Synthesis, structure and reactivity of a novel monocarbon hydridorhodacarborane $closo$-2,2-$(Ph_3P)_2$-2-H-1-(Me_3N)-2,1-$RhCB_{10}H_{10}$ Molecular structure of 16-electron $closo$-2-(Ph_3P)-2-Cl-1-(Me_3N)-2,1-$RhCB_{10}H_{10}$ and closely related 18-electron $closo$-3,3-$(Ph_3P)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11}$

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Abstract

A novel 12-vertex monocarbon hydridorhodacarborane $closo$-2,2-$(Ph_3P)_2$-2-H-1-(Me_3N)-2,1-$RhCB_{10}H_{10}$ **1** has been synthesized by the reaction of $Rh(PPh_3)_3Cl$ (**2**) with $nido$-$B_{10}H_{12}CNMe_3$ (**3**) under alkaline conditions. At low temperature **1** exists as a mixture of two preferred conformers in solution, both having C_s symmetry, in accord with the hindered rotation of the $(Ph_3P)_2RhH$ vertex with respect to the CB_4 face of the monocarbon carborane cage. Complex **1** readily reacts with chlorine-containing reagents to form mononuclear 16-electron $closo$-2-(Ph_3P)-2-Cl-1-(Me_3N)-2,1-$RhCB_{10}H_{10}$ (**5**), whose structure was unambiguously confirmed by an X-ray diffraction study. The results of an X-ray diffraction study of the closely related dicarbon carborane derivative $closo$-3,3-$(Ph_3P)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11}$ (**10**), prepared from $closo$-3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$ by analogy with **5**, are also reported. © 1997 Elsevier Science S.A.

Keywords: Rhodium; Boron; Carbaboranes; Crystal structure

1. Introduction

Despite the recent sustained efforts aimed at the development of monocarbon metallacarborane chemistry of transition metals, most of the documented research work has been focused on typical sandwich 18-electron clusters containing either two η^5-carbollyl or one η^5-carbollyl and one η^5-cyclopentadienyl ligands at the metal center [1]. Only limited data are available on 12-vertex closo clusters of this type possessing other than sandwich structures [2–5]. As part of our continuing research on monocarbon metallacarboranes of platinum group metals [3–5] we report herein the facile synthesis of novel $closo$-2,2-$(Ph_3P)_2$-2-H-1-

(Me_3N)-2,1-$RhCB_{10}H_{10}$ (**1**) and the study of its conformation and dynamic behavior in solution. Also presented are X-ray diffraction studies of $closo$-2-(Ph_3P)-2-Cl-1-(Me_3N)-2,1-$RhCB_{10}H_{10}$ (**5**) and $closo$-3,3-$(Ph_3P)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11}$ (**10**) which were obtained as principal products in the respective reactions of **1** and the closely related hydridorhodacarborane complex $closo$-3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$ (**9**) with chlorine-containing reagents.

2. Results and discussion

Recently, we prepared the first phosphine cage-substituted 18-electron monocarbon $closo$-hydridorhodacarborane, $closo$-2,7-$(Ph_3P)_2$-2-H-2-Cl-1-(Me_3N)-2,1-

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Scheme 1.
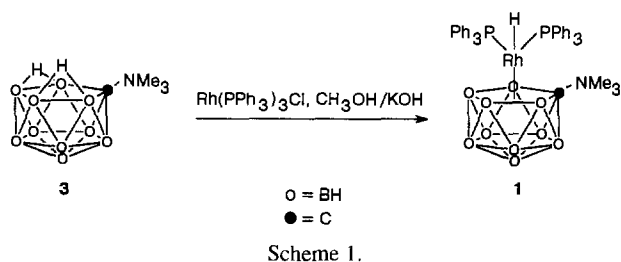
RhCB$_{10}$H$_9$ (6), which was obtained, together with a small amount of 5, on heating equimolar amounts of Rh(PPh$_3$)$_3$Cl (2) and *nido*-B$_{10}$H$_{12}$CNMe$_3$ (3) in methanol, wherein 5 was shown to play the role of intermediate in the formation of 6 [5]. We have now found that the reaction of 2 with 3, when carried out at ambient temperature in methanol for 4 h in the presence of an excess of crushed KOH, resulted in the formation of cluster 1 which was isolated as a light yellow solid in 75% yield (Scheme 1).

The structure and composition of 1 in the solid state agree well with IR spectroscopic and analytical data (see Section 3). However, the low-temperature (-30°C) ^{1}H NMR spectrum of a freshly prepared yellow solution of 1 in CD$_2$Cl$_2$ revealed the presence of a set of two highly resolved doublets of triplets at -9.14 and -11.62 ppm originating from terminal hydrido ligands of two metallacarborane species. The multiplicity of these signals confirmed clearly that the rhodium hydride in each species is coupling to two equivalent PPh$_3$ groups and a ^{103}Rh nucleus; however, the H–P and H–Rh coupling constants have different values (Fig. 1). A set of two slightly broadened singlets at 2.99 and 2.48 ppm originating from NMe$_3$ groups and overlapping multiplets at 7.0–7.45 ppm derived from PPh$_3$

groups were also observed in the spectrum. Approximately similar intensity ratios of 2:1 are observed within each pair of hydride and NMe$_3$ resonances, demonstrating that one of the species is predominant.

The ^{31}P{^{1}H} NMR spectrum of 1 (CD$_2$Cl$_2$, -30°C) also displayed a set of separate doublets of 2:1 intensity ratio at 39.4 ppm ($J_{\text{Rh–P}} = 135.5$ Hz) and 24.0 ppm ($J_{\text{Rh–P}} = 107.0$ Hz) respectively. This is apparently due to the equivalence of PPh$_3$ groups attached to the Rh atom in each of the two species, as may be expected when a mirror plane bisects both the P–Rh–P angle and the monocarbon carborane ligand in each species. Examination of the broad-band and selective decoupling ^{1}H{^{31}P} NMR spectra has confirmed the assignment of the phosphorus and hydride signals for each species and allowed the determination of values for the Rh–H coupling constants for rhodium hydride resonances at -9.14 ppm and -11.62 ppm as 4.0 Hz and 17.0 Hz respectively.

