than an NH_2 group. The other NMR data for **3** (Tables 2 and 3) were in accord with the formulation. However, to place the molecular structure of **3** on a firm basis, a single-crystal X-ray diffraction study was undertaken at 173 K. Selected bond distances and angles are given in Table 5, and the molecule is shown in Figure 2.

The *nido*-cage fragment adopts the customary η^5 -bonding mode for attachment to the rhodium, but the significant result of the study was confirmation that N(1) carries a single H(1) atom, its position being both located and refined. The C(1)–N(1) distance [1.438(3) Å] and the C(1)–N(1)–C(2) angle [128.4(2) $^\circ$] in **3** are essentially the same as those in **1a** [C(1)–N(1) 1.488(7) Å, C(1)–N(1)–C(2) 128.8(5) $^\circ$]. It is noteworthy that in the *nido*-carborane 7-NH $_{2\text{Bu}^t}$ -7-CB $_{10}\text{H}_{12}$ the cage C–N distance is 1.508(2) Å.¹¹ The Rh–P distance [2.3568(7) Å] is also similar to that in **1a**. The two CNBu^t groups are linearly bound to the rhodium (N–C–Rh average 176 $^\circ$). The various groups ligating the metal contribute 9 electrons, thus giving the metal atom an 18-electron configuration.

In further experiments with CNBu^t the compounds **1** were treated with 2 mol equiv of the isocyanide at room temperature but the product was isolated by column chromatography rather than by crystallization. This procedure yielded the 16-electron rhodium complex $[\text{Rh}(\text{CNBu}^t)(\text{PPh}_3)(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}\text{H}_{10})]$ (**4**), characterized by microanalysis (Table 1) and by the NMR data summarized in Tables 2 and 3. Not surprisingly, once isolated, compound **4** afforded **3** on treatment with CNBu^t in CH_2Cl_2 .

Since the formation of **4** again involved an unexpected ligand transformation from the charge-compensated moiety 7-NH $_{2\text{Bu}^t}$ -7-CB $_{10}\text{H}_{10}$ to the neutral 7-NH Bu^t -7-CB $_{10}\text{H}_{10}$, an X-ray diffraction study was made on this product. Selected bond distances and angles are given in Table 6, and the structure is shown in Figure 3. Atom H(1) atom attached to N(1) was located and its position refined. The C(1)–N(1) distance [1.413(4) Å] and C(1)–N(1)–C(2) angle [129.9(3) $^\circ$] are very similar to these same parameters for **3**. The CNBu^t ligand is essentially linearly bound to the metal [Rh–C(6)–N(7) 176.4(3) $^\circ$], as found for isocyanide groups in **3**, and the Rh–P bond length [2.354(1) Å] also shows little variation from that in **3** [2.3568(7) Å]. With the possible exception of the Rh–C(1) distances [**3**, 2.337(2); **4**, 2.103(3) Å] the connectivities between the rhodium and

the pentagonal CBBBB ring are also closely similar in the two compounds. Thus overall the structural parameters in common are not influenced by **3** being an 18-electron and **4** being a 16-electron species.

Some reactions between the compounds **1** and other donor ligands were next investigated. Treatment of **1a** in CH_2Cl_2 with 1 mol equiv of PEt_3 gave the 16-electron complex $[\text{RhBr}(\text{PEt}_3)(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}\text{H}_{10})]$ (**5**), there being no evidence of a stable 18-electron species $[\text{RhBr}(\text{PEt}_3)(\text{PPh}_3)(\eta^5\text{-7-NH}_2\text{Bu}^t\text{-7-CB}_{10}\text{H}_{10})]$. Existence of the latter is perhaps inhibited by steric effects, cone angles for PEt_3 and PPh_3 being 132 $^\circ$ and 145 $^\circ$, respectively.¹² The reaction between **1b** and an excess

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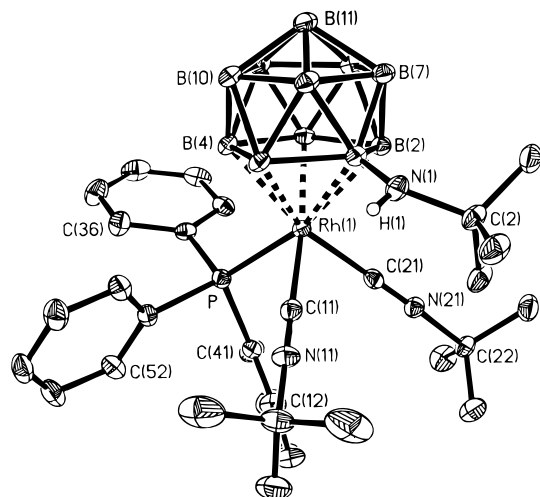
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Table 5. Selected Internuclear Distances (Å) and Angles (deg) for [Rh(CNBu^t)₂(PPh₃)(η^5 -7-NHBu^t-7-CB₁₀H₁₀)] (**3**) with Estimated Standard Deviations in Parentheses

