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Synthesis of Monocarbollide Complexes of Rhodium[†]

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The compounds $[RhX(PPh_3)_3]$ react with *nido*-7-NH_2Bu^t-7-$CB_{10}H_{12}$ in toluene to give the 16-electron complexes $[RhX(PPh_3)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**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, $\beta = 104.21(2)°$, 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 $\overline{CBBBB}$ 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 $[RhX(CNBu^t)(PPh_3)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**2a**, X = Br; **2b**, X = Cl) or $[Rh(CNBu^t)_2(PPh_3)(\eta^5\text{-}7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**3**) are obtained, or the 16-electron complex $[Rh(CNBu^t)(PPh_3)(\eta^5\text{-}7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**4**) is formed. Formation of **3** and **4**, in which the rhodium atoms are ligated by a *nido*-7-$NHBu^t$-7-$CB_{10}H_{10}$ cage, formally a 3 π-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, $\beta = 105.413(9)°$, and $Z = 4$, while those of **4** are triclinic, space group $P\bar{1}$, with $a = 9.840(3)$ Å, $b = 10.809(3)$ Å, $c = 17.287(3)$ Å, $\alpha = 88.49(2)°$, $\beta = 84.57(2)°$, $\gamma = 69.809(14)°$, 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-$NHBu^t$-7-$CB_{10}H_{10}$ 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, NC_5H_4Me-4, and tetrahydrofuran (thf) give the complexes $[RhBr(PEt_3)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**5**), $[RhCl(PMe_3)_2(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**6**), and $[RhBr(L)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**7a**, L = NC_5H_4Me-4; **7b**, L = thf), respectively. Prolonged refluxing of mixtures of $[CoCl(PPh_3)_3]$ and *nido*-7-NH_2Bu^t-7-$CB_{10}H_{12}$ in toluene gives the arene(carborane)−cobalt complex $[Co(\eta^6\text{-}C_6H_5Me)(\eta^5\text{-}7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**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, $\beta = 102.94(2)°$, 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 $7,8$-$C_2B_9H_{13}$ and 7-NR_3-7-$CB_{10}H_{12}$ ($NR_3 = NMe_3$, NH_2Bu^t, NMe_2Bu^t) react with $[Ru_3(CO)_{12}]$ to afford, respectively, the mononuclear ruthenium complex $[Ru(CO)_3(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ and the triruthenium complexes $[Ru_3(CO)_8(\eta^5\text{-}7\text{-}NR_3\text{-}7\text{-}CB_{10}H_{10})]$.[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-$CB_{10}H_{12}$ and the compounds $[RhX(PPh_3)_3]$ (X = Cl or Br) as a possible direct route to species with *closo*-$RhCB_{10}$ 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 $[RhX(PPh_3)_3]$ (X = Cl or Br) and *nido*-7-NH_2Bu^t-7-$CB_{10}H_{12}$ afford the mononuclear *closo*-rhodacarboranes $[RhX(PPh_3)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**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 η^5-7-NH_2Bu^t-7-$CB_{10}H_{10}$ group. They are closely related to the previously reported compounds $[RhBr(PPh_3)(\eta^5\text{-}7\text{-}NH_2(CH_2CH{=}CHMe)\text{-}7\text{-}CB_{10}H_{10})]$ and $[RhBr(PPh_3)(\eta^5\text{-}7\text{-}NH(CH_2CH{=}CHMe)_2\text{-}7\text{-}CB_{10}H_{10})]$, which were obtained by N-quaternization of the

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[†] 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^5-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.