The differences in magnitudes of $J_{\text{Rh–P}}$ (135.5 and 107.0 Hz) and $J_{\text{Rh–H}}$ (4.0 and 17.0 Hz) observed for two *closo*-hydridorhodacarborane species, which are similar in nature, suggested that 1 exists in CD$_2$Cl$_2$ solution as a mixture of A and B conformers, shown below. As shown previously, from the detailed study of dynamic ^{1}H and ^{31}P{^{1}H} FTNMR spectra of an extended series of 12-vertex *closo*-bis(phosphine)hydridometallacarboranes [6], the magnitudes of $J_{\text{Rh–P}}$ and $J_{\text{Rh–H}}$ depend markedly on the preferred conformation of the P$_2$RhH vertex, and, especially, on whether the phosphine and the hydride ligands are trans or cis with respect to carbon and boron atoms of the coordinating face of the carborane cage. Applying the empirical correlation [6] to the above conformers and taking
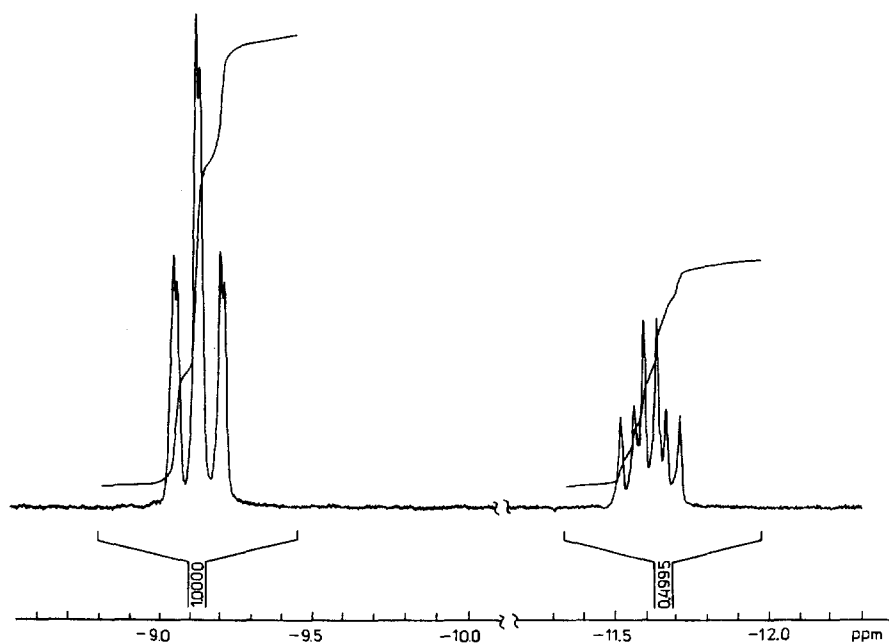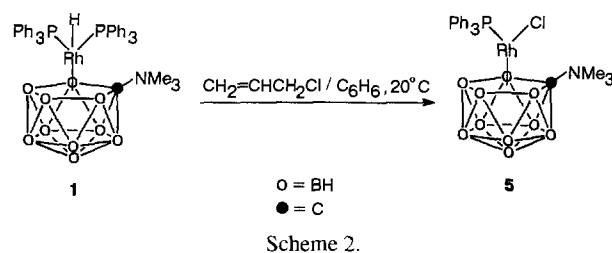

Fig. 1. The high-field region of the ^{1}H NMR spectrum of cluster 1 in CD$_2$Cl$_2$.

into account their overall C_s symmetry, we have concluded that in the predominant conformer **A** the hydride ligand eclipses a C–N bond ($J_{Rh-H} = 4.0\,Hz$) while both phosphine groups at the Rh atom are approximately trans to the corresponding C–B bonds ($J_{Rh-P} = 135.5\,Hz$). In the minor conformer **B**, on the basis of the observed values of $J_{Rh-H} = 17.0\,Hz$ and $J_{Rh-P} = 107.0\,Hz$, the rhodium hydride and two phosphine ligands are expected to be projected over, and to bisect, the B–B and C–B bonds of the carborane face respectively, so that the hydride ligand is trans to a CN vertex. Such assignment of conformers is supported by the argument that conformer **A** is indeed favored in solution, as would be predicted on the basis of steric requirements.

A   B
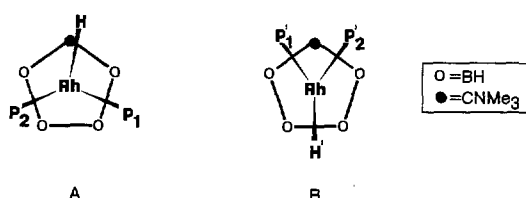
It is noteworthy that the relative concentration of conformers **A** and **B** in CD_2Cl_2 solution remains unchanged at temperatures below the ambient temperature. This observation suggests that a significant rotational barrier of the metal-containing group exists with respect to the open face of the monocarbon carborane ligand. However, our attempts to study the variable-temperature NMR spectra of **1** in order to estimate quantitatively the activation energy failed. It was evident from the NMR experiments that **1** in solution is chemically quite reactive, especially toward halogen-containing and coordinating [2] solvents; at the same time, it is almost insoluble in hydrocarbons, alcohols or aromatic solvents, even upon warming. Thus, an initially yellow solution of **1** in chlorinating solvents (CH_2Cl_2, $CHCl_3$) was found to change color after several minutes at room temperature, whereupon the solution turned dark red. Monitoring of this process by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy showed that in a solution of **1** in CD_2Cl_2 the facile dissociation of a phosphine ligand has occurred, and over ca. 1 h the initial hydride and phosphorus signals

