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An efficient synthesis of 12-vertex *closo*-rhodacarboranes [3-(η^5-C_5Me_5)-1-R^1-2-R^2-3,1,2-*closo*-$RhC_2B_9H_9$] (R^1, R^2 = H, Alk) via two-step reactions of [K][7-R^1-8-R^2-7,8-*nido*-$C_2B_9H_{10}$] mono-anions with [$Rh_2(\eta^5$-$C_5Me_5)_2Cl_4$]: structural characterization of the first purely *closo*-type metallacarborane with sterically demanding C,C′-dibenzylsubstituted carborane ligand

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ABSTRACT

The room temperature reactions between [$Rh_2(\eta^5$-$C_5Me_5)_2Cl_4$] (**1**) and [K][7-R^1-8-R^2-7,8-*nido*-$C_2B_9H_{10}$] (**2a–d**: **a**, $R^1 = R^2$ = H; **b**, $R^1 = R^2$ = Me; **c**, R^1 = H, R^2 = $PhCH_2$; **d**, $R^1 = R^2$ = $PhCH_2$) in solution of C_6H_6–EtOH mixture (4:1) to give [3-(η^5-C_5Me_5)-1-R^1-2-R^2-3,1,2-*closo*-$RhC_2B_9H_9$] (**3a–d**), respectively, have been shown to proceed through the formation of the first step ionic intermediates of the type [(η^5-C_5Me_5)$Rh(\mu$-Cl)$_3$$Rh(\eta^5$-$C_5Me_5$)][7-$R^1$-8-$R^2$-7,8-*nido*-$C_2B_9H_{10}$] (**4a–d**). All ionic compounds **4a–d** were isolated in the solid state and characterized by a combination of analytical, IR and multinuclear NMR data, including a single-crystal X-ray diffraction study of **4d**. The structure of **3d** ($R^1 = R^2$ = $PhCH_2$), the first 12-vertex *closo*-type metallacarborane species bearing sterically demanding C,C′-dibenzylsubstituted carborane ligand, has also been determined by an X-ray crystallography.

1. Introduction

The most widely employed synthetic routes to *closo*- and the related *pseudocloso*-rhodacarboranes with η^5-cyclopentadienyl-type ligands at the metal vertex rely on the reaction between the dimeric rhodium complexes [$Rh_2(\eta^5$-$C_5R_5)_2Cl_4$] (R = H or Me) and the open-faced dianions $[7,8\text{-}R'_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_9]^{2-}$ (where R′ is H or bulky substituent) [1,2]. The *nido*-carborane precursors are traditionally taken either as the di-Tl salts [1] or generated *in situ* from the mono-anions $[7,8\text{-}R'_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-$ (R′ = H) in the presence of a strong non-nucleophilic base such as proton sponge [2a]. Although these methods are mild and convenient, the isolated yields of the target rhodium complexes of either *closo* or *pseudocloso* structures are typically low, ranging from 8 to *c.a.* 35% [1–3]. We now report an efficient use of mono-, di-, and unsubstituted carborane {7,8-R^1,R^2-*nido*-C_2B_9}$^-$ mono-anion derivatives in the direct metallation reaction with [$Rh_2(\eta^5$-$C_5Me_5)_2Cl_4$] (**1**) to prepare 12-vertex {(η^5-C_5Me_5)-*closo*-RhC_2B_9} rhodacarborane systems in very high yields.

2. Results and discussion

We have found that, in contrast with the general trends observed for the reactions referred to above [1,2], treatment of **1** with 2.2–2.5 molar excess of the K^+ salts of the *nido*-carborane mono-anions $[7,8\text{-}R^1,R^2\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-$ (**2a–d**: **a**, $R^1 = R^2$ = H; **b**, $R^1 = R^2$ = Me; **c**, R^1 = H, R^2 = $PhCH_2$; **d**, $R^1 = R^2$ = $PhCH_2$) in solution of C_6H_6–EtOH (4:1) mixture for *c.a.* 5 days at ambient temperature afforded the desired *closo*-rhodacarboranes [3-(η^5-C_5Me_5)-1,2-R_2-3,1,2-*closo*-$RhC_2B_9H_9$] (**3a–d**), respectively, in *c.a.* 80–90% yields (Scheme 1, part **A**).