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Chart 1

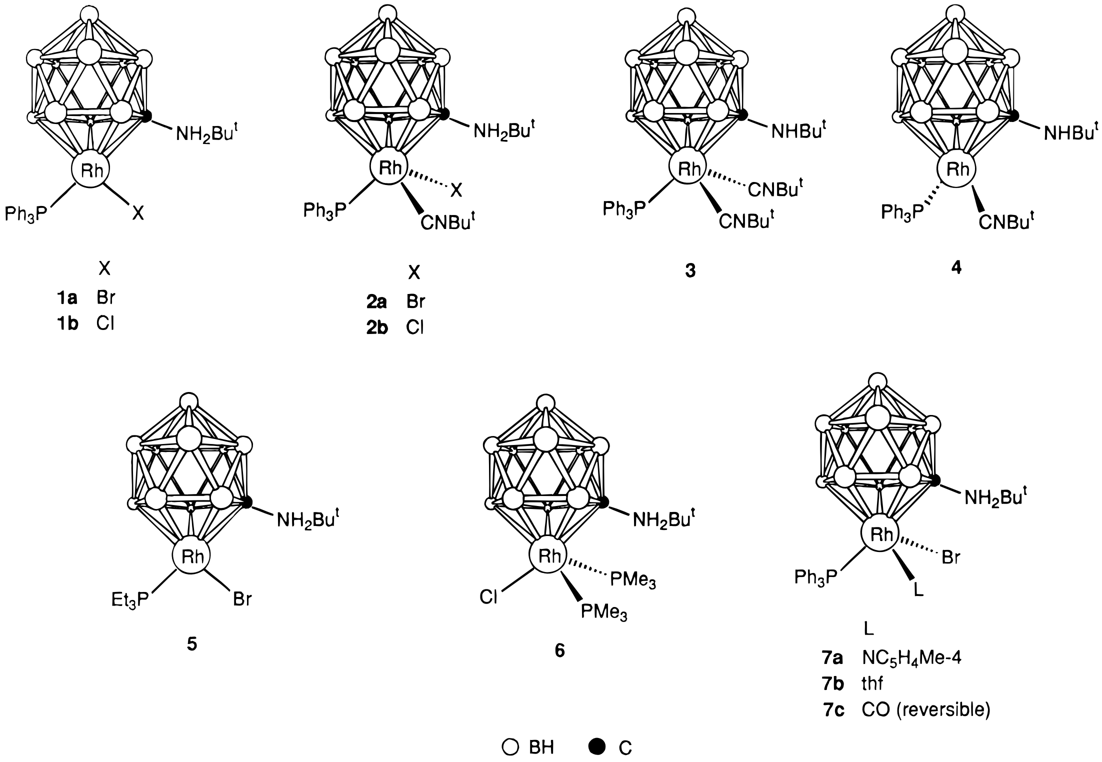

Table 1. Analytical and Physical Data

	compd[a]	color	yield/%	anal.[b]/% C	H	N
1a	$[RhBr(PPh_3)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$	red	56	42.2 (42.6)	5.5 (5.6)	2.1 (2.2)
1b	$[RhCl(PPh_3)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$	red	62	42.5 (41.8)	5.6 (5.5)	2.2 (2.0)[c]
2a	$[RhBr(CNBu^t)(PPh_3)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})$	orange	86	42.7 (42.6)	5.7 (5.8)	3.9 (3.4)[c]
2b	$[RhCl(CNBu^t)(PPh_3)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$	orange	85	45.2 (45.1)	6.4 (6.1)	3.6 (3.6)[c]
3	$[Rh(CNBu^t)_2(PPh_3)(\eta^5\text{-}7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10})]$	yellow	61[d]	53.9 (53.4)	7.9 (7.4)	5.6 (5.7)
4	$[Rh(CNBu^t)(PPh_3)(\eta^5\text{-}7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10})]$	red	80[e]	51.8 (51.6)	6.8 (6.9)	4.3 (4.3)
5	$[RhBr(PEt_3)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$	red	90	31.1 (31.1)	8.3 (8.5)	3.1 (3.3)
6	$[RhCl(PMe_3)_2(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$	red-orange	82	26.4 (25.8)	8.1 (7.4)	2.8 (2.5)
7a	$[RhBr(NC_5H_5Me\text{-}4)(PPh_3)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$	red	90	48.5 (49.9)	5.8 (5.9)	3.8 (3.6)[f]
7b	$[RhBr(thf)(PPh_3)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$	red	82	44.3 (45.0)	6.1 (6.1)	1.8 (1.9)
8	$[Co(\eta^6\text{-}C_6H_5Me)(\eta^5\text{-}7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10})]$	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 CH_2Cl_2, at ca. 2550 cm^{-1} due to B−H absorptions. There are also medium-intensity $\nu_{max}(NC)$ 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 CH_2Cl_2. [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 C_6H_6.

dimeric anion present in $[N(PPh_3)_2][Rh_2(\mu\text{-}H)(PPh_3)_2(\eta^5\text{-}7\text{-}NH_2\text{-}7\text{-}CB_{10}H_{10})_2]$ 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 PPh_3 [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*-$7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10}$ 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 $[RhBr(PPh_3)(\eta^5\text{-}7\text{-}NH(CH_2CH{=}CHMe)_2\text{-}7\text{-}CB_{10}H_{10})]$. 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 $[PHPh_3][RhBr_2(PPh_3)(\eta^5\text{-}7,8\text{-}C_2B_9H_{11})]$ [2.520(2) and 2.598(1) Å].[6]