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O = BH
● = C

Scheme 2.

have slowly disappeared from the spectra of **1**, being replaced in the $^{31}P\{^1H\}$ spectrum by a new doublet at 37.8 ppm attributed to a Ph_3P ligand bound to the Rh atom ($J_{Rh-P} = 152.0\,Hz$), and two sharp singlets derived from Ph_3PO (δ 28.4 ppm) and PPh_3 (δ −5.0 ppm). The spectroscopic data for this new species proved to be very similar to those observed earlier [5] for complex **5** as an intermediate species in the reaction of **2** and **3** under non-basic conditions; this complex could thus be formulated as $closo$-2-(Ph_3P)-2-Cl-1-(Me_3N)-2,1-$RhCB_{10}H_{10}$. Further, it has been found that complex **5** is formed nearly quantitatively as a stable crystalline solid in the reaction of **1** in benzene with allyl chloride, which serves as a source of a Cl ligand (Scheme 2).

In order to rule out the possible μ-chloro dimeric structure of **5**, an X-ray diffraction study was undertaken which confirmed that it is a mononuclear species. The full characterization of cluster **5** is especially important since it represents a rare type of 16-electron monocarbon metallacarborane complex, relatively few of which have been obtained and structurally characterized [4].

There are two crystallographically independent molecules in the crystal of **5** which show small differences in the bond distances and angles (see Fig. 2), possibly due to crystal packing effects. The structure of one of the independent molecules is shown in Fig. 2. The structural parameters of **5** are in most aspects similar to those found previously for $closo$-2-(Ph_3P)-2-Br-1-(R_2NH)-2,1-$RhCB_{10}H_{10}$ (**7**, R = crotyl) [4], with some differences induced by an intramolecular N–H $\cdots$ Br hydrogen bond in the latter complex. In both complexes **5** and **7** there is a quite noticeable distortion of the π-carbollyl ligand, in particular manifested in the folding of the CB_4 plane along the B(3) $\cdots$ B(6) line (6.3° or 8.5° and 8.3° in **5** (both independent molecules) and **7** respectively). Surprisingly, the conformations of the metal-containing groups with respect to the CB_4 open face of the carborane cage turn out to be very similar for both complexes **5** and **7**. Thus, in both species the halogen ligand projects approximately over the C–N bond and the phosphine groups are nearly trans to the CN vertices (the torsion angles XRhQC and PRhQC (X = halogen, Q = the centroid of the CB_4 face) are equal to 22.2° (37.9°); 178.4° (174.2°) and
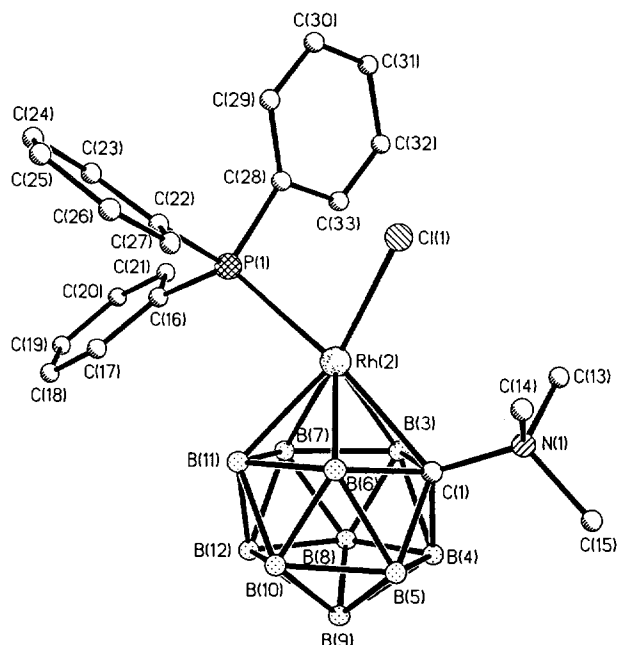

Fig. 2. The structure of one of the independent molecules of **5**. Selected interatomic distances (Å) and angles (deg) (values for both independent molecules are quoted): Rh(2)–Cl(1) 2.370(2), 2.417(2); Rh(2)–P(1) 2.357(2), 2.339(2); Rh(2)–C(1) 2.274(7), 2.236(7); Rh(2)–B(3) 2.126(9), 2.137(9); Rh(2)–B(6) 2.138(9), 2.142(9); Rh(2)–B(7) 2.193(8), 2.194(8); Rh(2)–B(11) 2.172(9), 2.144(8); C(1)–N(1) 1.517(9), 1.549(9); Cl(1)Rh(2)P(1) 83.30(8), 85.39(8); Cl(1)Rh(2)C(1) 104.6(2), 103.7(2); P(1)Rh(2)C(1) 172.1(2), 170.9(2); Rh(2)C(1)N(1) 115.3(5), 115.7(4).

9.8°; 176.6° in **5** and **7** respectively). These conformations, moreover, are strictly different from those found in closo-2,2-(^{t}BuNC)$_2$-1-(NMe$_3$)-2,1-PdCB$_{10}$H$_{10}$ [7]

and those derived by an extended Hückel calculation of such molecules performed by Mingos [8].