Compounds **3a–d** are crystalline materials, stable both in the solid state and in solution for long period in air; all gave satisfactory elemental analyses (see Section 4). Complexes **3a–d** were then characterized by IR and ^1H, $^{11}B/^{11}B\{^1H\}$ NMR spectroscopy, and in the case of **3c,d** by the $^{13}C\{^1H\}$ NMR data. In the ^1H NMR spectra of all these complexes **3a–d** signals characteristic of a η^5-C_5Me_5 ligand as well as resonances originating either from the cage substituent protons or the cluster CH protons have been revealed, of which each was observed in the expected integral ratio. On the basis of the NMR data obtained, together with the previously known NMR properties of complex **3a** [2a], all rhodacarboranes **3a–d** can be postulated to adopt 12-vertex *closo* geometry. Such a conclusion

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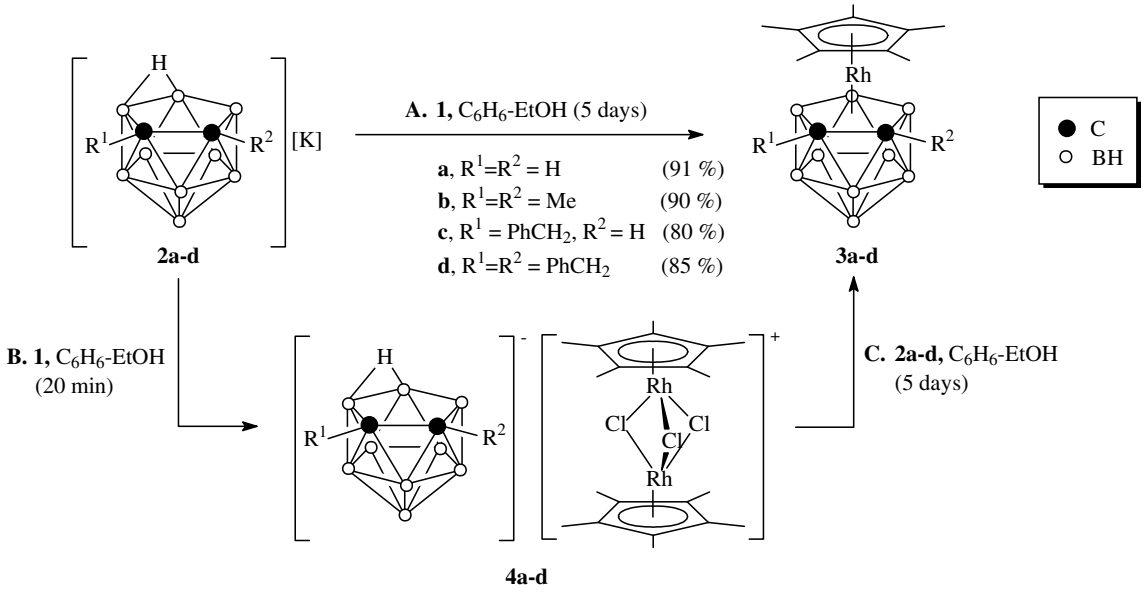

Scheme 1. Two-step reaction pathway of the dimeric complex **1** and the *nido*-carborane salts **2.**

is in agreement with the weighted average ^{11}B chemical shifts $\langle\delta(^{11}B)\rangle$ of −8.6 [2a], −5.0, −8.0, and −7.0 ppm calculated from the $^{11}B\{^1H\}$ NMR spectra of **3a–d**, respectively, which are indicative of typical *closo* structure [1c,4].

A single-crystal X-ray diffraction study of **3d** confirms this species can be formulated as 18-electron *closo*-rhodacarborane with non-distorted cluster geometry (Fig. 1). Notably, despite the presence of two bulky groups at the adjacent cluster carbons in **3d** the dimensions within the $\{RhC_2B_9\}$ core unit in this molecule are, in fact, similar to those observed in the known unsubstituted species **3a** [2a]. Nevertheless, evidence of an intramolecular crowding of **3d** has been obtained from the comparison of its molecular structure with that of **3a**. Although the Rh–B(8) distances are nearly the same in species **3a** and **3d** [2.173(6) and 2.173(1) Å, respectively], in the latter species the cluster Rh–C(1,2) distances [2.1885(9) and 2.1873(9) Å] are markedly longer than those found in **3a** (2.169 and 2.172 Å [2a]), respectively. Moreover, the fold angle of η^5-C_5Me_5 ligand with respect to η^5-C_2B_3 plane found in **3d** (11.1°) is somewhat greater than that observed in **3a** (8.1° [2a]). All these structural features reasonably suggest that the metal atom in **3a** is more intimately involved in the cluster coordination *via* the Rh–C_2B_3 bonding, giving thus more condensed face-capped cluster