An intramolecular N−H···Br hydrogen bond is present in $[RhBr(PPh_3)(\eta^5\text{-}7\text{-}NH(CH_2CH{=}CHMe)_2\text{-}7\text{-}CB_{10}H_{10})]$, 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 NH_2 protons were not located, but their inclusion in sensible calculated positions gives the shortest distance between the NH_2 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 NH_2 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	$^{1}H/\delta^{b}$	$^{13}C/\delta^{c,d}$
1a	1.65 (s, 9 H, CMe_3), 7.46−7.57 (m, 15 H, Ph), 9.80 (br s, 2 H, NH_2)	[e]135.6−129.1 (Ph), 76.5 ($CB_{10}H_{10}$), 66.0 ($N\mathit{C}Me_3$), 27.0 ($C\mathit{Me}_3$)
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 ($N\mathit{C}Me_3$), 27.2 ($C\mathit{Me}_3$)
2a	1.28, 1.51 (s × 2, 18 H, CMe_3), 6.75 [d, 1 H, NH_2, J(HH) = 13], 7.36−7.77 (m, 15 H, Ph), 7.95 [d, 1 H, NH_2, J(HH) = 13]	135.5−127.8 (Ph), 82.3 [d of d, $CB_{10}H_{10}$, J(PC) = 39, J(RhC) = 10], 66.6 ($N\mathit{C}Me_3$), 58.3 ($\mathit{C}Me_3$), 29.7, 27.6 ($C\mathit{Me}_3$)
2b	1.27, 1.50 (s × 2, 18 H, CMe_3), 6.85 [d, 1 H, NH_2, J(HH) = 13], 7.40−7.80 (m, 15 H, Ph), 8.32 [d, 1 H, NH_2, J(HH) = 13]	135.2−127.9 (Ph), 83.7 [d of d, $CB_{10}H_{10}$, J(PC) = 40, J(RhC) = 10], 65.9 ($N\mathit{C}Me_3$), 58.1 ($\mathit{C}Me_3$), 29.7, 27.6 ($C\mathit{Me}_3$)
3	1.26 (s, 18 H, $CNCMe_3$), 1.17 (s, 9 H, $NHC\mathit{Me}_3$), 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 ($\mathit{C}Me_3$), 30.8, 29.6 ($C\mathit{Me}_3$)
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 ($\mathit{C}Me_3$), 31.3, 29.7 ($C\mathit{Me}_3$)
5	1.13 (m, 9 H, $CH_2\mathit{Me}$), 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 ($\mathit{C}Me_3$), 27.1 ($C\mathit{Me}_3$), 17.5 [d, PCH_2, J(PC) = 30], 8.2 ($CH_2\mathit{Me}$)
6	1.38 (s, 9 H, CMe_3), 1.69 (m, 18 H, PMe), 7.25 (br s, 2 H, NH_2)	65.5 ($\mathit{C}Me_3$), 27.1 ($C\mathit{Me}_3$), 19.2 [d, PMe, J(PC) = 33]
7a	1.57 (s, 9 H, CMe_3), 2.35 (s, 3 H, $NC_5H_4\mathit{Me}$-4), 7.06−7.51 (m, 19 H, Ph and $NC_5\mathit{H}_4$Me-4), 8.55 (br s, 2 H, NH_2)	150.2−125.4 (Ph and $N\mathit{C}_5H_4$Me-4), 78.2 ($CB_{10}H_{10}$), 65.3 ($\mathit{C}Me_3$), 27.3 ($C\mathit{Me}_3$), 20.2 ($NC_5H_4\mathit{Me}$-4)
7b[f]	1.63 (s, 9 H, CMe_3), 1.84 (m, 4 H, CH_2), 3.69 (m, 4 H, CH_2O), 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_6H_5Me), 109.5, 108.8 (C^2, C^3, C_6H_5Me), 107.7 (C^4, C_6H_5Me), 56.5 ($\mathit{C}Me_3$), 30.4 ($C\mathit{Me}_3$), 20.7 ($C_6H_5\mathit{Me}$)

[a] Chemical shifts (δ) in ppm, coupling constants (J) in Hz, measurements at room temperature in CD_2Cl_2 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 $SiMe_4$. [d] Signals for *C*NBu^t nuclei not observed in spectra of compounds **2**, **3**, and **4**. [e] Measured in $(CD_3)_2CO$. [f] $^{13}C\{^1H\}$ not measured due to dissociation of thf ligand.