The spontaneous dissociation of the phosphine ligand is known to occur for closo-2,2-(Ph$_3$P)$_2$-2-H-2,1,7-RhC$_2$B$_9$H$_{11}$ which when heated in benzene in the presence of CCl$_4$ or when treated with concentrated HCl in CHCl$_3$ gives rise to closo-2-(Ph$_3$P)-2-Cl-2,1,7-RhC$_2$B$_9$H$_{11}$ (**8**) [9]. Surprisingly, such a reaction has never been observed for isomeric complexes derived from [nido-7,8-C$_2$B$_9$H$_{11}$]$^{2-}$. Thus, the reaction of closo-3,3-(Ph$_3$P)$_2$-3-H-3,1,2-RhC$_2$B$_9$H$_{11}$ (**9**) with HCl in CHCl$_3$ is known to form only an 18-electron complex, closo-3,3-(Ph$_3$P)$_2$-3-Cl-3,1,2-RhC$_2$B$_9$H$_{11}$ (**10**), and closo-3,3-(PhMe$_2$P)$_2$-3-H-3,1,2-RhC$_2$B$_9$H$_{11}$ produced the corresponding closo-3,3-(PhMe$_2$P)$_2$-3-Cl-3,1,2-RhC$_2$B$_9$H$_{11}$ by simple recrystallization from CH$_2$Cl$_2$ [9]. Another example of such processes has been reported recently by Stone and coworkers [10] for closo-3,3-(Me$_3$P)$_2$-3-Cl-1,2-Me$_2$-3,1,2-RhC$_2$B$_9$H$_9$ (**11**), which was obtained by treatment of closo-3-(η^3-C$_8$H$_{13}$)-1,2-Me$_2$-3,1,2-RhC$_2$B$_9$H$_9$ with PMe$_3$ in CH$_2$Cl$_2$. This latter reaction was shown to proceed via the intermediate complex closo-3,3-(Me$_3$P)$_2$-3-H-1,2-Me$_2$-3,1,2-RhC$_2$B$_9$H$_{11}$ and, therefore, may be considered to have a similar mechanism. In the present work we have also found that complex **9** reacts readily with allyl chloride in C$_6$H$_6$ at ambient temperature producing complex **10** (in 78% yield) whose structure was confirmed by an X-ray diffraction study.

The overall geometry of complex **10** confirmed clearly the 18-electron configuration of the rhodium atom which should be regarded as Rh^{III} (Fig. 3). The
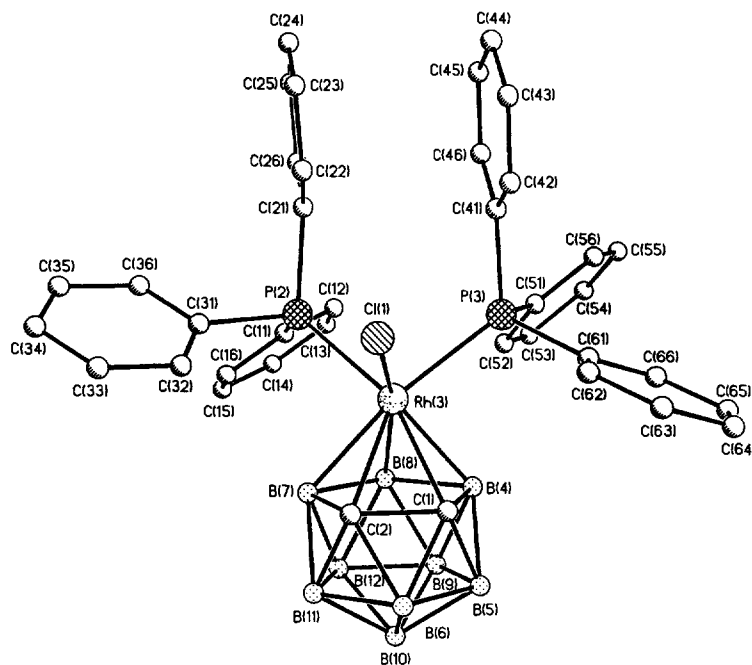

Fig. 3. Molecular structure of **10**. Selected bond lengths (Å) and angles (deg): Rh–Cl 2.422(2), Rh–P 2.371(2) and 2.391(2), Rh–C(1,2) 2.210(6) and 2.218(6), Rh–B(4,7,8) 2.231(7), 2.269(7), and 2.274(7); PRhP 99.6(1), ClRhP 89.9(1), 85.9(1).

metal center is coordinated by the η^5-dicarbollyl ligand and is additionally attached to the two triphenylphosphine groups and one chlorine ligand. The Rh–Cl bond length (2.422(2) Å) in **10** is close to those found in other related 18-electron *closo*-rhodacarborane clusters with terminal chlorine ligands (for instance, Rh–Cl 2.435(2) Å in **11** [10]; Rh–Cl 2.449(1) Å in **6** [5]). These distances are believed to be noticeably longer than those in 16-electron *closo*-metallacarboranes [10]. Thus, the Rh–Cl separation, 2.299(1) Å, found in complex **8** [9] is indeed significantly shorter than those in **10** and **11**. The geometry and bond lengths of the carborane ligand, as well as other fragments of molecule **10**, are quite normal and close to those observed in many representatives of the related *closo*-phosphinerhodacarboranes [11].

The chemical results obtained suggest that the π-carbollyl ligand is more capable of stabilizing 16-electron rhodium complexes than the related π-dicarbollyl ligand, *nido*-7,8-$C_2B_9H_{11}^{2-}$, presumably due to the stronger electron-donating capability of the former. As evidence of its greater donor ability, we may consider the fact of lowering the redox potential of *closo*-3-(η5-C_5H_5)-1,2-R_2-3,2,1-$CoC_2B_9H_9$ (R = H or Me) by approximately 0.3 eV in each case when a carbon atom moves out of the pentagonal open face to form isomeric 1,6- and 5,6-dicarbollyl complexes respectively [12]. The analogous spontaneous phosphine ligand dissociation which is observed for phosphinerhodium complexes with $[nido\text{-}B_{10}H_{10}CNMe_3]^{2-}$, $[nido\text{-}7,9\text{-}C_2B_9H_{11}]^{2-}$ [9] and $[nido\text{-}C_2B_7H_9]^{2-}$ [13] ligands may also indicate the similarity of electron donor abilities of these ligands.