Rh(1)–C(21)	2.010(2)	Rh(1)–C(11)	2.022(2)	Rh(1)–B(3)	2.211(2)	Rh(1)–B(5)	2.212(2)
Rh(1)–B(4)	2.220(2)	Rh(1)–B(2)	2.250(3)	Rh(1)–C(1)	2.337(2)	Rh(1)–P	2.3568(7)
B(2)–C(1)	1.727(3)	B(2)–B(8)	1.780(3)	B(2)–B(7)	1.792(4)	B(2)–B(3)	1.851(4)
B(3)–B(9)	1.777(3)	B(3)–B(8)	1.779(4)	B(3)–B(4)	1.851(3)	B(4)–B(10)	1.773(4)
B(4)–B(9)	1.775(3)	B(4)–B(5)	1.836(3)	B(5)–C(1)	1.773(3)	B(5)–B(10)	1.781(3)
B(5)–B(6)	1.792(4)	B(6)–C(1)	1.729(3)	B(6)–B(10)	1.755(4)	B(6)–B(7)	1.763(4)
B(6)–B(11)	1.767(4)	B(7)–C(1)	1.723(3)	B(7)–B(8)	1.758(4)	B(7)–B(11)	1.778(4)
B(8)–B(11)	1.777(4)	B(8)–B(9)	1.783(4)	B(9)–B(11)	1.766(4)	B(9)–B(10)	1.794(4)
B(10)–B(11)	1.772(4)	C(1)–N(1)	1.438(3)	N(1)–C(2)	1.485(3)	N(1)–H(1)	0.74 (0.03)
C(11)–N(11)	1.152(3)	N(11)–C(12)	1.470(3)	C(21)–N(21)	1.154(3)	N(21)–C(22)	1.461(3)
C(21)–Rh(1)–C(11)	90.53(9)	C(21)–Rh(1)–B(3)	99.78(9)	C(11)–Rh(1)–B(3)	168.81(9)s		
C(21)–Rh(1)–B(5)	155.06(9)	C(11)–Rh(1)–B(5)	85.93(9)	B(3)–Rh(1)–B(5)	82.88(9)		
C(21)–Rh(1)–B(4)	146.40(9)	C(11)–Rh(1)–B(4)	121.53(9)	B(3)–Rh(1)–B(4)	49.37(9)		
B(5)–Rh(1)–B(4)	48.94(9)	C(21)–Rh(1)–B(2)	83.64(9)	C(11)–Rh(1)–B(2)	128.96(9)		
B(3)–Rh(1)–B(2)	49.01(9)	B(5)–Rh(1)–B(2)	79.54(9)	B(4)–Rh(1)–B(2)	83.09(9)		
C(21)–Rh(1)–C(1)	109.91(8)	C(11)–Rh(1)–C(1)	92.68(8)	B(3)–Rh(1)–C(1)	79.78(8)		
B(5)–Rh(1)–C(1)	45.80(8)	B(4)–Rh(1)–C(1)	80.61(9)	B(2)–Rh(1)–C(1)	44.20(8)		
C(21)–Rh(1)–P	89.01(6)	C(11)–Rh(1)–P	89.04(7)	B(3)–Rh(1)–P	95.43(7)		
B(5)–Rh(1)–P	115.56(7)	B(4)–Rh(1)–P	82.35(7)	B(2)–Rh(1)–P	141.16(7)		
C(1)–Rh(1)–P	160.96(5)	N(1)–C(1)–B(7)	116.0(2)	N(1)–C(1)–B(2)	128.2(2)		
B(7)–C(1)–B(2)	62.57(14)	N(1)–C(1)–B(6)	110.0(2)	B(7)–C(1)–B(6)	61.41(14)		
B(2)–C(1)–B(6)	111.5(2)	N(1)–C(1)–B(5)	117.2(2)	B(7)–C(1)–B(5)	111.1(2)		
B(2)–C(1)–B(5)	109.2(2)	B(6)–C(1)–B(5)	61.51(14)	C(1)–N(1)–C(2)	128.4(2)		
C(1)–N(1)–H(1)	112. (2)	C(2)–N(1)–H(1)	112 (2)	N(11)–C(11)–Rh(1)	176.0(2)		
C(11)–N(11)–C(12)	177.7(2)	N(21)–C(21)–Rh(1)	176.4(2)	C(21)–N(21)–C(22)	173.7(2)		

**Figure 2.** Molecular structure of [Rh(CNBu^t)₂(PPh₃)(η^5 -7-NHBu^t-7-CB₁₀H₁₀)] (**3**), showing the crystallographic labeling scheme. Thermal ellipsoids are at the 40% probability level, and hydrogen atoms are omitted for clarity.

of the less sterically demanding PMe₃ (cone angle 118°), with the phosphine in excess, gave the 18-electron complex [RhCl(PMe₃)₂(η^5 -7-NH₂Bu^t-7-CB₁₀H₁₀)] (**6**). It is interesting that the reaction with PMe₃ did not afford a product containing the η^5 -7-NHBu^t-7-CB₁₀H₁₀ ligand as occurs in the formation of **3**. Data fully characterizing complexes **5** and **6** are given in Tables 1–3.

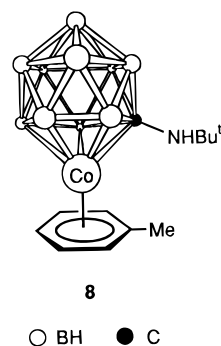
The reaction between **1a** and NC₅H₄Me-4 afforded the 18-electron complex [RhBr(NC₅H₄Me-4)(PPh₃)(η^5 -7-NH₂Bu^t-7-CB₁₀H₁₀)] (**7a**), data for which are given in Tables 1–3. Treatment of **1a** with thf (tetrahydrofuran) gave [RhBr(thf)(PPh₃)(η^5 -7-NH₂Bu^t-7-CB₁₀H₁₀)] (**7b**). However, although microanalytical data were obtained for this complex (Table 1), it readily dissociates in solution and satisfactory ¹³C{¹H}, ³¹P{¹H}, and ¹¹B{¹H} NMR spectra were not measured.

It was not possible to isolate an 18-electron complex [RhBr(CO)(PPh₃)(η^5 -7-NH₂Bu^t-7-CB₁₀H₁₀)] (**7c**) as a solid by treating **1a** with CO. However, red CH₂Cl₂ solutions of **1a** turned

yellow upon passage of a stream of CO gas, and formation of **7c** was suggested by the appearance of a strong CO band at 2076 cm^{−1} in the IR spectrum. Removal of solvent, however, regenerated **1a**. A similar reversible formation of a CO adduct has been observed on treatment of solutions of the 16-electron complex [RhCl(PPh₃)(η^5 -7,9-C₂B₉H₁₁)] with CO.⁷

Preparation of the rhodium compounds **1** directly from [RhX(PPh₃)₃] and *nido*-7-NH₂Bu^t-7-CB₁₀H₁₂ raised the possibility of synthesizing cobalt analogs. For a reaction to occur between *nido*-7-NH₂Bu^t-7-CB₁₀H₁₂ and [CoCl(PPh₃)₃] it was necessary to heat these reagents for several hours in toluene at reflux. Even under these forcing conditions the yield of product, a deep red crystalline complex, was low. It became apparent immediately from NMR spectra that although this product was diamagnetic it was not an analog of **1b**. Its true nature was only established by an X-ray diffraction study. There were two independent molecules in the asymmetric unit, and results for one are given in Table 7, with the molecule shown in Figure 4.

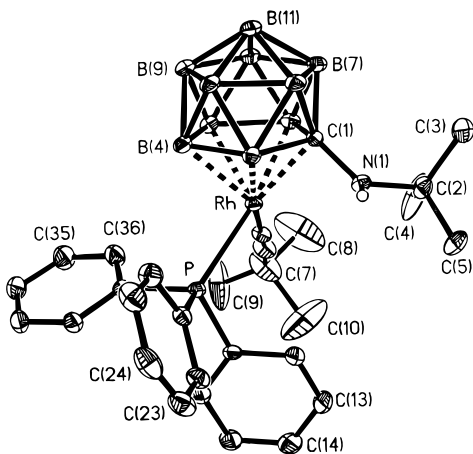
It is evident that the molecule is an arene(carborane)cobalt complex [Co(η^6 -C₆H₅Me)(η^5 -7-NHBu^t-7-CB₁₀H₁₀)] (**8**) in which



the cobalt atom attains an 18-electron valence shell, formally receiving 6 electrons from the toluene ligand and 3 from the *nido*-7-NHBu^t-7-CB₁₀H₁₀ cage. Although the H atom bonded to N(1) was not located in the X-ray diffraction pattern, its presence was revealed in the ¹H NMR spectrum as a broad resonance at δ 2.58 corresponding in intensity to a single proton. The C(11)–N(1) bond length [1.415(5) Å] may be compared

Table 6. Selected Internuclear Distances (Å) and Angles (deg) for [Rh(CNBu^t)(PPh₃)(η^5 -7-NHBu^t-7-CB₁₀H₁₀)] (**4**) with Estimated Standard Deviations in Parentheses