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

compd	$^{11}B/\delta^{b}$	$^{31}P/\delta^{c}$
1a	9.9 (3 B), 5.4 (2 B), −6.9 (1 B), −14.8 (4 B)	34.1 [d, J(RhP) = 160]
1b	9.1 (3 B), 5.9 (2 B), −6.5 (1 B), −15.1 (4 B)	33.8 [d, J(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, J(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, J(RhP) = 125]
3	13.4 (1 B), 1.6 (4 B), −9.2 (3 B), −13.6 (2 B)	39.2 [d, J(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, J(RhP) = 133]
5	7.9 (3 B), 3.8 (2 B), −7.4 (1 B), −15.5 (4 B)	38.1 [d, J(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, J(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, J(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 CD_2Cl_2, and at room temperature. [b] Hydrogen-1 decoupled; chemical shifts are positive to high frequency of $BF_3{\cdot}Et_2O$ (external). [c] Hydrogen-1 decoupled; chemical shifts are positive to high frequency of 85% H_3PO_4 (external).

Table 4. Selected Internuclear Distances (Å) and Angles (deg) for $[RhBr(PPh_3)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]{\cdot}CH_2Cl_2$ (**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 $^{13}C\{^1H\}$ NMR spectrum resonances at δ 76.5 (**1a**) and δ 75.8 (**1b**) are tentatively assigned to the carbon nuclei of the $CB_{10}H_{10}$ cages present in these molecules. At the present time there is a paucity of information on ^{13}C chemical shifts for carbon atoms in monocarboranes,[1b] the chemical shifts of which are likely to vary with the metal in the MCB_{10} framework and the character of any exo-polyhedral groups. The $^{31}P\{^1H\}$ NMR spectra for **1** have diagnostic doublet signals for the PPh_3 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

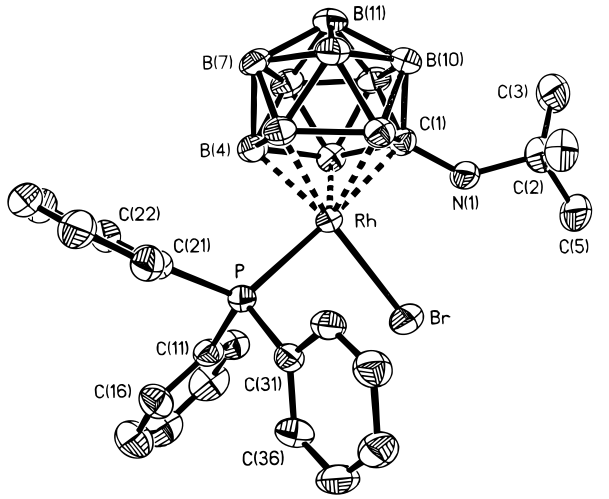

Figure 1. Molecular structure of [RhBr(PPh$_3$)(η^5-7-NH$_2$Bu^t-7-CB$_{10}$H$_{10}$)] (**1a**), showing the crystallographic labeling scheme. Thermal ellipsoids are at the 40% probability level, and hydrogen atoms are omitted for clarity.

with the previously reported dicarbon-rhodacarborane species [RhCl(PPh$_3$)(η^5-7,9-C$_2$B$_9$H$_{11}$)].[7] In the complexes **1**, as in [RhCl(PPh$_3$)(η^5-7,9-C$_2$B$_9$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$_2$Cl$_2$ at −20 °C with 1 mol equiv of CNBu^t gave the complexes [RhX(CNBu^t)(PPh$_3$)(η^5-7-NH$_2$Bu^t-7-CB$_{10}$H$_{10}$)] (**2a**, X = Br; **2b**, X = Cl). Data characterizing these products are summarized in Tables 1−3. The ^{1}H and ^{13}C{^{1}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 ^{1}H NMR spectra displaying two resonances for the diastereotopic protons of the NH$_2$ groups, and these occur as doublets [J(HH) = 13 Hz] at δ 6.75 and 7.95 for **2a** and at δ 6.85 and 8.32 for **2b**. The ^{13}C{^{1}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 *C*NBu^t ligand. These nuclei would be expected to resonate in the range δ ca. 130−180.[8−10] In the ^{13}C{^{1}H} NMR spectrum of the ruthenium cluster [Ru$_3$(CO)$_7$(CNBu^t)(η^5-7-NMe$_3$-7-CB$_{10}$H$_{10}$)] the *C*NBu^t resonance is at δ 189.4.[1b] Failure to observe peaks due to the *C*NBu^t nuclei in the ^{13}C{^{1}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$_2$Cl$_2$ gave the bis(isocyanide)rhodium complex [Rh(CNBu^t)$_2$(PPh$_3$)(η^5-7-NHBu^t-7-CB$_{10}$H$_{10}$)] (**3**) which was isolated by crystallization. In this product the *nido*-cage system 7-NHBu^t-7-CB$_{10}$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$_2$Bu^t-7-CB$_{10}$H$_{10}$ ligand in the species **1**. Evidently the reactions proceed with overall loss of HX via deprotonation of the CNH$_2$Bu^t group in the precursors **1**. Careful integration of the peaks in the ^{1}H 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)°] 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)°]. It is noteworthy that in the *nido*-carborane 7-NH$_2$Bu^t-7-CB$_{10}$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°). 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 [Rh(CNBu^t)(PPh$_3$)(η^5-7-NHBu^t-7-CB$_{10}$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$_2$Cl$_2$.