Table 1
Crystallographic details for *closo*-2-(Ph$_3$P)-2-Cl-1-(Me$_3$N)-2,1-RhCB$_{10}$H$_{10}$ (**5**) and *closo*-3,3-(Ph$_3$P)$_2$-3-Cl-3,1,2-RhC$_2$B$_9$H$_{11}$ (**10**)

Compound	5	10
Formula	C$_{22}$H$_{34}$B$_{10}$ClNPRh CH$_2$Cl$_2$	C$_{38}$H$_{41}$B$_{10}$ClP$_2$Rh 2C$_6$H$_{12}$ [a]
Mol. wt	674.9	974.5
Crystal colour, habit	red, parallelepiped	orange, parallelepiped
Crystal size (mm^3)	0.20 × 0.20 × 0.25	0.12 × 0.18 × 0.25
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
Cell constants:		
a (Å)	18.872(3)	11.590(1)
b (Å)	11.271(2)	13.179(1)
c (Å)	30.010(6)	15.414(1)
α (deg)	—	78.47(2)
β (deg)	101.26(1)	80.34(2)
γ (deg)	—	81.35(2)
V (Å^3)	6261	2258
Z	8	2
D_{calcd} (g cm^{-3})	1.432	1.370
Diffractometer	Siemens P3/PC	Huber
Reflections for cell determination	24	43
2θ range (deg)	$12 < \theta < 14$	$9 < 2\theta < 20$
Temperature (K)	296	298
Radiation	Mo Kα ($\lambda = 0.71073$)	Mo Kα ($\lambda = 0.71073$)
Scan mode	θ–2θ	θ–2θ
$2\theta_{max}$ (deg)	50	60
Total unique reflections	10582	13169
Abs. coeff., μ(Mo Kα), cm^{-1}	8.70	4.77
Structure solution	direct method	heavy atom method
Observed reflections	5961 ($I > 2\sigma(I)$)	7521 ($I > 3\sigma(I)$)
No. of parameters	975	389
R_I (on F for obs. reflections) [b]	0.0653	0.058
wR_2 (on F^2 for all reflections) [c]	0.2155	—
R_w [d]	—	0.078

[a] The crystals suitable for X-ray diffraction experiment were grown by slow evaporation of the cyclohexane–CH$_2$Cl$_2$ solution of **10** instead of *n*-hexane–CH$_2$Cl$_2$ mixture used for purification of **10** in synthetic procedure. Therefore, the sample of **10** employed for elemental analyses turned out to be the methylene cloride monosolvate (see Section 3).
[b] $R_1 = \Sigma|F_o - F_c|/\Sigma(F_o)$ for observed reflections.
[c] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ for all reflections.
[d] $R_w = \{[\Sigma w(|F_o| - |F_c|)^2]/\Sigma(wF_o^2)]\}^{1/2}$ for observed reflections.

3. Experimental details

3.1. General aspects

All syntheses were performed under dry argon. The organic solvents and reagents used were dried according to standard procedures. The ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker AMX-400 (^{1}H, 400.13 MHz, ^{31}P, 160 MHz) spectrometer and chemical shifts (δ ppm) were determined relative to external standards SiMe$_4$ and H$_3$PO$_4$ respectively, with high-field resonances being quoted as negative values. The IR spectra were obtained as KBr pellets and recorded on a Specord M-82 spectrometer. Microanalyses were carried out in the analytical laboratory of the Institute of Organoelement Compounds of the Russian Academy of

Science. The starting materials nido-B$_{10}$H$_{12}$CNMe$_3$ [14], Rh(PPh$_3$)$_3$Cl [15] and closo-3,3-(Ph$_3$P)$_2$-3-H-3,1,2-RhC$_2$B$_9$H$_{11}$ [9] were prepared by published methods.

3.2. Preparation of closo-2,2-(Ph$_3$P)$_2$-2-H-1-(Me$_3$N)-2,1-RhCB$_{10}$H$_{10}$ (1)

A suspension of 3 (0.206 g, 1.08 mmol) and carefully crushed KOH (0.170 g, 3.0 mmol) in 70 ml of absolute MeOH was stirred for 2 h at ambient temperature. To the resulting clear solution an equimolar amount of 2 (1.0 g, 1.08 mmol) was added as a solid and the mixture was stirred for an additional 4 h. A lemon yellow microcrystalline solid precipitate was filtered off, washed with absolute methanol and dried in vacuo to give

Table 2
Fractional atomic coordinates ($\times 10^4$) of non-hydrogen atoms and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$) in the structure of 5

