

Synthesis, structure and reactivity of a novel monocarbon
 hydridorhodacarborane *closo*-2,2-(Ph₃P)₂-2-*H*-1-(Me₃N)-2,1-RhCB₁₀H₁₀
 Molecular structure of 16-electron
closo-2-(Ph₃P)-2-Cl-1-(Me₃N)-2,1-RhCB₁₀H₁₀ and closely related
 18-electron *closo*-3,3-(Ph₃P)₂-3-Cl-3,1,2-RhC₂B₉H₁₁

Igor T. Chizhevsky ^{a,*}, Irina V. Pisareva ^a, Evgenii V. Vorontzov ^a, Vladimir I. Bregadze ^a,
 Fedor M. Dolgushin ^a, Alexandr I. Yanovsky ^a, Yuri T. Struchkov ^a, Carolyn B. Knobler ^b,
 M. Frederick Hawthorne ^{b,1}

^a A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova St. 28, 117813 Moscow, Russia

^b Department of Chemistry and Biochemistry, University of California at Los Angeles, Los Angeles, CA 90095-1569, USA

Received 19 June 1996; accepted 15 August 1996

Abstract

A novel 12-vertex monocarbon hydridorhodacarborane *closo*-2,2-(Ph₃P)₂-2-*H*-1-(Me₃N)-2,1-RhCB₁₀H₁₀ **1** has been synthesized by the reaction of Rh(PPh₃)₃Cl (**2**) with *nido*-B₁₀H₁₂CNMe₃ (**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 (Ph₃P)₂RhH vertex with respect to the CB₄ face of the monocarbon carborane cage. Complex **1** readily reacts with chlorine-containing reagents to form mononuclear 16-electron *closo*-2-(Ph₃P)-2-Cl-1-(Me₃N)-2,1-RhCB₁₀H₁₀ (**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-(Ph₃P)₂-3-Cl-3,1,2-RhC₂B₉H₁₁ (**10**), prepared from *closo*-3,3-(Ph₃P)₂-3-*H*-3,1,2-RhC₂B₉H₁₁ 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-(Ph₃P)₂-2-*H*-1-

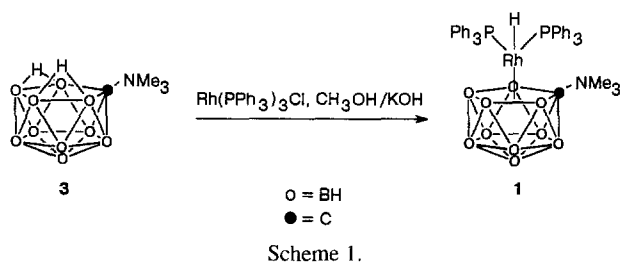
(Me₃N)-2,1-RhCB₁₀H₁₀ (**1**) and the study of its conformation and dynamic behavior in solution. Also presented are X-ray diffraction studies of *closo*-2-(Ph₃P)-2-Cl-1-(Me₃N)-2,1-RhCB₁₀H₁₀ (**5**) and *closo*-3,3-(Ph₃P)₂-3-Cl-3,1,2-RhC₂B₉H₁₁ (**10**) which were obtained as principal products in the respective reactions of **1** and the closely related hydridorhodacarborane complex *closo*-3,3-(Ph₃P)₂-3-*H*-3,1,2-RhC₂B₉H₁₁ (**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-(Ph₃P)₂-2-*H*-2-Cl-1-(Me₃N)-2,1-

* Corresponding author.

¹ Also corresponding author.