Since the formation of **4** again involved an unexpected ligand transformation from the charge-compensated moiety 7-NH$_2$Bu^t-7-CB$_{10}$H$_{10}$ to the neutral 7-NHBu^t-7-CB$_{10}$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)°] 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)°], 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 $\overline{\text{CBBBB}}$ 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$_2$Cl$_2$ with 1 mol equiv of PEt$_3$ gave the 16-electron complex [RhBr(PEt$_3$)(η^5-7-NH$_2$Bu^t-7-CB$_{10}$H$_{10}$)] (**5**), there being no evidence of a stable 18-electron species [RhBr(PEt$_3$)(PPh$_3$)(η^5-7-NH$_2$Bu^t-7-CB$_{10}$H$_{10}$)]. Existence of the latter is perhaps inhibited by steric effects, cone angles for PEt$_3$ and PPh$_3$ being 132° and 145°, respectively.[12] The reaction between **1b** and an excess

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Table 5. Selected Internuclear Distances (Å) and Angles (deg) for [Rh(CNBu^t)$_2$(PPh$_3$)(η^5-7-NHBu^t-7-CB$_{10}$H$_{10}$)] (**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)

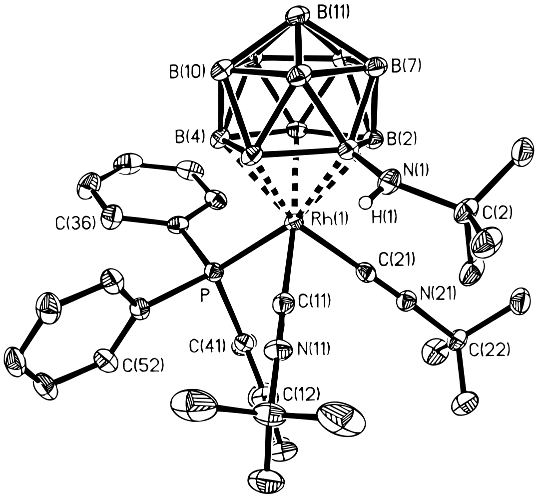


Figure 2. Molecular structure of [Rh(CNBu^t)$_2$(PPh$_3$)(η^5-7-NHBu^t-7-CB$_{10}$H$_{10}$)] (**3**), showing the crystallographic labeling scheme. Thermal ellipsoids are at the 40% probability level, and hydrogen atoms are omitted for clarity.

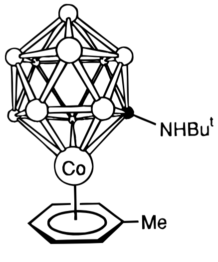
of the less sterically demanding PMe$_3$ (cone angle 118°), with the phosphine in excess, gave the 18-electron complex [RhCl(PMe$_3$)$_2$(η^5-7-NH$_2$Bu^t-7-CB$_{10}$H$_{10}$)] (**6**). It is interesting that the reaction with PMe$_3$ did not afford a product containing the η^5-7-NHBu^t-7-CB$_{10}$H$_{10}$ 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 NC$_5$H$_4$Me-4 afforded the 18-electron complex [RhBr(NC$_5$H$_4$Me-4)(PPh$_3$)(η^5-7-NH$_2$Bu^t-7-CB$_{10}$H$_{10}$)] (**7a**), data for which are given in Tables 1−3. Treatment of **1a** with thf (tetrahydrofuran) gave [RhBr(thf)(PPh$_3$)(η^5-7-NH$_2$Bu^t-7-CB$_{10}$H$_{10}$)] (**7b**). However, although microanalytical data were obtained for this complex (Table 1), it readily dissociates in solution and satisfactory ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{11}B{^{1}H} NMR spectra were not measured.