	Molecule A				Molecule B			
	x	y	z	U_{eq}	x	y	z	U_{eq}
Rh(2)	−3558(1)	−965(1)	868(1)	31(1)	1719(1)	4088(1)	1404(1)	28(1)
Cl(1)	−2343(1)	−836(2)	772(1)	69(1)	1991(1)	4112(2)	650(1)	53(1)
P(1)	−3259(1)	771(2)	1302(1)	32(1)	1127(1)	2298(2)	1182(1)	31(1)
N(1)	−3524(4)	−3127(6)	155(2)	41(2)	2908(3)	6191(5)	1538(2)	40(2)
C(1)	−3997(4)	−2623(6)	478(2)	33(2)	2247(4)	5736(6)	1726(2)	30(2)
B(3)	−4493(5)	−1312(8)	363(3)	36(2)	2312(5)	4474(8)	2070(3)	33(2)
B(4)	−4892(5)	−2771(9)	287(3)	39(2)	2340(5)	5949(9)	2301(3)	39(2)
B(5)	−4437(6)	−3666(9)	727(3)	41(2)	1745(6)	6819(8)	1914(3)	38(2)
B(6)	−3748(5)	−2739(8)	1067(3)	38(2)	1366(5)	5884(8)	1443(3)	37(2)
B(7)	−4702(5)	−658(7)	876(3)	29(2)	1419(5)	3848(7)	2069(3)	30(2)
B(8)	−5318(5)	−1602(8)	525(3)	36(2)	1854(5)	4816(8)	2507(3)	36(2)
B(9)	−5281(5)	−3058(9)	767(3)	41(2)	1475(5)	6266(8)	2399(3)	39(2)
B(10)	−4560(6)	−3034(9)	1248(3)	45(3)	872(5)	6219(8)	1870(4)	42(2)
B(11)	−4224(5)	−1559(9)	1338(3)	36(2)	813(5)	4712(8)	1671(3)	33(2)
B(12)	−5149(5)	−1790(9)	1129(3)	41(2)	928(6)	5003(9)	2265(3)	43(2)
C(13)	−3366(7)	−2180(11)	−169(4)	55(3)	3394(6)	5187(9)	1468(4)	56(3)
C(14)	−2837(6)	−3620(11)	416(4)	57(3)	2657(7)	6794(9)	1084(4)	60(3)
C(15)	−3873(7)	−4130(12)	−153(4)	67(3)	3379(8)	7058(9)	1854(6)	77(4)
C(16)	−3960(4)	1648(7)	1488(2)	33(2)	717(4)	1396(7)	1572(3)	35(2)
C(17)	−4276(6)	1244(8)	1834(3)	51(3)	70(5)	1741(8)	1673(4)	54(3)
C(18)	−4824(5)	1860(9)	1972(4)	58(3)	−252(6)	1087(9)	1964(4)	74(3)
C(19)	−5059(6)	2918(9)	1773(4)	63(3)	50(5)	59(9)	2151(4)	62(3)
C(20)	−4755(6)	3348(9)	1430(4)	59(3)	702(6)	−290(9)	2057(4)	58(3)
C(21)	−4209(6)	2726(8)	1285(3)	51(3)	1038(5)	370(7)	1769(3)	40(2)
C(22)	−2619(4)	522(7)	1833(3)	38(2)	385(4)	2370(7)	696(3)	38(2)
C(23)	−2441(5)	1442(9)	2140(3)	48(2)	−4(5)	1342(9)	551(4)	57(3)
C(24)	−1965(6)	1270(10)	2540(4)	61(3)	−579(6)	1385(9)	191(4)	80(4)
C(25)	−1669(6)	178(12)	2640(4)	67(3)	−777(6)	2423(9)	−28(3)	69(3)
C(26)	−1840(5)	−758(11)	2348(4)	65(3)	−412(5)	3424(9)	117(3)	61(3)
C(27)	−2301(5)	−584(8)	1944(3)	47(2)	168(5)	3422(9)	474(3)	47(2)
C(28)	−2845(4)	1793(6)	958(3)	33(2)	1829(4)	1365(7)	1036(3)	36(2)
C(29)	−2174(5)	2290(9)	1096(3)	54(3)	1772(5)	730(8)	637(3)	48(2)
C(30)	−1903(6)	3023(11)	805(4)	69(3)	2340(7)	69(9)	558(4)	63(3)
C(31)	−2272(6)	3276(9)	385(4)	56(3)	2963(7)	44(10)	852(4)	66(3)
C(32)	−2942(6)	2762(9)	236(3)	56(3)	3064(5)	650(9)	1256(4)	53(3)
C(33)	−3226(5)	2018(8)	524(3)	47(2)	2489(5)	1315(8)	1332(3)	46(2)
Cl(2)	−1705(4)	6296(7)	1694(2)	251(4)	−259(4)	8338(5)	947(2)	205(3)
Cl(3)	−1274(3)	4097(4)	2143(2)	154(2)	−831(2)	6064(4)	677(1)	126(1)
C(34)	−1143(9)	5323(16)	1841(6)	161(7)	−864(7)	7489(16)	578(7)	158(7)

sufficiently pure solid **1** (0.66 g, 75%). An analytically pure sample of **1**, in low yield, can be obtained by recrystallization from CH_2Cl_2–methanol at approximately 0 °C in the presence of an excess of PPh_3. Anal. Found: C, 54.62; H, 5.78; B, 12.12; Cl, 8.01. $C_{40}H_{50}NP_2Rh \cdot CH_2Cl_2$. Calc.: C, 54.55; H, 5.76; B, 11.97; Cl, 7.87%. IR (ν cm^{-1}): 2140 (RhH), 2508 (BH). ^{1}H NMR (CD_2Cl_2, −30 °C): δ 7.45–7.0 (m, 90 H, both Ph of **A** and **B** conformers), 2.99 (s, 18H, **A**–CH_3), 2.48 (s, 9H, **B**–CH_3), −9.14 (dt, J(HRh) = 4.0 Hz, 2H, **A**–RhH), −11.62 (dt, J(HRh) = 17.0 Hz, 1H, **B**–RhH). ^{31}P{^{1}H} NMR (CD_2Cl_2, −30 °C): δ 39.4 (d, J(PRh) = 135.5 Hz, 2P, **A**–PPh_3), 24.0 (d, J(PRh) = 107.0 Hz, 1P, **B**–PPh_3). (Integral intensities of all proton and phosphorus signals in the NMR spectra were taken relative to the minor conformer **B**.)

3.3. Preparation of closo-2-(Ph₃P)-2-Cl-1-(Me₃N)-2,1-RhCB₁₀H₁₀ (5) [5]

To a suspension of **1** (0.2 g, 0.24 mmol) in 30 ml of benzene was added allyl chloride (0.2 ml) and the mix-ture was stirred for 1 h at room temperature. The solvent was removed in vacuo and the residue was treated by column chromatography with silica gel as the packing material and CH_2Cl_2 as the eluent yielding the crude product **5**. It was recrystallized from a mixture of CH_2Cl_2–n-hexane to give crystals of **5** (0.13 g, 92%) which had an NMR spectra identical to that of an authentic sample [5]. IR (ν cm^{-1}): 2525 (BH). ^{1}H NMR (CD_2Cl_2, 22 °C): δ 7.3–7.6 (m, 30H, Ph), 3.70 (s, 9H, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 22 °C): δ 37.2 (d, J(RhP) = 152 Hz).