$\text{RhCB}_{10}\text{H}_9$ (**6**), which was obtained, together with a small amount of **5**, on heating equimolar amounts of $\text{Rh(PPh}_3)_3\text{Cl}$ (**2**) and *nido*- $\text{B}_{10}\text{H}_{12}\text{CNMe}_3$ (**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) ^1H NMR spectrum of a freshly prepared yellow solution of **1** in CD_2Cl_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 metallocarborane 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** (CD_2Cl_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 $^1\text{H}\{^{31}\text{P}\}$ 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_2Cl_2 solution as a mixture of **A** and **B** conformers, shown below. As shown previously, from the detailed study of dynamic ^1H and $^{31}\text{P}\{^1\text{H}\}$ FTNMR spectra of an extended series of 12-vertex *closo*-bis(phosphine)hydridometallocarboranes [6], the magnitudes of $J_{\text{Rh-P}}$ and $J_{\text{Rh-H}}$ depend markedly on the preferred conformation of the P_2RhH 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

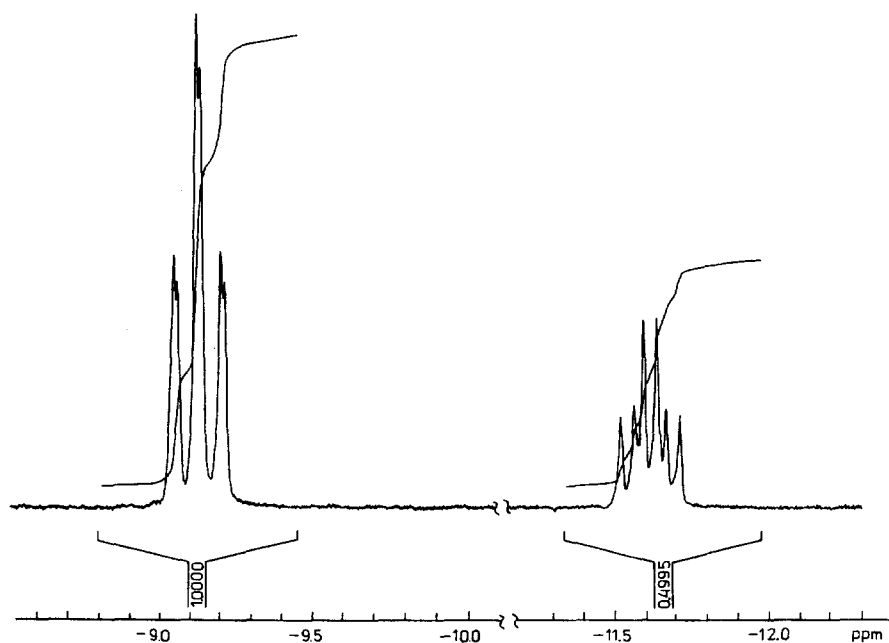
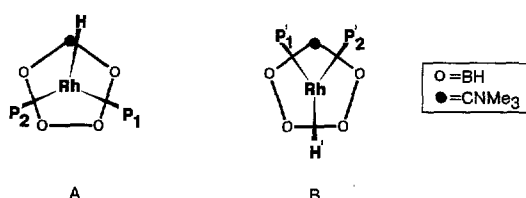


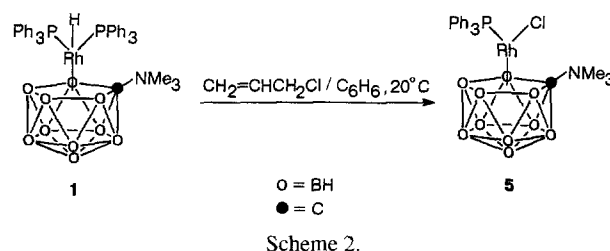
Fig. 1. The high-field region of the ^1H NMR spectrum of cluster **1** in CD_2Cl_2 .

into account their overall C_s symmetry, we have concluded that in the predominant conformer **A** the hydride ligand eclipses a C–N bond ($J_{\text{Rh-H}} = 4.0 \text{ Hz}$) while both phosphine groups at the Rh atom are approximately trans to the corresponding C–B bonds ($J_{\text{Rh-P}} = 135.5 \text{ Hz}$). In the minor conformer **B**, on the basis of the observed values of $J_{\text{Rh-H}} = 17.0 \text{ Hz}$ and $J_{\text{Rh-P}} = 107.0 \text{ Hz}$, 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.