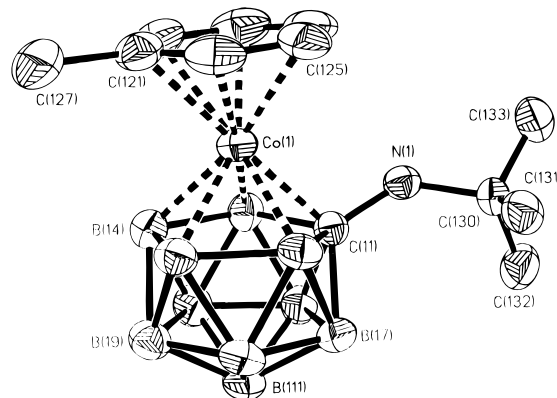
Rh—C(6)	1.998(3)	Rh—C(1)	2.103(3)	Rh—B(5)	2.171(3)	Rh—B(2)	2.200(3)
Rh—B(3)	2.204(4)	Rh—B(4)	2.218(3)	Rh—P	2.3542(10)	C(1)—N(1)	1.413(4)
C(1)—B(6)	1.710(4)	C(1)—B(7)	1.716(4)	C(1)—B(2)	1.747(4)	C(1)—B(5)	1.786(4)
B(2)—B(8)	1.750(5)	B(2)—B(7)	1.782(5)	B(2)—B(3)	1.850(5)	B(3)—B(9)	1.790(5)
B(3)—B(8)	1.806(5)	B(3)—B(4)	1.845(5)	B(4)—B(9)	1.781(5)	B(4)—B(10)	1.798(5)
B(4)—B(5)	1.812(5)	B(5)—B(10)	1.757(5)	B(5)—B(6)	1.783(5)	B(6)—B(11)	1.781(5)
B(6)—B(7)	1.784(5)	B(6)—B(10)	1.785(5)	B(7)—B(8)	1.771(5)	B(7)—B(11)	1.783(5)
B(8)—B(11)	1.778(5)	B(8)—B(9)	1.791(5)	B(9)—B(10)	1.780(5)	B(9)—B(11)	1.781(5)
B(10)—B(11)	1.778(5)	N(1)—C(2)	1.503(4)	N(1)—H(1)	0.83(4)	C(6)—N(7)	1.152(4)
N(7)—C(7)	1.453(5)	C(7)—C(8)	1.47(2)	C(7)—C(9)	1.371(11)	C(7)—C(10)	1.673(13)
C(7)—C(8A) ^a	1.380(11)	C(7)—C(9A)	1.675(14)	C(7)—C(10A)	1.460(14)		
C(6)—Rh—C(1)	123.96(12)	C(6)—Rh—B(5)	172.89(12)	C(1)—Rh—B(5)	49.37(12)		
C(6)—Rh—B(2)	87.38(13)	C(1)—Rh—B(2)	47.85(12)	B(5)—Rh—B(2)	85.71(13)		
C(6)—Rh—B(3)	92.01(14)	C(1)—Rh—B(3)	82.46(13)	B(5)—Rh—B(3)	84.78(14)		
B(2)—Rh—B(3)	49.68(14)	C(6)—Rh—B(4)	132.24(14)	C(1)—Rh—B(4)	82.85(12)		
B(5)—Rh—B(4)	48.76(13)	B(2)—Rh—B(4)	85.38(13)	B(3)—Rh—B(4)	49.31(13)		
C(6)—Rh—P	88.54(9)	C(1)—Rh—P	141.34(8)	B(5)—Rh—P	98.55(9)		
B(2)—Rh—P	168.84(10)	B(3)—Rh—P	120.16(10)	B(4)—Rh—P	89.69(9)		
C(1)—N(1)—C(2)	129.9(3)	H(1)—N(1)—C(1)	109(2)	C(2)—N(1)—H(1)	112(2)		
N(7)—C(6)—Rh	176.4(3)	C(6)—N(7)—C(7)	176.5(4)	C(9)—C(7)—N(7)	114.8(8)		
C(8A)—C(7)—C(10A)	125.7(11)	C(9)—C(7)—C(8)	122.8(12)	N(7)—C(7)—C(8)	109.4(9)		
C(9)—C(7)—C(10)	103.2(11)	N(7)—C(7)—C(10)	100.3(5)	C(8)—C(7)—C(10)	102.5(11)		
C(8A)—C(7)—C(9A)	107.1(9)	C(10A)—C(7)—C(9A)	102.6(11)				

^a Disordered component of the CNBu^t ligand (see Experimental Section).**Figure 3.** Molecular structure of [Rh(CNBu^t)(PPh₃)(η^5 -7-NHBu^t-7-CB₁₀H₁₀)] (**4**), showing the crystallographic labeling scheme. Thermal ellipsoids are at the 40% probability level, and hydrogen atoms are omitted for clarity.

with the corresponding C—N distances in **3** [1.438(3) Å] and **4** [1.413(4) Å], all three being perceptibly shorter than that [1.508(2) Å] in *nido*-7-NH₂Bu^t-7-CB₁₀H₁₂.¹¹

In addition to resonances due to the C₆H₅Me and Bu^t groups, the ¹³C{¹H} NMR spectrum of **8** displayed a broad weak peak at δ 121.6, the band profile being typical of that for a cage-carbon nucleus. The chemical shift may be compared with the corresponding cage-carbon signals in the ¹³C{¹H} NMR spectra of **3** (δ 106.5) and **4** (δ 118.7), which also contain the η^5 -7-NHBu^t-CB₁₀H₁₀ ligand. Noteworthy, the resonances for the cage-carbons in the species having the charge-compensated η^5 -7-NH₂Bu^t-7-CB₁₀H₁₀ ligand are appreciably more shielded (Table 2).^{1b}

As far as we are aware, only two species structurally related to **8** have been reported: [Co(η^6 -C₁₀H₁₀)(CB₁₀H₁₁)]¹³ and [Co(η^6 -C₆H₅Me)(η^5 -7-CH(SiMe₃)₂-7-CB₁₀H₁₀)]¹⁴. The former was obtained in ca. 9% yield as an unexpected product of

**Figure 4.** Molecular structure of [Co(η^6 -C₆H₅Me)(η^5 -7-NHBu^t-7-CB₁₀H₁₀)] (**8**), showing the crystallographic labeling scheme. Thermal ellipsoids are at the 40% probability level, and hydrogen atoms are omitted for clarity.

treating Na[Co(η^5 -C₅H₅)(η^5 -CB₁₀H₁₁)] with sodium naphthalide in tetrahydrofuran, followed by addition of NaC₅H₅ and NiBr₂ with air oxidation of the mixture. The latter was prepared in ca. 6% yield by reacting *nido*-7-CH(SiMe₃)₂-9-SMe₂-7-CB₁₀H₁₁ in toluene with cobalt vapor. Its structure was determined by X-ray diffraction. The connectivities between the cobalt atom and the atoms of the CBBBB pentagonal ring ranged from 2.07(1) to 2.143(9) Å with the longest distance being to the carbon atom.¹⁴ These data compare well with those for **8** in which the connectivities between the metal atom and the CB₄ atoms of the cage are 2.069(5)–2.138(4) Å, with again the longest being to the ring carbon. The cobalt–carbon distances involved in attachment of the η^6 -C₆H₅Me ligand in the two molecules are also very similar being in the range 2.126(4)–2.175(4) Å for **8** and 2.10(1)–2.17(1) Å for [Co(η^6 -C₆H₅Me)(η^5 -7-CH(SiMe₃)₂-7-CB₁₀H₁₀)].