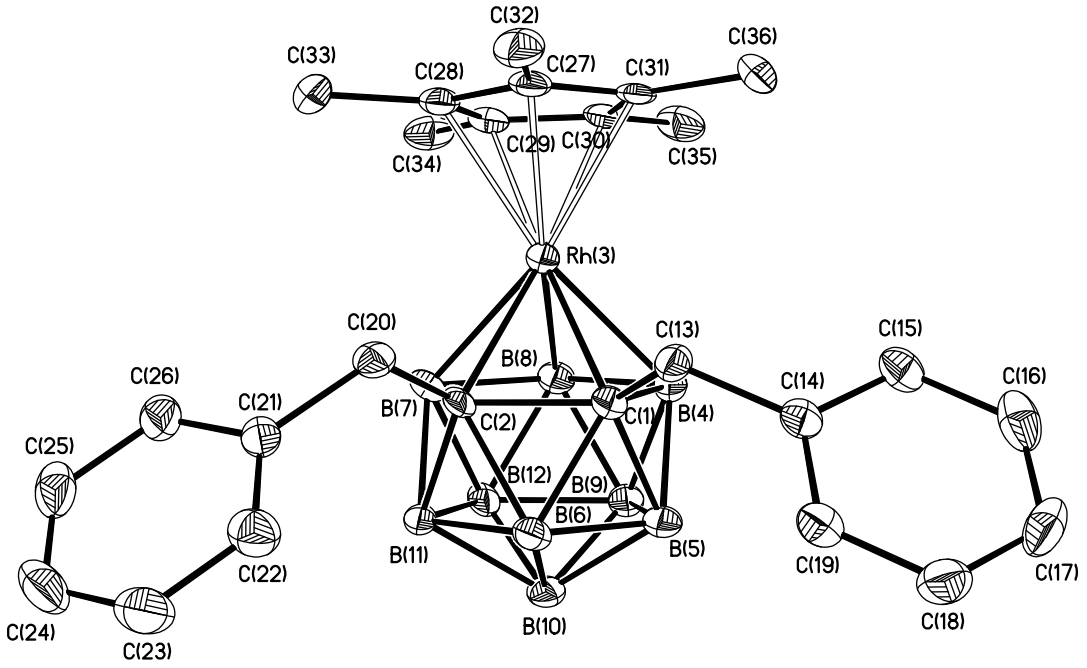

Fig. 1. ORTEP drawing of the molecular structure of complex **3d** with thermal ellipsoids at 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Rh(3)–C(1) 2.1885(9); Rh(3)–C(2) 2.1873(9); Rh(3)–B(4) 2.1766(10); Rh(3)–B(7) 2.1719(10); Rh(3)–B(8) 2.1731(10); Rh(3)–C(27) 2.2599(8); Rh(3)–C(28) 2.2147(9); Rh(3)–C(29) 2.1662(9); Rh(3)–C(30) 2.1693(9); Rh(3)–C(31) 2.2256(8); C(1)–C(2) 1.7397(12); C(2)–C(1)–B(4) 110.36(6); C(1)–C(2)–B(7) 109.98(6); C(1)–B(4)–B(8) 106.70(7); C(2)–B(7)–B(8) 106.58(7); B(4)–B(8)–B(7) 106.33(7).