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 $^{31}\text{P}\{^1\text{H}\}$ 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

² On dissolution of **1** in coordinating solvents such as acetone, THF, or CH_3CN , the solvent-promoted dissociation of one of the PPh_3 ligands proceeds rapidly, even at low temperature, to give at least four rhodacarborane species, two of which are believed to contain a coordinated solvent molecule. This process, as well as intermolecular solvent exchange, significantly complicate the study of the variable-temperature NMR spectra of **1**.



have slowly disappeared from the spectra of **1**, being replaced in the $^{31}\text{P}\{^1\text{H}\}$ spectrum by a new doublet at 37.8 ppm attributed to a Ph_3P ligand bound to the Rh atom ($J_{\text{Rh-P}} = 152.0 \text{ Hz}$), 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-RhCB₁₀H₁₀. 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-RhCB₁₀H₁₀ (**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 CB₄ 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 CB₄ 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 CB₄ face) are equal to 22.2° (37.9°); 178.4° (174.2°) and

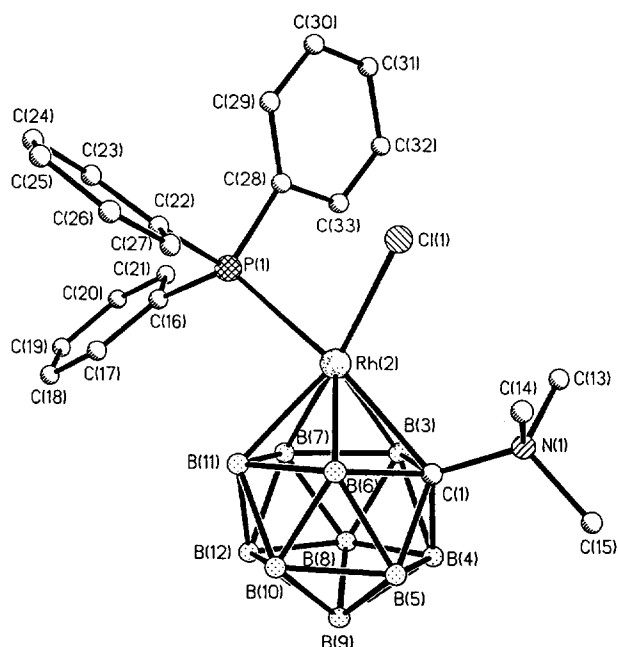


Fig. 2. The structure of one of the independent molecules of **5**. Selected interatomic distances (Å) and angles (deg) (values for both independent molecules are quoted): Rh(2)–Cl(1) 2.370(2), 2.417(2); Rh(2)–P(1) 2.357(2), 2.339(2); Rh(2)–C(1) 2.274(7), 2.236(7); Rh(2)–B(3) 2.126(9), 2.137(9); Rh(2)–B(6) 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-(^tBuNC)₂-1-(NMe₃)-2,1-PdCB₁₀H₁₀ [**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-(Ph₃P)₂-2-*H*-2,1,7-RhC₂B₉H₁₁ which when heated in benzene in the presence of CCl₄ or when treated with concentrated HCl in CHCl₃ gives rise to *closo*-2-(Ph₃P)-2-Cl-2,1,7-RhC₂B₉H₁₁ (**8**) [9]. Surprisingly, such a reaction has never been observed for isomeric complexes derived from [nido-7,8-C₂B₉H₁₁]²⁻. Thus, the reaction of *closo*-3,3-(Ph₃P)₂-3-*H*-3,1,2-RhC₂B₉H₁₁ (**9**) with HCl in CHCl₃ is known to form only an 18-electron complex, *closo*-3,3-(Ph₃P)₂-3-Cl-3,1,2-RhC₂B₉H₁₁ (**10**), and *closo*-3,3-(PhMe₂P)₂-3-*H*-3,1,2-RhC₂B₉H₁₁ produced the corresponding *closo*-3,3-(PhMe₂P)₂-3-Cl-3,1,2-RhC₂B₉H₁₁ by simple recrystallization from CH₂Cl₂ [9]. Another example of such processes has been reported recently by Stone and coworkers [10] for *closo*-3,3-(Me₃P)₂-3-Cl-1,2-Me₂-3,1,2-RhC₂B₉H₉ (**11**), which was obtained by treatment of *closo*-3-(η^3 -C₈H₁₃)-1,2-Me₂-3,1,2-RhC₂B₉H₉ with PMe₃ in CH₂Cl₂. This latter reaction was shown to proceed via the intermediate complex *closo*-3,3-(Me₃P)₂-3-*H*-1,2-Me₂-3,1,2-RhC₂B₉H₁₁ 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 C₆H₆ 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