Conclusions

It has been shown that the complexes **1** can be conveniently obtained directly from *nido*-7-NH₂Bu^t-7-CB₁₀H₁₂ and [RhX(PPh₃)₃], and that these species provide a convenient entry route to several other monocarbon rhodacarborane complexes in which

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Table 7. Selected Internuclear Distances (Å) and Angles (deg) for One of the Crystallographically Independent Molecules of [Co(η^6 -C₆H₅Me)(η^5 -7-NHBu^t-7-CB₁₀H₁₀)] (**8**) with Estimated Standard Deviations in Parentheses

Co(1)–C(11)	2.138(4)	Co(1)–B(12)	2.069(5)	Co(1)–B(13)	2.100(4)	Co(1)–B(14)	2.104(5)
Co(1)–B(15)	2.086(5)	Co(1)–C(121)	2.175(4)	Co(1)–C(122)	2.143(4)	Co(1)–C(123)	2.158(5)
Co(1)–C(124)	2.168(5)	Co(1)–C(125)	2.143(4)	Co(1)–C(126)	2.126(4)	C(11)–N(1)	1.415(5)
C(11)–B(17)	1.716(6)	C(11)–B(15)	1.719(5)	C(11)–B(16)	1.723(5)	C(11)–B(12)	1.748(5)
B(12)–B(18)	1.766(6)	B(12)–B(17)	1.798(6)	B(12)–B(13)	1.813(6)	B(13)–B(18)	1.771(7)
B(13)–B(19)	1.773(6)	B(13)–B(14)	1.801(7)	B(14)–B(110)	1.772(7)	B(14)–B(19)	1.774(7)
B(14)–B(15)	1.809(6)	B(15)–B(110)	1.769(7)	B(15)–B(16)	1.775(6)	B(16)–B(17)	1.757(7)
B(16)–B(111)	1.765(7)	B(16)–B(110)	1.770(7)	B(17)–B(18)	1.775(7)	B(17)–B(111)	1.784(7)
B(18)–B(111)	1.782(7)	B(18)–B(19)	1.783(7)	B(19)–B(111)	1.759(7)	B(19)–B(110)	1.777(7)
B(110)–B(111)	1.770(7)	N(1)–C(130)	1.480(5)	C(130)–C(133)	1.524(5)	C(130)–C(131)	1.525(5)
C(130)–C(132)	1.535(5)	C(121)–C(122)	1.387(6)	C(121)–C(126)	1.395(6)	C(121)–C(127)	1.510(6)
C(122)–C(123)	1.385(7)	C(123)–C(124)	1.365(8)	C(124)–C(125)	1.386(7)	C(125)–C(126)	1.393(7)
B(12)–Co(1)–B(15)	85.7(2)	B(12)–Co(1)–B(13)	51.6(2)	B(15)–Co(1)–B(13)	87.4(2)		
B(12)–Co(1)–B(14)	87.8(2)	B(15)–Co(1)–B(14)	51.2(2)	B(13)–Co(1)–B(14)	50.7(2)		
B(12)–Co(1)–C(126)	100.8(2)	B(15)–Co(1)–C(126)	173.2(2)	B(13)–Co(1)–C(126)	95.0(2)		
B(14)–Co(1)–C(126)	126.4(2)	B(12)–Co(1)–C(11)	49.1(2)	B(15)–Co(1)–C(11)	48.0(2)		
B(13)–Co(1)–C(11)	86.0(2)	B(14)–Co(1)–C(11)	85.5(2)	C(126)–Co(1)–C(11)	138.4(2)		
B(12)–Co(1)–C(125)	96.5(2)	B(15)–Co(1)–C(125)	143.9(2)	B(13)–Co(1)–C(125)	122.0(2)		
B(14)–Co(1)–C(125)	164.4(2)	C(126)–Co(1)–C(125)	38.1(2)	C(11)–Co(1)–C(125)	108.7(2)		
B(12)–Co(1)–C(122)	165.4(2)	B(15)–Co(1)–C(122)	105.5(2)	B(13)–Co(1)–C(122)	118.5(2)		
B(14)–Co(1)–C(122)	92.0(2)	C(126)–Co(1)–C(122)	67.8(2)	C(11)–Co(1)–C(122)	145.4(2)		
C(125)–Co(1)–C(122)	80.1(2)	B(12)–Co(1)–C(123)	152.8(2)	B(15)–Co(1)–C(123)	95.0(2)		
B(13)–Co(1)–C(123)	155.5(2)	B(14)–Co(1)–C(123)	113.7(2)	C(126)–Co(1)–C(123)	80.2(2)		
C(11)–Co(1)–C(123)	113.6(2)	C(125)–Co(1)–C(123)	67.3(2)	C(122)–Co(1)–C(123)	37.6(2)		
B(12)–Co(1)–C(124)	118.2(2)	B(15)–Co(1)–C(124)	110.9(2)	B(13)–Co(1)–C(124)	159.4(2)		
B(14)–Co(1)–C(124)	149.1(2)	C(126)–Co(1)–C(124)	68.0(2)	C(11)–Co(1)–C(124)	99.0(2)		
C(125)–Co(1)–C(124)	37.5(2)	C(122)–Co(1)–C(124)	67.1(2)	C(123)–Co(1)–C(124)	36.8(2)		
B(12)–Co(1)–C(121)	128.1(2)	B(15)–Co(1)–C(121)	135.8(2)	B(13)–Co(1)–C(121)	93.6(2)		
B(14)–Co(1)–C(121)	97.2(2)	C(126)–Co(1)–C(121)	37.8(2)	C(11)–Co(1)–C(121)	176.2(2)		
C(125)–Co(1)–C(121)	68.4(2)	C(122)–Co(1)–C(121)	37.5(2)	C(123)–Co(1)–C(121)	67.8(2)		
C(124)–Co(1)–C(121)	80.1(2)	C(11)–N(1)–C(130)	130.5(3)				