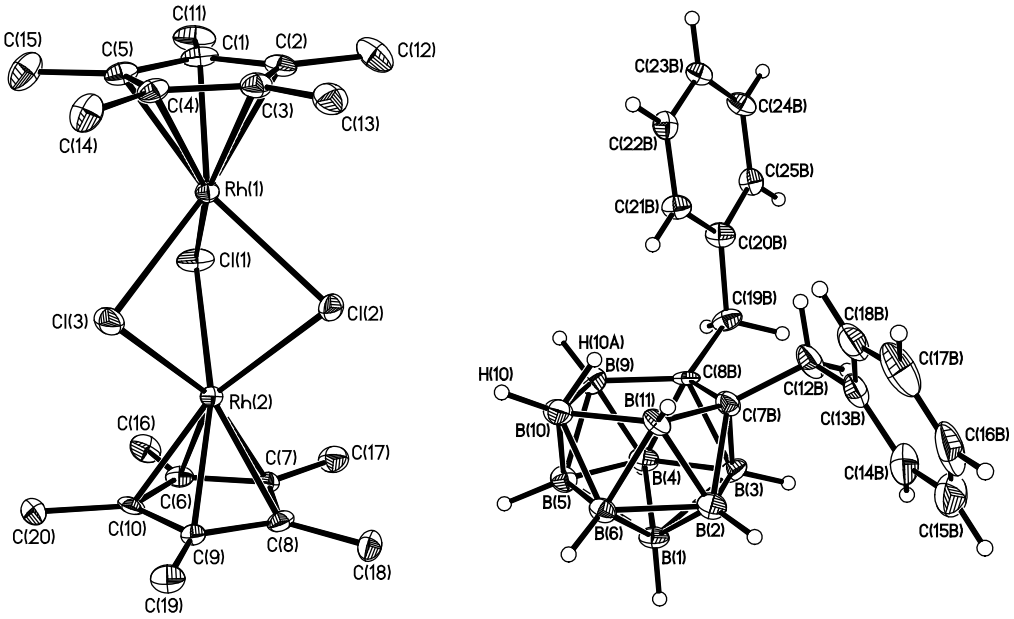

Fig. 2. ORTEP drawing of the molecular structure of ionic complex **4d** with thermal ellipsoids at 50% probability level. Excluding $C_2B_9H_{10}$ unit, the hydrogen atoms, as well as minor component of disordered anion species have been omitted for clarity. Selected bond lengths (Å) and angles (deg.): Rh(1)···Rh(2) 3.1864(4), Rh–Cl 2.4240(9)–2.4716(8), Rh–C_{Cp} 2.109(3)–2.145(3), C(7B)–C(8B) 1.572(6), C(7B)–B(11) 1.653(5), C(8B)–B(9) 1.592(6), B(9)–B(10) 1.803(6), B(10)–B(11) 1.831(6), Rh(1)–Cl(1)–Rh(2) 81.11(3), Rh(1)–Cl(2)–Rh(2) 80.30(2), Rh(1)–Cl(3)–Rh(2) 81.78(3), C(8B)–C(7B)–B(11) 110.0(3), C(7B)–C(8B)–B(9) 115.5(3), C(8B)–B(9)–B(10) 106.0(3), B(9)–B(10)–B(11) 102.2(3), C(7B)–B(11)–B(10) 106.0(3).

geometry than in **3d**. At the same time, slippage distortions in complexes **3a,d** remain marginally close to each other.

We note in this context that the only reported C,C′-dibenzylsubstituted metallacarboranes containing group 4 metals [5] and early lanthanides [6] were found to adopt far more reasonable "heavily slipped" *closo* or *exo-nido* structures, strongly indicating that benzyl substituents are functioned here as sterically demanding groups. In this respect, the structurally characterized complex **3d** is thus the first example which lends unambiguous support to the fact that two carbon-bound benzyl substituents, although are bulky, may not produce any noticeable distortion of metallacarborane *closo* geometry, as it is usually observed for other bulky cage substituents [7].

Particular noteworthy feature of the reactions discussed above is that the formation of *closo*-rhodacarborane complexes **3a–d** proceeds by the two-step pathway (Scheme 1, parts **B** and **C**). Thus, monitoring the reaction of **1** with **2a** by TLC showed the formation of an additional band of a new complex after the first 20 min. This new species slowly disappeared from the reaction mixture upon stirring of the reagents for a longer period of time, exhibiting properties of an apparent intermediate. When the reaction of **1** with **2a** was terminated at the first stage two products could be isolated using column chromatography on silica gel. Of these products, one, which is formed in a less quantity, has been identified, by comparison with the authentic sample, as **3a**, and another one was an intermediate ionic species of presumed formulation $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)_3Rh(\eta^5\text{-}C_5Me_5)][7\text{-}R^1\text{-}8\text{-}R^2\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]$ (**4a**, $R^1 = R^2 = H$).

By a procedure similar to that described for **4a**, other respective ionic intermediates **4b–d** were successfully isolated from the reaction of **1** with **2b–d**, respectively. All compounds **4b–d** gave satisfactory microanalyses and, in addition, good-quality single crystals of complex **4d** were obtained for an X-ray diffraction study. As can be seen in the drawing (see Fig. 2), the crystallographic study clearly established that **4d** is the ionic species formally built from a cationic dirhodium unit $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)_3Rh(\eta^5\text{-}C_5Me_5)]^+$ counteracted by *nido*-carborane $[7,8\text{-}(PhCH_2)_2\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-$ mono-anion in non-associated manner. Each rhodium atom in **4d** is symmetrically coordinated by a $\eta^5\text{-}C_5Me_5$ ligand to form two structural units which are held together via the three μ-chloride bridges {Rh-(μ-Cl)-Rh}.

Solution NMR data of **4d** are fully consistent with its solid-state structure. The ^1H NMR spectrum of **4d** displays both a characteristic broad resonance at *c.a.* −2.59 ppm, indicating the presence of a B–H–B bridging hydrogen atom of the anionic {*nido*-C_2B_9}-carborane moiety, the resonance at 1.65 ppm related with the two $\eta^5\text{-}C_5Me_5$ ligands, seen as a sharp singlet, and the corresponding resonances derived from the two equivalent cage benzyl substituents. Accordingly, the ^{11}B NMR spectrum of **4d** exhibits a set of six doublets with *J*(B,H) coupling of *c.a.* 130–170 Hz in the region from −9.6 to −36.8 ppm as expected for the carborane $\{nido\text{-}C_2B_9\}^-$ mono-anion. Similar ^1H and ^{11}B NMR spectra were observed for complexes **4a–c**.

To further confirm that species **4a–d** are the first step intermediates on the way to complexes **3a–d**, rather than side products formed during metallation reactions, we examined reactions of selected complexes **4b,d** with the corresponding *nido*-carborane mono-anions **2b** and **2d**, respectively. Indeed, on treatment with 5–15% molar excess of **2b,d** both species **4b** and **4d** led to mononuclear products in high yields, which from analysis of their ^1H and $^{11}B\{^1H\}$ NMR spectra were deduced to be *closo*-rhodacarboranes **3b,d**, respectively.