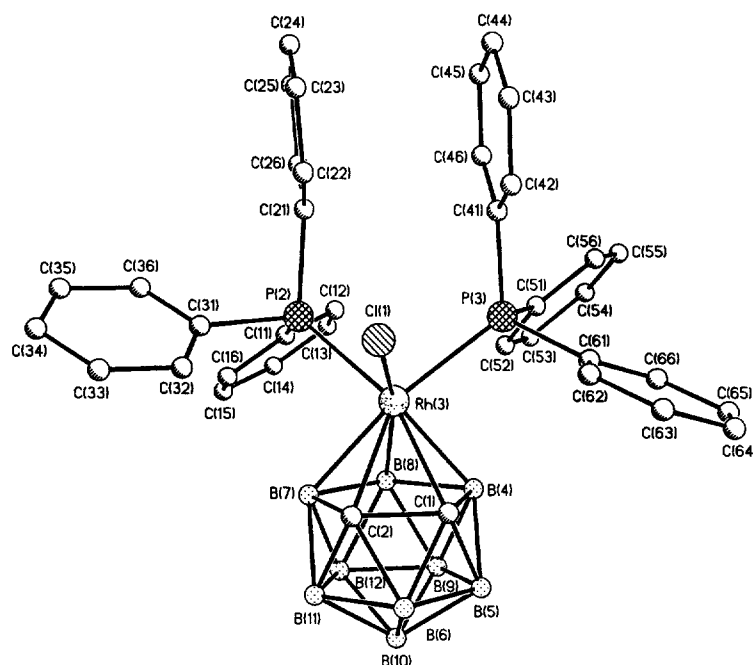


Fig. 3. Molecular structure of **10**. Selected bond lengths (Å) and angles (deg): Rh–Cl 2.422(2), Rh–P 2.371(2) and 2.391(2), Rh–C(1,2) 2.210(6) and 2.218(6), Rh–B(4,7,8) 2.231(7), 2.269(7), and 2.274(7); PRhP 99.6(1), ClRhP 89.9(1), 85.9(1).

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-(η^5 - 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*- $B_{10}H_{10}CNMe_3$] $^{2-}$, [*nido*-7,9- $C_2B_9H_{11}$] $^{2-}$ [9] and [*nido*- $C_2B_7H_9$] $^{2-}$ [13] ligands may also indicate the similarity of electron donor abilities of these ligands.