3.4. Preparation of closo-3,3-(Ph₃P)₂-3-Cl-3,1,2-RhC₂B₉H₁₁ (10) [9,16]

Complex **10** was prepared from **9** (0.2 g, 0.26 mmol) and allyl chloride (0.1 ml) using the same procedure as for compound **5**; recrystallization of the crude product from CH_2Cl_2–n-hexane afforded orange crystals of **10** (0.16 g, 78%). Anal. Found: C, 52.00; H, 5.16; B, 10.53; Cl, 12.43; P, 6.68. $C_{38}H_{41}B_9ClP_2Rh \cdot CH_2Cl_2$. Calc.: C, 53.20; H, 4.88; B, 11.05; Cl, 12.11; P, 7.05%.

Table 3
Fractional atomic coordinates ($\times 10^3$) and isotropic displacement parameters ($\mathring{A} \times 10^2$) of hydrogen atoms in the structure of **5**

	Molecule A				Molecule B			
	x	y	z	U_{eq}	x	y	z	U_{eq}
H(3)	−438(3)	−74(5)	2(2)	2(2)	273(3)	400(5)	213(2)	2(2)
H(4)	−508(3)	300(6)	−8(2)	3(2)	286(3)	629(6)	253(2)	3(2)
H(5)	−429(4)	−454(7)	65(2)	4(2)	188(3)	774(6)	185(2)	2(2)
H(6)	−320(3)	−311(6)	122(2)	3(2)	122(3)	614(6)	114(2)	2(2)
H(7)	−484(3)	30(5)	91(2)	2(2)	136(3)	299(5)	217(2)	2(2)
H(8)	−576(4)	−134(6)	38(2)	3(2)	208(5)	440(8)	286(3)	8(3)
H(9)	−573(3)	361(6)	72(2)	2(2)	140(3)	682(6)	266(2)	3(2)
H(10)	−456(4)	−364(7)	157(3)	6(3)	42(4)	673(7)	179(3)	6(3)
H(11)	−396(4)	−126(7)	170(3)	6(2)	26(4)	447(6)	143(2)	5(2)
H(12)	−565(4)	−164(6)	136(2)	5(2)	49(4)	478(7)	247(3)	6(3)
H(131)	−308(5)	−162(9)	−1(3)	8(4)	313(6)	472(9)	127(4)	9(4)
H(132)	−299(4)	−251(6)	−30(2)	3(2)	378(5)	561(8)	135(3)	6(3)
H(133)	−382(4)	−188(6)	−33(2)	2(2)	357(5)	496(8)	177(3)	6(3)
H(141)	−292(4)	−419(7)	61(3)	4(3)	307(4)	701(7)	95(2)	4(2)
H(143)	−252(4)	−376(6)	23(2)	2(2)	238(4)	615(7)	87(2)	3(2)
H(151)	−350(5)	−439(8)	−28(3)	6(3)	305(5)	780(9)	184(3)	8(4)
H(152)	−400(4)	−457(6)	0(2)	1(2)	373(7)	650(9)	205(4)	11(5)
H(153)	−424(6)	−365(9)	−41(4)	10(4)	360(4)	731(7)	169(3)	3(3)
H(17)	−417(5)	68(8)	198(3)	6(3)	−10(4)	241(7)	157(3)	4(2)
H(18)	−503(4)	154(7)	222(3)	5(2)	−64(5)	127(8)	204(3)	7(3)
H(19)	−550(6)	339(9)	188(3)	10(3)	−18(4)	−51(7)	240(2)	5(2)
H(20)	−492(4)	388(7)	131(3)	4(3)	88(5)	−86(8)	214(3)	6(3)
H(21)	−405(4)	292(8)	108(3)	5(3)	150(3)	11(5)	171(2)	1(1)
H(23)	−261(4)	223(7)	205(2)	3(2)	7(5)	73(8)	78(3)	7(3)
H(24)	−177(4)	189(8)	272(3)	5(3)	−81(6)	81(9)	12(4)	9(4)
H(25)	−137(4)	5(7)	287(2)	3(2)	−119(4)	255(6)	−26(2)	2(2)
H(26)	−165(6)	−148(9)	240(3)	9(4)	−55(5)	414(8)	−1(3)	7(3)
H(27)	−242(4)	−120(7)	174(3)	4(2)	44(4)	414(7)	57(2)	5(2)
H(29)	−190(4)	208(7)	137(3)	5(2)	139(4)	85(7)	44(2)	4(2)
H(30)	−145(5)	324(9)	92(3)	7(3)	226(4)	−25(8)	31(3)	5(3)
H(31)	−212(5)	373(8)	16(3)	6(3)	329(4)	−31(6)	83(2)	1(2)
H(32)	−325(5)	298(8)	−4(3)	8(3)	352(5)	59(8)	144(3)	7(3)
H(33)	−371(5)	163(9)	43(3)	8(3)	247(3)	160(5)	156(2)	0(2)

Table 4
Fractional atomic coordinates ($\times 10^4$; for Rh atom $\times 10^5$) and their isotropic (or equivalent isotropic) temperature factors ($\times 10^3$; for Rh, Cl, P $\times 10^4$) in the structure of **10**