3. Conclusion

A short series of four *closo*-rhodacarborane complexes of general formula $[3\text{-}(\eta^5\text{-}C_5Me_5)\text{-}1\text{-}R^1\text{-}2\text{-}R^2\text{-}3,1,2\text{-}closo\text{-}RhC_2B_9H_9]$, **3a–d**, have been efficiently prepared starting from $[Rh_2(\eta^5\text{-}C_5Me_5)_2Cl_4]$, **1**, and the corresponding *nido*-carborane mono-anions $[K][nido\text{-}7\text{-}R^1\text{-}8\text{-}R^2\text{-}7,8\text{-}C_2B_9H_{10}]$ (**2a–d**: **a**, $R^1 = R^2 = H$; **b**, $R^1 = R^2 = Me$; **c**, $R^1 = H$, $R^2 = PhCH_2$; **d**, $R^1 = R^2 = PhCH_2$) in a mixture of solvents C_6H_6–EtOH. One of the ionic intermediates, $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)_3Rh(\eta^5\text{-}C_5Me_5)][nido\text{-}7,8\text{-}(PhCH_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]$,

4d, formed in the course of the reaction of **1** with **2d**, as well as the final product of this metallation reaction, *closo* complex **3d**, were structurally characterized by single-crystal X-ray diffraction studies.

4. Experimental

4.1. General comments

All reactions and manipulations, except for column chromatography, were carried out under an atmosphere of dry argon using standard Schlenk techniques. All solvents were dried over appropriate drying agents and distilled under an argon atmosphere prior to use. Silica gel Merck (230–400 mesh) was used for column chromatography. Starting reagents $[Rh_2(\eta^5\text{-}C_5Me_5)_2Cl_4]$ [8], [K][7,8-*nido*-$C_2B_9H_{12}$] [9], [K][7,8-Me_2-7,8-*nido*-$C_2B_9H_{10}$] [10], [K][7-$PhCH_2$-7,8-*nido*-$C_2B_9H_{11}$] [10], and [K][7,8-$(PhCH_2)_2$-7,8-*nido*-$C_2B_9H_{10}$] [6a] were prepared according to the literature methods or by analogy. The ^1H, ^{11}B, and ^{13}C NMR spectra were obtained on a Bruker AMX-400 and Avance-600 instruments (*J* values are given in Hz). IR spectra in hexachlorobutadiene were recorded on a Bruker IFS-25 spectrometer. Elemental analyses were performed by the Analytical Laboratory of the Institute of Organoelement Compounds of the RAS.

4.2. General procedure for the preparation of closo-rhodacarboranes [3-(η^5-C_5Me_5)-1-R^1-2-R^2-3,1,2-closo-$RhC_2B_9H_9$] (**3a–d**) without isolation of ionic intermediate complexes

4.2.1. Synthesis of [3-(η^5-C_5Me_5)-3,1,2-closo-$RhC_2B_9H_{11}$] (**3a**) [**2a**]

A suspension of dimeric complex **1** (0.050 g, 0.081 mmol) and **2a** (0.031 g, 0.18 mmol) in 16 ml of a C_6H_6–EtOH (4:1) mixture were stirred at room temperature for 5 days. After the solvent was removed under reduced pressure, the crude solid obtained was purified by column chromatography on silica gel (eluent *n*-hexane–CH_2Cl_2 mixture, 3:2) to give pure complex **3a** (0.055 g, 91%) as a pale-yellow crystalline solid. Anal. Calc. for $C_{12}H_{26}B_9Rh$: C, 38.90; H, 7.07; B, 26.26. Found: C, 38.84; H, 7.07; B, 26.20%. IR spectrum (ν_{max}/cm^{-1}): 2560 (BH). ^1H NMR (400.13 MHz, C_6D_6): δ = 3.27 (2H, br s, CH_{carb}), 2.03 (15H, s, C_5Me_5).

4.2.2. Synthesis of [3-(η^5-C_5Me_5)-1,2-Me_2-3,1,2-closo-$RhC_2B_9H_9$] (**3b**)

The complex **3b** (0.035 g, 90%) was synthesized from **1** (0.030 g, 0.049 mmol) and the salt **2b** (0.022 g, 0.11 mmol) in 16 ml of C_6H_6–EtOH (4:1) mixture using similar reaction conditions and purification procedure as those described above for **3a**. Anal. Calc. for $C_{14}H_{30}B_9Rh$: C, 42.19; H, 7.59; B, 24.41. Found: C, 42.24; H, 7.55; B, 24.36%. IR spectrum (ν_{max}/cm^{-1}): 2514 (BH). ^1H NMR (400.13 MHz, C_6D_6): δ = 1.77 (6H, s, CH_3), 1.44 (15H, s, C_5Me_5). ^{11}B NMR (128.33 MHz, C_6D_6, $J = J(^{11}B,^1H)$): δ = 9.4 (1B, d, *J* = 145), 1.0 (3B, d, *J* = 147), −8.6 (2B, d, *J* = 144), −13.5 (3B, d, *J* = 151).