Table 8. Crystallographic Data

	1a ·CH ₂ Cl ₂	3	4	8
formula	C ₂₄ H ₃₈ B ₁₀ BrCl ₂ NPRh	C ₃₃ H ₅₃ B ₁₀ N ₃ PRh	C ₂₈ H ₄₄ B ₁₀ N ₂ PRh	C ₁₂ H ₂₈ B ₁₀ NCo
<i>M_r</i>	733.34	733.76	650.63	353.38
<i>T</i> /K	293	173	173	293
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	12.937(3)	10.533(2)	9.840(3)	16.332(5)
<i>b</i> (Å)	18.101(4)	19.110(4)	10.809(3)	10.397(2)
<i>c</i> (Å)	14.695(4)	19.707(4)	17.287(3)	22.186(6)
α (deg)			88.49(2)	
β (deg)	104.21(2)	105.413(9)	84.57(2)	102.94(2)
γ (deg)			69.809(14)	
<i>V</i> (Å ³)	3335.8(14)	3824.0(14)	1717.8(8)	3671(2)
<i>Z</i>	4	4	2	8
<i>d</i> _{calc} /g cm ^{−3}	1.460	1.275	1.258	1.279
μ (Mo K α) / mm ^{−1}	1.936	0.516	0.565	0.926
<i>F</i> (000)/e	1472	1528	672	1472
crystal dimensions (mm)	0.25 × 0.30 × 0.30	0.45 × 0.1 × 0.1	0.60 × 0.40 × 0.40	0.15 × 0.20 × 0.25
crystal color, shape	red prism	yellow needle	red prism	red prism
reflens measured	14659	17402	7830	13397
independent reflens	5849	6720	5836	5221
2 θ range (deg)	5.0–50.0	4.0–50.0	5.0–50.0	3.0–46.5
refinement method	full-matrix least squares on all <i>F</i> ² data	full-matrix least squares on all <i>F</i> ² data	full-matrix least squares on all <i>F</i> ² data	full-matrix least squares on all <i>F</i> ² data
final residuals	w <i>R</i> ₂ = 0.131 ^a (<i>R</i> ₁ = 0.051) ^b	w <i>R</i> ₂ = 0.104 ^a (<i>R</i> ₁ = 0.039) ^b	w <i>R</i> ₂ = 0.067 ^a (<i>R</i> ₁ = 0.027) ^b	w <i>R</i> ₂ = 0.115 ^a (<i>R</i> ₁ = 0.052) ^b
weighting factors	<i>a</i> = 0.0394; <i>b</i> = 11.54 ^a	<i>a</i> = 0.0602; <i>b</i> = 2.0925 ^a	<i>a</i> = 0.0205; <i>b</i> = 3.3801 ^a	<i>a</i> = 0.0265; <i>b</i> = 3.6239 ^a
goodness of fit on <i>F</i> ²	1.120	1.079	1.101	1.198
final electron density diff features (max/min)/e Å ^{−3}	0.65, −1.02	0.70, −1.14	0.29, −0.41	0.21, −0.23

^a Structure was refined on *F*_o² using all data: w*R*₂ = [Σ(*wF*_o² − *F*_c²)/Σ(*wF*_o²)]^{1/2}, where *w*^{−1} = [$\sigma^2(F_o^2) + (aP)^2 + bP$] and *P* = [max(*F*_o², 0) + 2*F*_c²]/3. ^b The value in parentheses is given for comparison with refinements based on *F*_o with a typical threshold of *F* ≥ 4 σ (*F*) and *R*₁ = Σ|*F*_o − |*F*_c||/Σ|*F*_o| and *w*^{−1} = [$\sigma^2(F_o) + gF_o^2$].

the metal adopts either 16- or 18-electron configurations in the valence shell. Reactions with CNBu^t in which neutral charge-compensated carbon-substituted *clos*-1-NH₂Bu^t-2,1-RhCB₁₀H₁₀ frameworks are transformed into polyhedra with *clos*-1-NHBu^t-2,1-RhCB₁₀H₁₀ cage structures are without precedent. The

synthesis of the cobalt complex **8** is novel and must at some stage in the reaction involve deprotonation of an η^5 -7-NH₂Bu^t-7-CB₁₀H₁₀ four-electron donor ligand into a three-electron donor η^5 -7-NHBu^t-7-CB₁₀H₁₀ group. Together the three compounds [Co(η^6 -C₁₀H₁₀)(CB₁₀H₁₁)],¹³ [Co(η^6 -C₆H₅Me)(η^5 -7-CH(SiMe₃)₂-

Table 9. Atomic Positional Parameters (Fractional Coordinates $\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for the Atoms of **1a**

atom	x	y	z	$U(\text{eq})^a$
Rh	2809(1)	319(1)	2824(1)	35(1)
Br	2711(1)	1666(1)	2387(1)	65(1)
P	3492(1)	39(1)	1534(1)	38(1)
C(11)	2577(5)	217(3)	400(4)	45(1)
C(12)	1570(5)	486(3)	340(5)	55(2)
C(13)	879(6)	621(4)	-531(5)	72(2)
C(14)	1213(7)	486(5)	-1337(5)	80(3)
C(15)	2212(7)	217(5)	-1280(5)	79(2)
C(16)	2900(6)	66(4)	-428(4)	61(2)
C(21)	3984(5)	-885(3)	1398(4)	41(1)
C(22)	3268(5)	-1446(4)	1045(4)	54(2)
C(23)	3610(7)	-2171(4)	1000(5)	65(2)
C(24)	4678(7)	-2332(4)	1292(5)	65(2)
C(25)	5395(6)	-1787(4)	1622(5)	63(2)
C(26)	5058(5)	-1058(4)	1671(4)	55(2)
C(31)	4630(4)	654(3)	1651(4)	39(1)
C(32)	5399(5)	652(3)	2490(4)	46(1)
C(33)	6254(5)	1127(4)	2641(4)	56(2)
C(34)	6335(6)	1629(4)	1950(5)	63(2)
C(35)	5570(6)	1647(4)	1125(5)	61(2)
C(36)	4720(5)	1159(3)	959(4)	49(1)
C(1)	2212(4)	473(3)	4118(4)	40(1)
B(2)	3459(5)	81(4)	4270(4)	42(2)
B(3)	3370(5)	-731(3)	3496(4)	41(1)
B(4)	2026(5)	-751(4)	2777(5)	43(2)
B(5)	1342(5)	57(4)	3163(5)	44(2)
B(6)	3318(6)	-823(4)	4683(5)	45(2)
B(7)	2410(6)	-1330(4)	3789(5)	46(2)
B(8)	1166(6)	-841(4)	3556(5)	50(2)
B(9)	1282(6)	-105(4)	4358(5)	49(2)
B(10)	2609(6)	-89(4)	5055(4)	45(2)
B(11)	1959(6)	-943(4)	4731(5)	52(2)
N(1)	2017(4)	1273(3)	4239(3)	51(1)
C(2)	2320(7)	1746(4)	5140(5)	71(2)
C(3)	1643(8)	1522(5)	5807(6)	96(3)
C(4)	3558(7)	1690(5)	5550(6)	86(2)
C(5)	2023(8)	2531(4)	4770(6)	88(3)
C(60)	291(11)	-2144(7)	-2066(14)	168(8)
Cl(1)	641(3)	-1816(3)	-3084(3)	163(2)
Cl(2)	771(5)	-1598(4)	-1147(4)	203(3)

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

7-CB₁₀H₁₀],¹⁴ and **8** form a family of complexes where monocarbon ligands, formally [RCB₁₀H₁₀]³⁻, are bound to Co³⁺.

