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Metallacarborane diene π-complexes. I. Synthesis of rhodacarboranes with a η^2,η^3-2-methylenenorbornadienyl ligand at the rhodium vertex

L.I. Zakharkin *, I.T. Chizhevsky, G.G. Zhigareva, P.V. Petrovskii, A.V. Polyakov, A.I. Yanovsky and Yu.T. Struchkov

A.N. Nesmeyanov Institute of Organoelement Compounds, Academy of Sciences, 28 Vavilov St., Moscow (U.S.S.R.)

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Abstract

Novel 18-electron rhodacarboranes with a 2-methylenenorbornadienyl ligand, η^2,η^3-coordinated to a rhodium atom of closo-3,3-(η^2,η^3-$C_7H_7CH_2$)-1,2-R^1R^2-3,1,2-$RhC_2B_9H_9$ (IIIa–IIId, $R^1 = R^2 = H$ (a), $R^1 = R^2 = Me$ (b), $R^1 = Me$ or Ph, $R^2 = H$ (c,d) and closo-2,2-(η^2,η^3-$C_7H_7CH_2$)-2,1,7-$RhC_2B_9H_{11}$ (VIII) have been prepared. The structures of IIIa–IIId, and VIII were deduced from their IR, ^1H NMR and ^{13}C NMR spectra. Two alternative synthetic routes to the above complexes have been suggested: (a) reactions of 16-electron complexes of (η^4-C_7H_7-2-CH_2OH)-Rh(acac) or [(η^4-C_7H_7-2-CH_2OH)RhCl]$_2$ with appropriate dicarbollide anions with a subsequent acidification by HPF_6 and (b) reactions of unsubstituted and C-monosubstituted closo-bis(triphenylphosphine)hydridorhodacarboranes with 2-(hydroxymethyl)norbornadiene on heating in benzene. The possible mechanisms of these reactions are discussed. An X-ray study of complex IIIb, $R^1 = R^2 = Me$, confirms that there is allylolefin type metal–ligand bonding.

Introduction

It is well known that nido-undecaborate anion $(C_2B_9H_{11})^{2-}$ is capable of formally replacing the η^5-cyclopentadienyl or η^5-pentamethylcyclopentadienyl ligand in a variety of transition metal π-complexes. In respect of the electron-donor ability and steric requirements this anion resembles most closely the permethylated cyclopentadienyl group [1]. These similarities have led to the synthesis of carborane analogues of most metallocene, arene and other known types of metal complexes [2]. However in the literature there are but a few examples of (π-diene)metallacarboranes that have scarcely been investigated. A number of anionic dienerhodacarboranes with a 1,5-cyclooctadiene [3], and a norbornadiene [4] ligand at the metal

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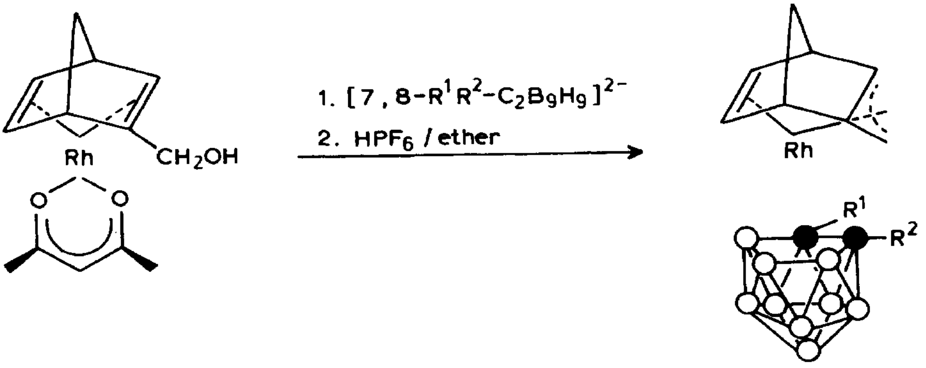
vertex were synthesized recently by Hawthorne and co-workers. They found that these complexes show significantly different chemical behaviour to that of isoelectronic η^5-cyclopentadienyl analogues. Thus, an unusual polyhedral rearrangement of η^4-norbornadiene to η^5-ethylcyclopentadienyl moiety was observed in the [closo-3,3-(η^4-norbornadiene)-1,2-Me_2-3,1,2-$RhC_2B_9H_9]^-$ PPN^+ complex under the action of CF_3COOH [4]. In view of our interest in metallacarborane chemistry [5,6] as well as the chemistry of transition metal diene π-complexes [7,8] it seemed quite natural to extend these studies and to carry out a systematic and detailed comparative investigation of reactions of the diene π-complexes having carboranyl or cyclopentadienyl ligands.