4.2.3. Synthesis of [3-(η^5-C_5Me_5)-1-($C_6H_5CH_2$)-3,1,2-closo-$RhC_2B_9H_{10}$] (**3c**)

In a procedure similar to that for **3a**, complex **1** (0.030 g, 0.049 mmol) reacted with the salt **2c** (0.030 g, 0.11 mmol) in 15 ml of C_6H_6-EtOH (4:1) mixture to give complex **3c** (0.032 g, 80%) as a pale yellow solid. Anal. Calc. for $C_{14}H_{30}B_9Rh$: C, 49.54; H, 7.00; B, 21.12. Found: C, 49.58; H, 6.99; B, 21.12%. IR spectrum (ν_{max}/cm^{-1}): 2565 (BH). ^1H NMR (400.13 MHz, CD_2Cl_2): δ = 7.28 (3H, m, C_6H_5-*meta* + *para*), 7.05 (2H, dd-like, C_6H_5-*ortho*). $^{11}B/^{11}B\{^1H\}$ NMR (128.33 MHz, CD_2Cl_2, $J = J(^{11}B,^1H)$): δ = 9.2 (1B, d, *J* = 132), −1.3 (2B, d, *J* = 143), −3.3 (1B, d, *J* = 157), −8.5 (1B, d, *J* = 138), −10.5 (1B, d, *J* = 140), −16.8 (1B, d, *J* = 178), −18.3 (1B, d, *J* = 170), −21.2 (1B, d, *J* = 168). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, $J = J(^{103}Rh,^{13}C)$): δ = 137.9 (s, C_6H_5), 130.6 (s, C_6H_5), 127.8 (s, C_6H_5), 127.1 (s, C_6H_5), 103.5 (d, C_5Me_5, *J* = 8), 74.7 (m, C_{carb}), 59.6 (m, C_{carb}), 48.5 (s, CH_2), 9.3 (s, C_5Me_5).

4.2.4. Synthesis of [3-(η^5-C_5Me_5)-1,2-($C_6H_5CH_2$)$_2$-3,1,2-closo-$RhC_2B_9H_9$] (**3d**)

The complex **3d** (0.076 g, 85%) was synthesized from **1** (0.050 g, 0.081 mmol) and the salt **2d** (0.065 g, 0.20 mmol) in 20 ml of C_6H_6–EtOH (4:1) mixture using similar reaction conditions and purification procedure as those for **3a**. Anal. Calc. for $C_{26}H_{38}B_9Rh$: C, 56.70; H, 6.95; B, 17.66. Found: C, 56.65; H, 6.99; B, 17.68%. IR spectrum (ν_{max}/cm^{-1}): 2550 (BH). ^1H NMR (400.13 MHz, C_6D_6): δ = 7.33 (6H, m, C_6H_5); 7.18 (4H, m, C_6H_5); 3.67 (4H, s, CH_2); 2.04 (15H, s, C_5Me_5). ^{11}B NMR (128.33 MHz, CD_2Cl_2, $J = J(^{11}B,^1H)$): δ = 10.0 (1B, d, *J* = 130); −0.8 (3B, d, *J* = 135); −9.3 (2B, d, *J* = 138); −15.7 (2B, d, *J* = 150); −20.4 (1B, d, *J* = 154). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, $J = J(^{103}Rh,^{13}C)$): δ = 137.8 (s, C_6H_4), 130.7 (s, C_6H_4), 127.9 (s, C_6H_4), 127.2 (s, C_6H_4), 103.9 (d, C_5Me_5, *J* = 6), 82.4 (m, C_{carb}), 44.9 (s, CH_2), 9.0 (s, C_5Me_5).

4.3. Isolation of the intermediate ionic complexes [(η^5-C_5Me_5)$_2$$Rh_2$($\mu$-Cl)$_3$][7-$R^1$-8-$R^2$-7,8-nido-$C_2B_9H_{10}$] (**4a–d**) and their transformation to closo-rhodacarboranes (**3a–d**)

4.3.1. Synthesis of [(η^5-C_5Me_5)$_2$$Rh_2$($\mu$-Cl)$_3$][7,8-nido-$C_2B_9H_{12}$] (**4a**) and (**3a**)

Complex **1** (0.040 g, 0.065 mmol) and the K^+-salt **2a** (0.012 g, 0.069 mmol) in 6 ml of a C_6H_6–C_2H_5OH (4:1) mixture were stirred for 20 min at room temperature. Solvent was evaporated under reduced pressure, and the solid obtained was extracted with a CH_2Cl_2–THF–*n*-hexane (2:1:1) mixture, followed by column chromatography on silica gel. The first mobile band eluted from the column using the same mixture of solvents as eluent was found to contain crude complex **3a** (0.010 g, 21%). The second orange broad band was then eluted with a CH_2Cl_2–THF–*n*-hexane (4:3:2) mixture to afford, followed by evaporation and recrystallization of the residue from a CH_2Cl_2 solution layered by *n*-hexane, ionic complex **4a** (0.020 g, 43%) as deep orange solid. Anal. Calc. for $C_{22}H_{42}B_9Cl_3Rh_2$: C, 36.90; H, 5.91; B, 13.59. Found: C, 36.85; H, 5.91; B, 13.68. IR spectrum (ν_{max}/cm^{-1}): 2527 (BH). ^1H NMR (400.13 MHz, CD_2Cl_2): δ = 1.70 (32H, br s, C_5Me_5 + $2CH_{carb}$), −2.92 (1H, br m, H-*endo*). $^{11}B\{^1H\}$ NMR (192.57 MHz, CD_2Cl_2, $J = J(^{11}B,^1H)$): δ = − 11.4 (2B, s, *J* = 130), −17.2 (2B, s, *J* = 141), −22.1 (2B, s, *J* = 113), −33.2 (1B, s, *J* = 134), −38.0 (1B, s, *J* = 132), −39.1 (1B, s, *J* = 136).