Experimental Section

General Considerations. 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. Light petroleum refers to that fraction of boiling point 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 the following frequencies: ¹H at 360.13, ¹³C at 90.56, ¹¹B at 115.55, and ³¹P at 145.78 MHz. The reagents [7-NH₂Bu^t-*nido*-7-CB₁₀H₁₂],^{1b,15} [RhX(PPh₃)₃] (X = Br, Cl),¹⁶ and [CoCl(PPh₃)₃]¹⁷ were made by procedures previously described.

Syntheses of the Compounds [RhX(PPh₃)(η^5 -7-NH₂Bu^t-7-CB₁₀H₁₀)] (1, X = Br, Cl). (i) A mixture of the compounds [RhBr(PPh₃)₃] (0.97 g, 1.0 mmol) and *nido*-7-NH₂Bu^t-7-CB₁₀H₁₂ (0.20 g, 1.0 mmol) was refluxed in toluene (20 mL) for 3 h. Solvent was removed *in vacuo*, and the residue was dissolved in CH₂Cl₂ (5 mL) and then chromatographed. Elution with CH₂Cl₂–light petroleum (3:1) removed a deep red fraction. The solvent was removed *in vacuo* and the residue crystallized from toluene (10 mL) to give red microcrystals of [RhBr(PPh₃)(η^5 -7-NH₂Bu^t-7-CB₁₀H₁₀)] (**1a**) (0.36 g).

Table 10. Atomic Positional Parameters (Fractional Coordinates $\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for the Atoms of **3**

atom	x	y	z	$U(\text{eq})^a$
Rh(1)	7691(1)	8429(1)	2324(1)	17(1)
B(2)	5734(2)	7877(1)	2069(1)	21(1)
B(3)	6008(2)	8463(1)	1374(1)	20(1)
B(4)	7584(2)	8189(1)	1208(1)	20(1)
B(5)	8180(3)	7466(1)	1824(1)	21(1)
B(6)	7037(3)	6759(1)	1564(1)	23(1)
B(7)	5521(3)	7010(1)	1710(1)	23(1)
B(8)	4928(3)	7732(1)	1165(1)	23(1)
B(9)	6049(2)	7916(1)	651(1)	22(1)
B(10)	7384(3)	7307(1)	921(1)	23(1)
B(11)	5741(3)	7041(1)	847(1)	24(1)
C(1)	6986(2)	7266(1)	2283(1)	20(1)
N(1)	7416(2)	6862(1)	2918(1)	25(1)
C(2)	6862(2)	6852(1)	3537(1)	27(1)
C(3)	7710(3)	6328(1)	4049(1)	37(1)
C(4)	6926(3)	7561(1)	3901(1)	33(1)
C(5)	5437(3)	6592(1)	3340(1)	34(1)
C(11)	9332(2)	8229(1)	3106(1)	23(1)
N(11)	10254(2)	8075(1)	3542(1)	28(1)
C(12)	11447(2)	7907(1)	4101(1)	35(1)
C(13)	12475(3)	7635(2)	3751(2)	65(1)
C(14)	11077(3)	7369(2)	4582(2)	67(1)
C(15)	11905(3)	8587(2)	4497(2)	46(1)
C(21)	6928(2)	8977(1)	2992(1)	21(1)
N(21)	6510(2)	9264(1)	3401(1)	23(1)
C(22)	6087(2)	9584(1)	3978(1)	25(1)
C(23)	7193(3)	9472(2)	4646(1)	38(1)
C(24)	5847(3)	10353(1)	3803(2)	39(1)
C(25)	4833(2)	9214(1)	4025(1)	36(1)
P	8687(1)	9463(1)	2065(1)	20(1)
C(31)	8015(2)	9916(1)	1229(1)	22(1)
C(32)	6730(2)	10170(1)	1054(1)	26(1)
C(33)	6238(3)	10535(1)	431(1)	32(1)
C(34)	7003(3)	10644(1)	-26(1)	38(1)
C(35)	8265(3)	10393(2)	137(1)	41(1)
C(36)	8779(3)	10028(1)	761(1)	32(1)
C(41)	8790(2)	10171(1)	2712(1)	23(1)
C(42)	8259(3)	10833(1)	2541(1)	34(1)
C(43)	8448(3)	11361(2)	3042(2)	44(1)
C(44)	9182(3)	11237(2)	3719(2)	43(1)
C(45)	9699(3)	10579(2)	3901(1)	43(1)
C(46)	9505(2)	10048(2)	3407(1)	34(1)
C(51)	10431(2)	9351(1)	2094(1)	23(1)
C(52)	11289(2)	9923(1)	2252(1)	29(1)
C(53)	12588(2)	9851(2)	2229(1)	36(1)
C(54)	13038(3)	9221(2)	2048(1)	37(1)
C(55)	12204(2)	8650(2)	1899(1)	36(1)
C(56)	10902(2)	8712(1)	1923(1)	30(1)

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

(ii) By use of a similar procedure [RhCl(PPh₃)₃] (0.93 g, 1.0 mmol) and *nido*-7-NH₂Bu^t-7-CB₁₀H₁₂ (0.20 g, 1.0 mmol) gave red microcrystals of [RhCl(PPh₃)(η^5 -7-NH₂Bu^t-7-CB₁₀H₁₀)] (**1b**) (0.35 g).

Reactions of the Complexes [RhX(PPh₃)(η^5 -7-NH₂Bu^t-7-CB₁₀H₁₀)] (X = Br or Cl) with CNBu^t. (i) Compound **1a** (0.20 g, 0.30 mmol) was dissolved in CH₂Cl₂ (15 mL) and the solution maintained at -20 °C. A solution of CNBu^t (0.025 g, 0.30 mmol) in CH₂Cl₂ (5 mL) was added dropwise and then the mixture allowed to warm gradually to room temperature. Solvent was removed *in vacuo*, and crystallization from CH₂Cl₂–light petroleum (1:8, 10 mL) afforded orange microcrystals of [RhBr(CNBu^t)(PPh₃)(η^5 -7-NH₂Bu^t-7-CB₁₀H₁₀)] (**2a**) (0.19 g). (ii) Similarly **1b** (0.13 g, 0.21 mmol) and CNBu^t (0.017 g, 0.21 mmol) gave orange microcrystals of [RhCl(CNBu^t)(PPh₃)(η^5 -7-NH₂Bu^t-7-CB₁₀H₁₀)] (**2b**) (0.12 g).

(iii) Compound **1a** (0.16 g, 0.26 mmol) was dissolved in CH₂Cl₂ (5 mL). To this solution was added CNBu^t (0.04 g, 0.52 mmol) in CH₂Cl₂ (5 mL), causing a color change from red to yellow. Removal of solvent *in vacuo* followed by crystallization from CH₂Cl₂–light petroleum (1:6, 15 mL) afforded yellow microcrystals of [Rh(CNBu^t)₂(PPh₃)(η^5 -7-NH₂Bu^t-7-CB₁₀H₁₀)] (**3**) (0.11 g).