It was not possible to isolate an 18-electron complex [RhBr(CO)(PPh$_3$)(η^5-7-NH$_2$Bu^t-7-CB$_{10}$H$_{10}$)] (**7c**) as a solid by treating **1a** with CO. However, red CH$_2$Cl$_2$ 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(PPh$_3$)(η^5-7,9-C$_2$B$_9$H$_{11}$)] with CO.[7]

Preparation of the rhodium compounds **1** directly from [RhX(PPh$_3$)$_3$] and *nido*-7-NH$_2$Bu^t-7-CB$_{10}$H$_{12}$ raised the possibility of synthesizing cobalt analogs. For a reaction to occur between *nido*-7-NH$_2$Bu^t-7-CB$_{10}$H$_{12}$ and [CoCl(PPh$_3$)$_3$] 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-C$_6$H$_5$Me)(η^5-7-NHBu^t-7-CB$_{10}$H$_{10}$)] (**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-CB$_{10}$H$_{10}$ cage. Although the H atom bonded to N(1) was not located in the X-ray diffraction pattern, its presence was revealed in the ^{1}H 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



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○ BH ● C

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Table 6. Selected Internuclear Distances (Å) and Angles (deg) for [Rh(CNBu^t)(PPh$_3$)(η^5-7-NHBu^t-7-CB$_{10}$H$_{10}$)] (**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).

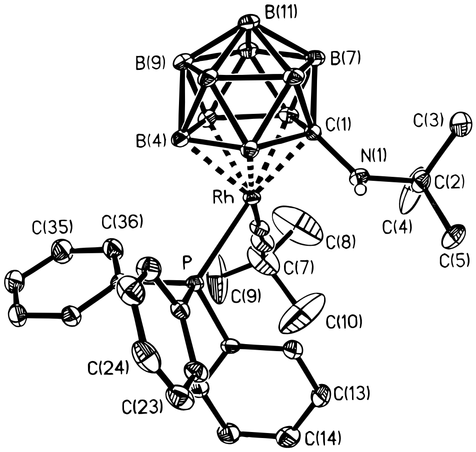

Figure 3. Molecular structure of [Rh(CNBu^t)(PPh$_3$)(η^5-7-NHBu^t-7-CB$_{10}$H$_{10}$)] (**4**), showing the crystallographic labeling scheme. Thermal ellipsoids are at the 40% probability level, and hydrogen atoms are omitted for clarity.

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-NH$_2$Bu^t-7-CB$_{10}$H$_{12}$.[11]

In addition to resonances due to the C$_6$H$_5$Me and Bu^t groups, the ^{13}C{^{1}H} 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 ^{13}C{^{1}H} NMR spectra of **3** (δ 106.5) and **4** (δ 118.7), which also contain the η^5-7-NHBu^t-CB$_{10}$H$_{10}$ ligand. Noteworthy, the resonances for the cage-carbons in the species having the charge-compensated η^5-7-NH$_2$Bu^t-7-CB$_{10}$H$_{10}$ 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-C$_{10}$H$_{10}$)(CB$_{10}$H$_{11}$)][13] and [Co(η^6-C$_6$H$_5$Me)(η^5-7-CH(SiMe$_3$)$_2$-7-CB$_{10}$H$_{10}$)].[14] The former was obtained in ca. 9% yield as an unexpected product of treating Na[Co(η^5-C$_5$H$_5$)(η^5-CB$_{10}$H$_{11}$)] with sodium naphthalide in tetrahydrofuran, followed by addition of NaC$_5$H$_5$ and NiBr$_2$ with air oxidation of the mixture. The latter was prepared in ca. 6% yield by reacting *nido*-7-CH(SiMe$_3$)$_2$-9-SMe$_2$-7-CB$_{10}$H$_{11}$ in toluene with cobalt vapor. Its structure was determined by X-ray diffraction. The connectivities between the cobalt atom and the atoms of the $\overline{\text{CBBBB}}$ 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 CB$_4$ 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-C$_6$H$_5$Me 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-C$_6$H$_5$Me)(η^5-7-CH(SiMe$_3$)$_2$-7-CB$_{10}$H$_{10}$)].