Atom	x	y	z	U_{iso}/U_{eq}	Atom	x	y	z	U_{iso}/U_{eq}
Rh(3)	21347(4)	29983(3)	30568(3)	269(1)	C(41)	562(4)	1028(3)	2552(2)	36(1)
Cl(1)	1712(1)	1621(1)	4321(1)	415(3)	C(42)	40(4)	451(3)	3340(2)	45(2)
P(2)	3788(1)	1905(1)	2489(1)	313(3)	C(43)	−26(4)	−609(3)	3396(2)	57(2)
P(3)	627(1)	2446(1)	2437(1)	329(3)	C(44)	429(4)	−1091(3)	2662(2)	61(2)
C(1)	1118(5)	4210(4)	3779(4)	35(1) [a]	C(45)	951(4)	−513(3)	1873(2)	59(2)
C(2)	2444(5)	3884(4)	4061(4)	34(1) [a]	C(46)	1017(4)	547(3)	1818(2)	45(2)
B(4)	1181(6)	4573(5)	2624(4)	35(1) [a]	C(51)	513(3)	2908(3)	1244(3)	40(1)
B(5)	874(7)	5503(6)	3368(5)	45(2) [a]	C(52)	1257(3)	3605(3)	720(3)	44(2)
B(6)	1667(6)	5054(6)	4293(5)	43(2) [a]	C(53)	1146(3)	3963(3)	−180(3)	57(2)
B(7)	3532(6)	3986(5)	3160(4)	35(1) [a]	C(54)	291(3)	3625(3)	−557(3)	63(2)
B(8)	2757(6)	4479(5)	2190(4)	35(1) [a]	C(55)	−452(3)	2928(3)	−33(3)	66(2)
B(9)	1944(6)	5696(6)	2382(5)	40(2) [a]	C(56)	−341(3)	2570(3)	867(3)	54(2)
B(10)	2239(7)	5995(6)	3387(5)	43(2) [a]	C(61)	−837(3)	2956(3)	3004(2)	38(1)
B(11)	3201(6)	4935(6)	3889(5)	41(2) [a]	C(62)	−1117(3)	2695(3)	3931(2)	47(2)
B(12)	3375(6)	5340(5)	2703(5)	39(2) [a]	C(63)	−2213(3)	3070(3)	4355(2)	54(2)
C(11)	4573(3)	2557(3)	1445(3)	36(1)	C(64)	−3029(3)	3706(3)	3852(2)	60(2)
C(12)	4097(3)	2669(3)	653(3)	50(2)	C(65)	−2749(3)	3968(3)	2925(2)	68(2)
C(13)	4647(3)	3216(3)	−141(3)	63(2)	C(66)	−1653(3)	3593(3)	2501(2)	55(2)
C(14)	5673(3)	3651(3)	−142(3)	77(2)	C(1H) [b]	5596(16)	6813(14)	4017(12)	56(5) [a]
C(15)	6149(3)	3539(3)	650(3)	72(2)	C(2H) [b]	5917(22)	−3418(19)	3379(17)	101(8) [a]
C(16)	5599(3)	2992(3)	1443(3)	51(2)	C(3H) [b]	7038(40)	−3167(34)	2611(31)	172(18) [a]
C(21)	3660(4)	596(3)	2272(2)	36(1)	C(4H) [b]	7651(27)	−3020(24)	3096(21)	145(10) [a]
C(22)	3250(4)	−121(3)	3014(2)	45(2)	C(5H) [b]	7462(13)	7734(10)	3624(9)	38(3) [a]
C(23)	3287(4)	−1165(3)	2945(2)	58(2)	C(6H) [b]	6607(29)	7600(24)	3476(21)	158(11) [a]
C(24)	3733(4)	−1493(3)	2135(2)	65(2)	C(7H) [b]	5548(15)	6589(13)	3812(13)	45(4) [a]
C(25)	4142(4)	−776(3)	1393(2)	65(2)	C(8H) [b]	−2470(41)	−1503(36)	1114(28)	352(22) [a]
C(26)	4106(4)	268(3)	1461(2)	53(2)	C(1S) [b]	−2470(41)	−1503(36)	1114(28)	352(22) [a]
C(31)	4920(3)	1473(3)	3239(3)	39(1)	C(2S) [b]	−2660(7)	−1373(7)	688(6)	65(2) [a]
C(32)	4721(3)	1586(3)	4135(3)	45(2)	C(3S) [b]	−2405(84)	−393(76)	1117(67)	428(82) [a]
C(33)	5593(3)	1192(3)	4679(3)	61(2)	C(4S) [b]	−1588(34)	−709(34)	856(25)	316(15) [a]
C(34)	6663(3)	686(3)	4328(3)	65(2)	C(5S) [b]	−1981(10)	557(9)	695(7)	92(3) [a]
C(35)	6861(3)	573(3)	3432(3)	78(3)	C(6S) [b]	−2554(8)	884(6)	531(5)	60(2) [a]
C(36)	5989(3)	967(3)	2888(3)	64(2)					

[a] Atom was refined isotropically; the value of the isotropic temperature factor is given.
[b] Atom belongs to one of the solvating cyclohexane molecules.

^{1}H NMR (CD$_2$Cl$_2$, 20 °C): δ 7.1–7.7 (m, 30H, Ph), 5.34 (s, CH$_2$Cl$_2$), 3.77 (s.br, 2H, CH$_{cb}$).

3.5. X-ray structure determination

Details of crystal parameters, data collection and structure refinement for complexes **5** and **10** are given in Table 1. Both structures were refined by the full-matrix least-squares technique. The non-H atoms in **5** were refined in the anisotropic approximation; the H-atoms of the complex were located in a difference Fourier synthesis and included in the refinement in an isotropic approximation; the H-atoms of the solvating methylene chloride molecules were refined with the help of a riding motion model. All non-H atoms in molecule **10**, with the exceptions of the C$_2$B$_9$ atoms of the carborane cage and the atoms of two solvating and partially disordered cyclohexane molecules, were refined in an anisotropic approximation. All H-atoms of the complex molecule were placed in geometrically calculated posi-

tions and used in structure factor calculations as fixed contributions. All calculations for **5** were performed using SHELXTL PLUS 5 (gamma version) programs on an IBM PC computer; calculations for **10** were carried out by means of the UCLA Crystallographic Program Package on a VAX 3100 computer. Atomic coordinates and their temperature factors for the structure of **5** are listed in Tables 2 and 3; atomic coordinates for the structure of **10** are given in Table 4.

Tables of anisotropic thermal parameters, hydrogen atom coordinates and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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