Table 1

Crystallographic details for *closo*-2-(Ph_3P) $_2$ -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**)

Compound	5	10
Formula	C $_{22}H_{34}B_{10}ClNPRh$	C $_{38}H_{41}B_{10}ClP_2Rh$
Mol. wt	CH $_2Cl_2$ 674.9	2C $_6H_{12}$ ^a 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:		
<i>a</i> (Å)	18.872(3)	11.590(1)
<i>b</i> (Å)	11.271(2)	13.179(1)
<i>c</i> (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)
<i>V</i> (Å ³)	6261	2258
<i>Z</i>	8	2
<i>D</i> _{calcd} (g cm ⁻³)	1.432	1.370
Diffractometer	Siemens P3/PC	Huber
Reflections for cell determination	24	43
2 θ range (deg)	12 < θ < 14	9 < 2 θ < 20
Temperature (K)	296	298
Radiation	Mo K α ($\lambda = 0.71073$)	Mo K α ($\lambda = 0.71073$)
Scan mode	θ -2 θ	θ -2 θ
2 θ_{max} (deg)	50	60
Total unique reflections	10582	13169
Abs. coeff., μ (Mo K α), 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_1 (on <i>F</i> 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 $_2Cl_2$ solution of **10** instead of *n*-hexane–CH $_2Cl_2$ mixture used for purification of **10** in synthetic procedure. Therefore, the sample of **10** employed for elemental analyses turned out to be the methylene chloride monosolvate (see Section 3).

^b $R_1 = \sum |F_o - F_c| / \sum (F_o)$ for observed reflections.

^c $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ for all reflections.

^d $R_w = \{ [\sum w(|F_o| - |F_c|)^2] / \sum (wF_o^2) \}^{1/2}$ 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 ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker AMX-400 (^1H , 400.13 MHz, ^{31}P , 160 MHz) spectrometer and chemical shifts (δ ppm) were determined relative to external standards SiMe_4 and H_3PO_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*- $\text{B}_{10}\text{H}_{12}\text{CNMe}_3$ [14], $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ [15] and *closo*-3,3-(Ph_3P) $_2$ -3-*H*-3,1,2- $\text{RhC}_2\text{B}_9\text{H}_{11}$ [9] were prepared by published methods.

3.2. Preparation of *closo*-2,2-(Ph_3P) $_2$ -2-*H*-1-(Me_3N)-2,1- $\text{RhCB}_{10}\text{H}_{10}$ (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 ($\text{\AA}^2 \times 10^3$) 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(5)	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(3)	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. $\text{C}_{40}\text{H}_{50}\text{NP}_2\text{Rh} \cdot \text{CH}_2\text{Cl}_2$. Calc.: C, 54.55; H, 5.76; B, 11.97; Cl, 7.87%. IR ($\nu \text{ cm}^{-1}$): 2140 (RhH), 2508 (BH). ^1H 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, $J(\text{HRh}) = 4.0 \text{ Hz}$, 2H, A–RhH), -11.62 (dt, $J(\text{HRh}) = 17.0 \text{ Hz}$, 1H, B–RhH). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -30°C): δ 39.4 (d, $J(\text{PRh}) = 135.5 \text{ Hz}$, 2P, A– PPh_3), 24.0 (d, $J(\text{PRh}) = 107.0 \text{ Hz}$, 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-(Ph_3P)-2-Cl-1-(Me_3N)-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 ($\nu \text{ cm}^{-1}$): 2525 (BH). ^1H NMR (CD_2Cl_2 , 22°C): δ 7.3–7.6 (m, 30H, Ph), 3.70 (s, 9H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 22°C): δ 37.2 (d, $J(\text{RhP}) = 152 \text{ Hz}$).

3.4. Preparation of *closo*-3,3-(Ph_3P)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. $\text{C}_{38}\text{H}_{41}\text{B}_9\text{ClP}_2\text{Rh} \cdot \text{CH}_2\text{Cl}_2$. 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 ($\text{\AA}^2 \times 10^2$) 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	$U_{\text{iso}}/U_{\text{eq}}$	Atom	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$
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.

¹H NMR (CD₂Cl₂, 20°C): δ 7.1–7.7 (m, 30H, Ph), 5.34 (s, CH₂Cl₂), 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 C₂B₉ 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.