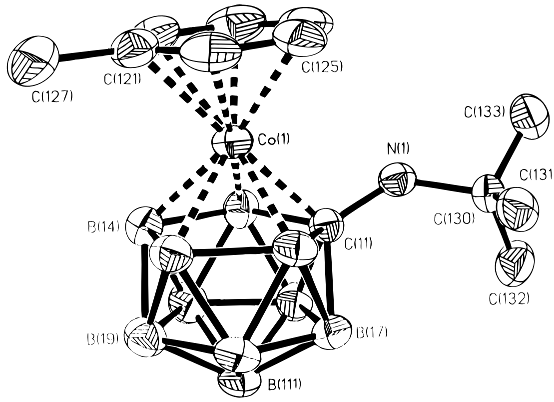

Figure 4. Molecular structure of [Co(η^6-C$_6$H$_5$Me)(η^5-7-NHBu^t-7-CB$_{10}$H$_{10}$)] (**8**), showing the crystallographic labeling scheme. Thermal ellipsoids are at the 40% probability level, and hydrogen atoms are omitted for clarity.

Conclusions

It has been shown that the complexes **1** can be conveniently obtained directly from *nido*-7-NH$_2$Bu^t-7-CB$_{10}$H$_{12}$ and [RhX(PPh$_3$)$_3$], 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-C_6H_5Me)(η^5-7-NHBu^t-7-$CB_{10}H_{10}$)] (**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_2Cl_2	**3**	**4**	**8**
formula	$C_{24}H_{38}B_{10}BrCl_2NPRh$	$C_{33}H_{53}B_{10}N_3PRh$	$C_{28}H_{44}B_{10}N_2PRh$	$C_{12}H_{28}B_{10}NCo$
M_r	733.34	733.76	650.63	353.38
T/K	293	173	173	293
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	12.937(3)	10.533(2)	9.840(3)	16.332(5)
b (Å)	18.101(4)	19.110(4)	10.809(3)	10.397(2)
c (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)	
V (Å^3)	3335.8(14)	3824.0(14)	1717.8(8)	3671(2)
Z	4	4	2	8
d_{calcd}/g cm^{-3}	1.460	1.275	1.258	1.279
μ(Mo Kα) / mm^{-1}	1.936	0.516	0.565	0.926
F(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
reflcns measured	14659	17402	7830	13397
independent reflcns	5849	6720	5836	5221
2θ 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 F^2 data	full-matrix least squares on all F^2 data	full-matrix least squares on all F^2 data	full-matrix least squares on all F^2 data
final residuals	$wR_2 = 0.131^a$ ($R_1 = 0.051$)^b	$wR_2 = 0.104^a$ ($R_1 = 0.039$)^b	$wR_2 = 0.067^a$ ($R_1 = 0.027$)^b	$wR_2 = 0.115^a$ ($R_1 = 0.052$)^b
weighting factors	a = 0.0394; b = 11.54^a	a = 0.0602; b = 2.0925^a	a = 0.0205; b = 3.3801^a	a = 0.0265; b = 3.6239^a
goodness of fit on F^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_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 $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ 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 $w^{-1} = [\sigma^2(F_o) + gF_o^2]$.

the metal adopts either 16- or 18-electron configurations in the valence shell. Reactions with CNBu^t in which neutral charge-compensated carbon-substituted *closo*-1-NH$_2$Bu^t-2,1-RhCB$_{10}$H$_{10}$ frameworks are transformed into polyhedra with *closo*-1-NHBu^t-2,1-RhCB$_{10}$H$_{10}$ 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-NH$_2$Bu^t-7-CB$_{10}$H$_{10}$ four-electron donor ligand into a three-electron donor η^5-7-NHBu^t-7-CB$_{10}$H$_{10}$ group. Together the three compounds [Co(η^6-$C_{10}H_{10}$)($CB_{10}H_{11}$)],[13] [Co(η^6-C_6H_5Me)(η^5-7-CH(SiMe$_3$)$_2$-

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

atom	x	y	z	U(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.

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

atom	x	y	z	U(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.

7-$CB_{10}H_{10}$)],[14] and **8** form a family of complexes where monocarbon ligands, formally $[RCB_{10}H_{10}]^{3-}$, are bound to Co^{3+}.

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, ^{13}C at 90.56, ^{11}B at 115.55, and ^{31}P at 145.78 MHz. The reagents [7-NH_2Bu^t-*nido*-7-$CB_{10}H_{12}$],[1b,15] $[RhX(PPh_3)_3]$ (X = Br, Cl),[16] and $[CoCl(PPh_3)_3]$[17] were made by procedures previously described.