Treatment of **4a** (0.020 g, 0.028 mmol) with the salt **2a** (0.005 g, 0.029 mmol) in 5 ml of C_6H_6–EtOH (4:1) mixture for 5 days with stirring afforded, after purification procedure, complex **3a** (0.020 g, 97%).

4.3.2. Synthesis of [(η^5-C_5Me_5)$_2$$Rh_2$($\mu$-Cl)$_3$][7,8-$Me_2$-7,8-nido-$C_2B_9H_{10}$] (**4b**) and (**3b**)

The complex was prepared from **1** (0.040 g, 0.065 mmol) and the salt **2b** (0.015 g, 0.075 mmol) with stirring of the reagents in 10 ml of C_6H_6–EtOH (4:1) mixture for 20 min at room temperature. Using the same purification procedure as for the unsubstituted species **4a**, pure ionic complex **4b** (0.030 g, 62%), along with a small amount of **3b** (0.008 g, 17%), was thus obtained. Anal. Calc. for $C_{24}H_{46}B_9Cl_3Rh_2$: C, 38.74; H, 6.23; B, 13.08. Found: C, 38.79; H, 6.11; B, 12.99%. IR spectrum (ν_{max}/cm^{-1}): 2526 (BH). ^1H NMR (400.13 MHz, CD_2Cl_2): δ = 1.68 (30H, s, C_5Me_5), 1.31 (6H, s, Me), −2.74 (1H, br m, H-*endo*). $^{11}B\{^1H\}$ NMR (128.33 MHz, $CDCl_3$): δ = − 9.6 (3B, d), −18.5 (4B, d), −34.8 (1B, d), −37.1 (1B, d).

A mixture of **4b** (0.020 g, 0.027 mmol) and the salt **2b** (0.006 g, 0.030 mmol) in 5 ml of C_6H_6–EtOH (4:1) mixture was stirred for 5 days at ambient temperature. Solvent was removed, and the residue was purified by column chromatography similarly to that described above, affording yellow-orange crystalline product, which on the basis of its ^{1}H NMR spectrum was deduced to be complex **3b** (0.019 g, 96%).

*4.3.3. Synthesis of [(η^5-C_5Me_5)$_2$Rh$_2$(μ-Cl)$_3$][7-($C_6H_5CH_2$)-7,8-nido-$C_2B_9H_{11}$] (**4c**) and (**3c**)*

Ionic complex **4c** was prepared from **1** (0.040 g, 0.065 mmol) and the salt **2c** (0.020 g, 0.076 mmol) with stirring of the reagents in 10 ml of C_6H_6–EtOH (4:1) mixture for 20 min at room temperature. Similar treatment of the reaction product by column chromatography afforded **4c** (0.040 g, 76%) along with minor amount of the complex **3c** (<0.05 g). Complex **4c** was recrystallized by slow diffusion of pentane into its $CHCl_3$ solution to give analytically pure red crystals. Anal. Calc. for $C_{29}H_{48}B_9Cl_3Rh_2 \cdot CHCl_3$: C, 38.93; H, 5.34. Found: C, 38.57; H, 5.39%. IR spectrum (ν_{max}/cm^{-1}): 2528 (BH). ^{1}H NMR (400.13 MHz, CD_2Cl_2, $J = J(^1H,^1H)$, Hz): δ = 7.28 (1H, s-like, C_6H_5), 7.27 (s, $CHCl_3$ as a solvate), 7.22 (3H, m, C_6H_5), 7.14 (1H, m, C_6H_5), 3.04 (1H, d, CH_2, J = 15), 2.78 (1H, d, CH_2, J = 15), 1.81 (1H, br s, C_{carb}H), 1.69 (30H, s, C_5Me_5), −2.76 (1H, br m, H-*endo*). ^{11}B{^{1}H} NMR (128.33 MHz, $CDCl_3$, $J = J(^{11}B, ^1H)$): δ = − 10.5 (1B, d, J = 122), −11.1 (1B, d, J = 133), −13.5 (1B, d, J = 156), −16.9 (1B, d, J = 149), −18.7 (2B, d, J = 133), −21.9 (1B, d, J = 141), −33.4 (1B, dd, $J_1 \approx 125$, $J_2 \approx 42$), −37.0 (1B, d, J = 137).