Acknowledgements

This research was supported in part by National Science Foundation (Grant CHE-91-11437). I.T.C., I.V.P., E.V.V., V.I.B., F.M.D. and A.I.Y. gratefully

acknowledge the financial support of the Russian Foundation for Basic Research (Grant Nos. 96-03-08831 and 94-03-08338) and International Science Foundation (Grant Nos M4P000 and M04000).

References

- [1] (a) B. Štibr, J. Plešek and S. Hermánek, in J.F. Liebman, A. Greenberg, R.E. Williams (eds.) *Advances in Boron and the Boranes*, VCH, New York, 1988, Chapter 3, p. 35. (b) A.K. Saxena and N.S. Hosmane, *Chem. Rev.*, **93** (1993) 1081. (c) R.N. Grimes, in E.W. Abel, F.G.A. Stone and G. Wilkinson (eds.), *Comprehensive Organometallic Chemistry II*, Vol. 1, Pergamon, Oxford, 1995, Chapter 9, p. 373.
- [2] (a) P.A. Wegner, L.J. Guggenberger and E.L. Muettertles, *J. Am. Chem. Soc.*, **92** (1970) 3473. (b) C.G. Salentine and M.F. Hawthorne, *J. Am. Chem. Soc.*, **97** (1975) 6382. (c) W. Quintana, R.L. Ernest, P.J. Carroll and L.G. Sneddon, *Organometallics*, **7** (1988) 166. (g) V.N. Lebedev, D.F. Mullica, E.L. Sappenfield and F.G.A. Stone, *Organometallics*, **15** (1996) 1669.
- [3] J.A. Walker, C.A. O'Con, L. Zheng, C.B. Knobler and M.F. Hawthorne, *J. Chem. Soc. Chem. Commun.*, (1983) 803.
- [4] I.T. Chizhevsky, I.V. Pisavera, P.V. Petrovskii, V.I. Bregadze, A.I. Yanovsky, Yu.T. Struchkov, C.B. Knobler and M.F. Hawthorne, *Inorg. Chem.*, **32** (1993) 3393.
- [5] I.T. Chizhevsky, I.V. Pisareva, P.V. Petrovskii, V.I. Bregadze, F.M. Dolgushin, A.I. Yanovsky, Yu.T. Struchkov and M.F. Hawthorne, *Inorg. Chem.*, **35** (1996) 1386.
- [6] T.B. Marder, R.T. Baker, J.A. Long, J.A. Doi and M.F. Hawthorne, *J. Chem. Soc.*, **103** (1981) 2988.
- [7] W.E. Carroll, M. Green, F.G.A. Stone and A.J. Welch, *J. Chem. Soc. Dalton Trans.*, (1975) 2265.
- [8] D.M.P. Mingos, *J. Chem. Soc. Dalton Trans.*, (1977) 602.
- [9] R.T. Baker, M.S. Delaney, R.E. King, C.B. Knobler, J.A. Long, T.B. Marder, T.E. Paxson, R.G. Teller and M.F. Hawthorne, *J. Am. Chem. Soc.*, **104** (1984) 2965.
- [10] J.C. Jeffery, F.G.A. Stone and I. Topaloglu, *Polyhedron*, **12** (1993) 319.
- [11] A.I. Yanovsky, *Russ. Chem. Rev.*, **54** (1985) 515 (English translation *Uspekhi Khimii*, **54** (1985) 881).
- [12] M.K. Kaloustian, R.J. Wiersema and M.F. Hawthorne, *J. Am. Chem. Soc.*, **94** (1972) 6679.
- [13] C.W. Jung, R.T. Baker and M.F. Hawthorne, *J. Am. Chem. Soc.*, **103** (1981) 810.
- [14] W.H. Knoth, *Inorg. Chem.*, **10** (1971) 598.
- [15] J. Osborn and G. Wilkinson, *Inorg. Synth.*, **10** (1967) 67.
- [16] A.R. Siedle, *J. Organomet. Chem.*, **90** (1975) 249.