Syntheses of the Compounds [RhX(PPh_3)(η^5-7-NH_2Bu^t-7-$CB_{10}H_{10}$)] (1, X = Br, Cl). (i) A mixture of the compounds $[RhBr(PPh_3)_3]$ (0.97 g, 1.0 mmol) and *nido*-7-NH_2Bu^t-7-$CB_{10}H_{12}$ (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 CH_2Cl_2 (5 mL) and then chromatographed. Elution with CH_2Cl_2−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(PPh_3)(η^5-7-NH_2Bu^t-7-$CB_{10}H_{10}$)] (**1a**) (0.36 g).

(ii) By use of a similar procedure $[RhCl(PPh_3)_3]$ (0.93 g, 1.0 mmol) and *nido*-7-NH_2Bu^t-7-$CB_{10}H_{12}$ (0.20 g, 1.0 mmol) gave red microcrystals of [RhCl(PPh_3)(η^5-7-NH_2Bu^t-7-$CB_{10}H_{10}$)] (**1b**) (0.35 g).

Reactions of the Complexes [RhX(PPh_3)(η^5-7-NH_2Bu^t-7-$CB_{10}H_{10}$)] (X = Br or Cl) with $CNBu^t$. (i) Compound **1a** (0.20 g, 0.30 mmol) was dissolved in CH_2Cl_2 (15 mL) and the solution maintained at −20 °C. A solution of $CNBu^t$ (0.025 g, 0.30 mmol) in CH_2Cl_2 (5 mL) was added dropwise and then the mixture allowed to warm gradually to room temperature. Solvent was removed *in vacuo*, and crystallization from CH_2Cl_2−light petroleum (1:8, 10 mL) afforded orange microcrystals of [RhBr($CNBu^t$)(PPh_3)(η^5-7-NH_2Bu^t-7-$CB_{10}H_{10}$)] (**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($CNBu^t$)(PPh_3)(η^5-7-NH_2Bu^t-7-$CB_{10}H_{10}$)] (**2b**) (0.12 g).

(iii) Compound **1a** (0.16 g, 0.26 mmol) was dissolved in CH_2Cl_2 (5 mL). To this solution was added $CNBu^t$ (0.04 g, 0.52 mmol) in CH_2Cl_2 (5 mL), causing a color change from red to yellow. Removal of solvent *in vacuo* followed by crystallization from CH_2Cl_2−light petroleum (1:6, 15 mL) afforded yellow microcrystals of [Rh($CNBu^t$)$_2$(PPh_3)(η^5-7-$NHBu^t$-7-$CB_{10}H_{10}$)] (**3**) (0.11 g).

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

atom	*x*	*y*	*z*	*U*(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 $CNBu^t$ (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 $CNBu^t$ (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 $[Rh(CNBu^t)(PPh_3)(\eta^5\text{-}7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**4**) (0.14 g).

(vi) Similarly, a mixture of **1b** (0.20 g, 0.33 mmol) and $CNBu^t$ (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 $CNBu^t$ (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 $[RhX(PPh_3)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$ with PR_3 (R = 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 $[RhBr(PEt_3)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**5**) (0.05 g).

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

atom	*x*	*y*	*z*	*U*(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 $[RhCl(PMe_3)_2(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**6**) (0.04 g).

Reactions of the Compound $[RhBr(PPh_3)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$ with 4-Picoline and thf. (i) A mixture of compound **1a** (0.09 g, 0.14 mmol) and $NC_5H_4Me\text{-}4$ (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 $[RhBr(PPh_3)(NC_5H_4Me\text{-}4)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**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 $[RhBr(thf)(PPh_3)(\eta^5\text{-}7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{10})]$ (**7b**) (0.09 g).

Synthesis of the Cobalt Compound $[Co(\eta^6\text{-}C_6H_5Me)(\eta^5\text{-}7\text{-}NHBu^t\text{-}7\text{-}CB_{10}H_{10})]$. A mixture of $[CoCl(PPh_3)_3]$ (0.88 g, 1.0 mmol) and *nido*-$7\text{-}NH_2Bu^t\text{-}7\text{-}CB_{10}H_{12}$ (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 [Co(η^6-C_6H_5Me)(η^5-7-$NHBu^t$-7-$CB_{10}H_{10}$)] (**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 Mo K_α X-radiation $\bar{\lambda} = 0.71073$. 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 ($U_{\mathrm{iso}} = 1.2U_{\mathrm{iso\ equiv}}$ of the parent atom except for Me protons where $U_{\mathrm{iso}} = 1.3U_{\mathrm{iso\ equiv}}$). 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 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.