A mixture of **4c** (0.030 g, 0.037 mmol) and the salt **2c** (0.020 g, 0.076 mmol) in 10 ml of C_6H_6–EtOH mixture for 5 days afforded, after purification, pure complex **3c** (0.020 g, 66%).

*4.3.4. Synthesis of [(η^5-C_5Me_5)$_2$Rh$_2$(μ-Cl)$_3$][7,8-($C_6H_5CH_2$)$_2$-7,8-nido-$C_2B_9H_{10}$] (**4d**) and (**3d**)*

The compound **1** (0.050 g, 0.081 mmol) and the salt **2c** (0.030 g, 0.085 mmol) were stirred in 12 ml of C_6H_6–EtOH (4:1) mixture for 20 min. The reaction products were similarly treated by column chromatography to give ionic complex **4d** (0.050 g, 69%), along with complex **3d** (0.010 g, 11%). Anal. Calc. for $C_{36}H_{54}B_9Cl_3Rh_2$: C, 48.24; H, 6.07; B, 10.85. Found: C, 48.72; H, 6.34; B, 11.07%. IR spectrum (ν_{max}/cm^{-1}): 2523 (BH). ^{1}H NMR (600.13 MHz, CD_2Cl_2, $J = J$(H,H)): δ = 7.17 (8H, m, C_6H_5), 7.09 (2H, m, C_6H_5), 3.10 (2H, d, CH_2, J_{AB} = 15), 2.96 (2H, d, CH_2, J_{AB} = 15), 1.65 (15H, s, C_5Me_5), −2.59 (1H, br m, H-*endo*). ^{11}B NMR (192.57 MHz, CD_2Cl_2, $J = J(^{11}B, ^1H)$): δ = − 9.6 (2B, d, J = 134), −10.8 (1B, d, J = 140), −17.8 (2B, d, J = 141), −18.6 (2B, d, J = 169), −34.1 (1B, d, J = 136), −36.8 (1B, d, J = 142).

Complex **4d** (0.020 g, 0.022 mmol) was suspended in the mixture of C_6H_6–EtOH (4:1) and then the salt **2d** (0.009 g, 0.025 mmol) was added. The reaction mixture was stirred for 5 days at room temperature, solvent was evaporated and the residue subjected to purification via column chromatography, affording yellow crystalline solid, which on the basis of the ^{1}H NMR spectrum was deduced to be complex **3d** (0.020 g, 81%).

*4.4. X-ray studies of **3d** and **4d***

Crystal data and the details of data collection and structure refinement parameters for complexes **3d** and **4d** are listed in Table 1. Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART APEX II diffractometer (graphite monochromated Mo Kα radiation, λ = 0.71073 Å, ω-scan technique, T = 100 K). The APEX II software [11] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling and absorption correction, and SHELXTL [12] for space group and structure determination, refinements, graphics, and structure reporting. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with the anisotropic temperature factors for all non-hydrogen atoms. One of two carbon atoms of the *nido*-carborane mono-anion in **4d** is disordered over two positions with 0.7/0.3 occupancies. All hydrogen atoms in structures of **3d** and **4d** were located from difference Fourier maps and within of the carborane moieties were refined isotropically, the rest hydrogen atoms were refined in rigid body approximation.

Table 1
Crystallographic and experimental parameters of **3d** and **4d**

Complex	**3d**	**4d**
Molecular formula	$C_{26}H_{38}B_9Rh$	$C_{36}H_{54}B_9Cl_3Rh_2$
Formula weight	550.76	896.25
Dimension, mm	0.50 × 0.14 × 0.14	0.25 × 0.13 × 0.03
Crystal system	Orthorhombic	Triclinic
Space group	$P2_12_12_1$	$P1$
a, Å	10.1140(1)	11.3857(6)
b, Å	15.0574(2)	12.6933(6)
c, Å	17.4684(2)	14.1952(7)
α, °		80.488(1)
β, °		88.650(1)
γ, °		87.546(1)
V, Å^3	2660.27(5)	2021.2(2)
Z	4	2
ρ_{calc}, g cm^{-3}	1.375	1.473
$2\theta_{max}$, °	64	60
Linear absorption (μ), cm^{-1}	6.57	10.41
No. unique reflection (R_{int})	9184 (0.0432)	11707 (0.0605)
No. observed reflection ($I > 2\sigma(I)$)	9034	8087
No. parameters	366	469
Flack parameter	−0.010(8)	
R_1 (on F for observed reflection)[a]	0.0134	0.0436
wR_2 (on F^2 for all reflection)[b]	0.0339	0.0801
Goodness-of-fit	1.073	0.974

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

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Appendix A. Supplementary material

CCDC 663084 and 663085 contains the supplementary crystallographic data for **3d** and **4d**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.06.018.

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