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Table 11. Atomic Positional Parameters (Fractional Coordinates $\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for the Atoms of **4**

atom	x	y	z	$U(\text{eq})^a$
Rh	9498(1)	6817(1)	7355(1)	23(1)
P	8983(1)	9109(1)	7278(1)	24(1)
C(1)	9880(3)	5154(3)	6650(2)	23(1)
B(2)	9685(4)	4770(3)	7633(2)	28(1)
B(3)	7948(4)	6027(4)	8010(2)	32(1)
B(4)	7192(4)	7122(3)	7203(2)	30(1)
B(5)	8458(4)	6567(3)	6347(2)	27(1)
B(6)	8607(4)	4925(3)	6117(2)	29(1)
B(7)	9322(4)	3843(3)	6892(2)	28(1)
B(8)	8088(4)	4386(4)	7730(2)	33(1)
B(9)	6587(4)	5785(4)	7476(2)	34(1)
B(10)	6905(4)	6108(4)	6472(2)	32(1)
B(11)	7413(4)	4454(4)	6806(2)	33(1)
N(1)	11203(3)	5250(2)	6309(2)	26(1)
C(2)	12728(3)	4286(3)	6309(2)	37(1)
C(3)	12813(5)	3000(5)	5921(4)	88(2)
C(4)	13234(5)	4103(8)	7111(3)	101(3)
C(5)	13661(4)	4890(4)	5792(2)	47(1)
C(6)	10533(4)	6804(3)	8297(2)	33(1)
N(7)	11085(4)	6763(3)	8861(2)	42(1)
C(7)	11737(7)	6799(5)	9576(3)	81(2)
C(8)	12337(33)	5460(17)	9878(14)	203(19)
C(9)	11007(18)	7871(19)	10045(10)	131(11)
C(10)	13232(17)	7103(29)	9221(8)	168(11)
C(8A)	12977(14)	5725(16)	9661(9)	95(7)
C(9A)	10421(15)	6616(24)	10208(6)	135(7)
C(10A)	11583(33)	8176(16)	9692(14)	199(18)
C(11)	10584(3)	9510(3)	7479(2)	28(1)
C(12)	11933(4)	8669(3)	7157(2)	38(1)
C(13)	13184(4)	8922(4)	7268(3)	52(1)
C(14)	13112(4)	9996(4)	7708(3)	53(1)
C(15)	11785(4)	10827(4)	8032(2)	45(1)
C(16)	10506(4)	10589(3)	7917(2)	35(1)
C(21)	8451(3)	9985(3)	6372(2)	29(1)
C(22)	9188(4)	10768(3)	6019(2)	37(1)
C(23)	8702(5)	11482(4)	5356(2)	47(1)
C(24)	7496(5)	11416(4)	5043(2)	51(1)
C(25)	6769(5)	10629(4)	5384(2)	50(1)
C(26)	7233(4)	9913(4)	6045(2)	42(1)
C(31)	7556(3)	10062(3)	8011(2)	29(1)
C(32)	6750(4)	11378(3)	7900(2)	36(1)
C(33)	5718(4)	12090(4)	8477(2)	44(1)
C(34)	5507(5)	11496(4)	9175(3)	55(1)
C(35)	6359(5)	10198(4)	9303(3)	57(1)
C(36)	7353(4)	9474(4)	8713(2)	48(1)

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

(iv) Similarly **1b** (0.10 g, 0.16 mmol) and CNBu^+ (0.026 g, 0.32 mmol) gave **3** (0.08 g, yield 66%).

(v) A solution of **1a** (0.17 g, 0.26 mmol) in CH_2Cl_2 (20 mL) was treated with CNBu^+ (0.021 g, 0.26 mmol) and the mixture stirred for 1 h. Solvent was then reduced *in vacuo* to a volume of 3 mL and the solution chromatographed. Elution with CH_2Cl_2 –light petroleum (4:1) removed a red fraction. Solvent was removed *in vacuo*, and crystallization of the residue from CH_2Cl_2 –light petroleum (1:7, 15 mL) gave red microcrystals of $[\text{Rh}(\text{CNBu}^+)(\text{PPh}_3)(\eta^5\text{-7-NHBu}^+\text{-7-CB}_{10}\text{H}_{10})]$ (**4**) (0.14 g).

(vi) Similarly, a mixture of **1b** (0.20 g, 0.33 mmol) and CNBu^+ (0.027 g, 0.33 mmol) in CH_2Cl_2 (25 mL) gave **4** (0.13 g, yield 54%).

(vii) By use of the same procedure, compound **4** (0.05 g, 0.08 mmol) and CNBu^+ (0.006 g, 0.08 mmol) in CH_2Cl_2 (5 mL) afforded microcrystals of **3** (0.04 g, yield 71%).

Reactions of the Compounds $[\text{RhX}(\text{PPh}_3)(\eta^5\text{-7-NH}_2\text{Bu}^+\text{-7-CB}_{10}\text{H}_{10})]$ with PR_3 ($\text{R} = \text{Me}$ or Et). (i) A solution of compound **1a** (0.08 g, 0.12 mmol) in CH_2Cl_2 (15 mL) was treated with PEt_3 (0.02 g, 0.12 mmol) and the mixture stirred for 2 h. Solvent was then removed *in vacuo* and crystallization of the residue from CH_2Cl_2 –light petroleum (1:6, 10 mL) yielded red microcrystals of $[\text{RhBr}(\text{PEt}_3)(\eta^5\text{-7-NH}_2\text{Bu}^+\text{-7-CB}_{10}\text{H}_{10})]$ (**5**) (0.05 g).

Table 12. Atomic Positional Parameters (Fractional Coordinates $\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for the Atoms of **8**

atom	x	y	z	$U(\text{eq})^a$
Co(1)	4725(1)	870(1)	3560(1)	45(1)
C(11)	5799(2)	2091(3)	3656(2)	42(1)
B(12)	5786(3)	1037(4)	4267(2)	46(1)
B(13)	5577(3)	−572(4)	3955(2)	49(1)
B(14)	5403(3)	−422(4)	3127(2)	53(1)
B(15)	5523(3)	1266(4)	2969(2)	48(1)
B(16)	6583(3)	1707(5)	3281(2)	51(1)
B(17)	6749(3)	1583(5)	4089(2)	51(1)
B(18)	6617(3)	−54(5)	4274(2)	54(1)
B(19)	6388(3)	−947(5)	3570(2)	56(1)
B(110)	6343(3)	162(5)	2954(2)	56(1)
B(111)	7104(3)	340(5)	3655(2)	61(1)
N(1)	5522(2)	3382(3)	3648(2)	47(1)
C(130)	5846(2)	4471(4)	4062(2)	49(1)
C(131)	5915(3)	4127(4)	4740(2)	61(1)
C(132)	6693(3)	4956(4)	3963(2)	69(1)
C(133)	5193(3)	5532(4)	3881(2)	67(1)
C(121)	3631(3)	−344(4)	3526(2)	60(1)
C(122)	3554(3)	305(5)	2969(2)	70(1)
C(123)	3614(3)	1632(6)	2948(3)	82(2)
C(124)	3760(3)	2332(5)	3482(4)	87(2)
C(125)	3868(3)	1717(6)	4049(3)	83(2)
C(126)	3809(3)	381(5)	4068(2)	68(1)
C(127)	3546(3)	−1789(5)	3544(3)	98(2)
Co(2)	281(1)	9523(1)	1487(1)	42(1)
C(21)	−795(2)	8301(3)	1324(2)	41(1)
B(22)	−590(3)	9113(4)	2019(2)	44(1)
B(23)	−458(3)	10812(4)	1871(2)	50(1)
B(24)	−543(3)	10965(4)	1050(2)	49(1)
B(25)	−714(3)	9362(4)	730(2)	45(1)
B(26)	−1630(3)	8673(4)	1653(2)	47(1)
B(27)	−1431(3)	10219(5)	1991(2)	52(1)
B(28)	−1411(3)	11339(5)	1384(2)	54(1)
B(29)	−1565(3)	10442(4)	680(2)	49(1)
B(210)	−1712(3)	8813(5)	852(2)	48(1)
B(211)	−2127(3)	10040(5)	1253(2)	54(1)
N(2)	−514(2)	7011(3)	1345(1)	46(1)
C(230)	−813(3)	5924(4)	923(2)	50(1)
C(231)	−1682(3)	5447(4)	978(2)	66(1)
C(232)	−821(3)	6257(4)	249(2)	65(1)
C(233)	−171(3)	4858(4)	1134(2)	70(1)
C(221)	1385(2)	10748(4)	1568(2)	54(1)
C(222)	1258(2)	10010(5)	1032(2)	60(1)
C(223)	1202(3)	8669(6)	1054(3)	76(2)
C(224)	1256(3)	8052(5)	1612(3)	80(2)
C(225)	1347(3)	8779(5)	2149(2)	73(1)
C(226)	1408(2)	10109(5)	2127(2)	61(1)
C(227)	1472(3)	12187(4)	1557(2)	78(2)

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

(ii) Using a similar procedure, a mixture of compound **1b** (0.06 g, 0.1 mmol) and PMe_3 (0.4 mL of a 1.0 M solution in *thf*, 0.4 mmol) gave orange-red microcrystals of $[\text{RhCl}(\text{PMe}_3)_2(\eta^5\text{-7-NH}_2\text{Bu}^+\text{-7-CB}_{10}\text{H}_{10})]$ (**6**) (0.04 g).

Reactions of the Compound $[\text{RhBr}(\text{PPh}_3)(\eta^5\text{-7-NH}_2\text{Bu}^+\text{-7-CB}_{10}\text{H}_{10})]$ with 4-Picoline and *thf*. (i) A mixture of compound **1a** (0.09 g, 0.14 mmol) and $\text{NC}_5\text{H}_4\text{Me-4}$ (0.01 g, 0.14 mmol) was stirred in CH_2Cl_2 (10 mL) for 6 h. Solvent was then removed *in vacuo* and the residue crystallized from benzene–light petroleum (1:5, 15 mL) to give red microcrystals of $[\text{RhBr}(\text{PPh}_3)(\text{NC}_5\text{H}_4\text{Me-4})(\eta^5\text{-7-NH}_2\text{Bu}^+\text{-7-CB}_{10}\text{H}_{10})]$ (**7a**) (0.09 g).

(ii) Similarly compound **1a** (0.10 g, 0.14 mmol) was stirred in *thf* (5 mL) for 7 h to give red microcrystals of $[\text{RhBr}(\text{thf})(\text{PPh}_3)(\eta^5\text{-7-NH}_2\text{Bu}^+\text{-7-CB}_{10}\text{H}_{10})]$ (**7b**) (0.09 g).

Synthesis of the Cobalt Compound $[\text{Co}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\eta^5\text{-7-NH}_2\text{Bu}^+\text{-7-CB}_{10}\text{H}_{10})]$. A mixture of $[\text{CoCl}(\text{PPh}_3)_3]$ (0.88 g, 1.0 mmol) and *nido*-7- $\text{NH}_2\text{Bu}^+\text{-7-CB}_{10}\text{H}_{12}$ (0.20 g, 1.0 mmol) was refluxed in toluene (20 mL) for 6 h. Solvent was removed *in vacuo* and the residue taken up in CH_2Cl_2 (15 mL) and chromatographed. Elution with CH_2Cl_2 –light

petroleum (1:10) removed a deep red fraction. Evaporation of solvent and crystallization from CH_2Cl_2 –light petroleum (1:8, 15 mL) gave deep red microcrystals of $[\text{Co}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\eta^5\text{-7-NHBu}^t\text{-7-CB}_{10}\text{H}_{10})]$ (**8**) (0.15 g).

Crystal Structure Determinations and Refinements

Crystals were grown by diffusion of light petroleum into CH_2Cl_2 solutions of the complexes.

Low-temperature data sets for **3** and **4** were collected with the crystals mounted on glass fibers. The ambient temperature data sets for **1a** and **8** were collected with the crystals sealed in capillary tubes. Complex **1a** crystallized with a molecule of CH_2Cl_2 per molecule of the complex.

Data (Table 8) were collected on a Siemens SMART CCD area-detector three-circle diffractometer using $\text{Mo K}\alpha$ X-radiation $\lambda = 0.71073$. For three settings of ϕ , narrow data “frames” were collected for 0.3° increments in ω . In all cases 1271 frames of data were collected, affording rather more than a hemisphere of data for each complex. The substantial redundancy in data allows empirical absorption corrections to be applied using multiple measurements of equivalent reflections. Data frames were collected for 10–60 s per frame giving overall data collection times of between ca. 6 and 25 h. The data frames were integrated using SAINT,¹⁸ and the structures were solved by conventional direct methods or heavy atom

procedures. The structures were refined by full-matrix least-squares on all F^2 data using Siemens SHELXTL 5.03,¹⁸ and with anisotropic thermal parameters for all non-hydrogen atoms. The NH protons in **3** and **8** were located from final electron density difference syntheses, and their positions were refined. All other hydrogen atoms were included in calculated positions and allowed to ride on the parent boron or carbon atoms with isotropic thermal parameters ($U_{\text{iso}} = 1.2U_{\text{iso equiv}}$ of the parent atom except for Me protons where $U_{\text{iso}} = 1.3U_{\text{iso equiv}}$). For **4** the methyl groups of the CNBu^t ligand are disordered (1:1) over two sites such that the two sets of methyl substituents are staggered about the $\text{Rh-C}(7)$ bond. For clarity only one of the disordered components is shown in Figure 3. For **8** there are two essentially similar crystallographically independent molecules in the asymmetric unit. Only one of these molecules is shown in Figure 4 and discussed in the text. Atomic positional parameters for complexes **1a**, **3**, **4**, and **8** are listed in Tables 9–12. All calculations were carried out 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 **1a**, **3**, **4**, and **8** (36 pages). Ordering information is given on any current masthead page.

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