Results and discussion

{2-(Hydroxymethyl)norbornadiene}acetylacetonatorhodium (I) reacts readily with mono- and di-substituted dicarbollide anions $[7,8\text{-}R^1R^2C_2B_9H_9]^{2-}$ (IIa–IId), (generated in situ from [nido-7,8-$R^1R^2C_2B_9H_{10}$]K and sodium isopropoxide in i-PrOH and after acidification with 70% HPF_6 gives the novel 18-electron rhodacarboranes, closo-3,3-(η^2,η^3-$C_7H_7CH_2$)-1,2-R^1R^2-3,1,2-$RhC_2B_9H_9$ (IIIa–IIId).

Complexes IIIa–IIId are air-stable, coloured (from yellow to dark red), crystalline substances that are moderately soluble in polar solvents and insoluble in hydrocarbon solvents. They do not have sharp melting points.

Substitution at the 2(3) or 5(6) position of the norbornadiene molecule gives chiral compounds, the chirality being retained on coordination of the transition metal by the monosubstituted norbornadiene [9]. The rhodacarboranes (IIIa, IIIb)



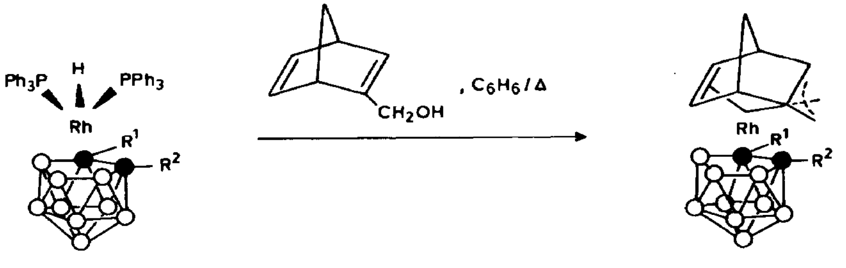
(IIIa : $R^1 = R^2 = H$;
IIIb : $R^1 = R^2 = Me$;
IIIc : $R^{1(2)} = Me$,
$R^{2(1)} = H$;
IIId : $R^{1(2)} = Ph$,
$R^{2(1)} = H$)

thus are racemic, whereas (IIIc, IIId) are diastereomeric mixtures, owing to additional asymmetry introduced by the dicarbollide anions (IIc, IId). As has been shown by ^1H NMR spectroscopy the ratio of diastereomers in the mixtures IIIc, IIId is equal to 1/1.

Replacement of an acetylacetonate ligand in the 16-electron dieneacetylacetonatorhodium complexes by an undecaborate anion, though very promising because of the availability of initial complexes, is not the only synthetic route to the title compounds. In particular the μ-halide dimeric complexes of rhodium $[(\eta^4$-cyclodiene)$RhCl]_2$, were also used to synthesize the anionic (π-diene)rhodacarboranes [2,3]. Usually, such μ-halide dimers are prepared directly by heating $RhCl_3 \cdot 3H_2O$ with dienes in alcohol under reflux. However, in the case of functionally substituted norbornadienes, this method either fails to provide satisfactory results [10], or requires a large excess of diene. So in order to prepare μ-halide dimeric rhodium complexes, we used the reaction between $[(C_8H_{14})_2RhCl]_2$ with 2-*R*-norbornadiene (in 1/1 molar ratio) in hexane affording the complexes $[(\eta^4$-C_7H_7-2-$CH_2R)RhCl]_2$ (IVa, IVb, R = OH or OAc) in high yields and under milder conditions.

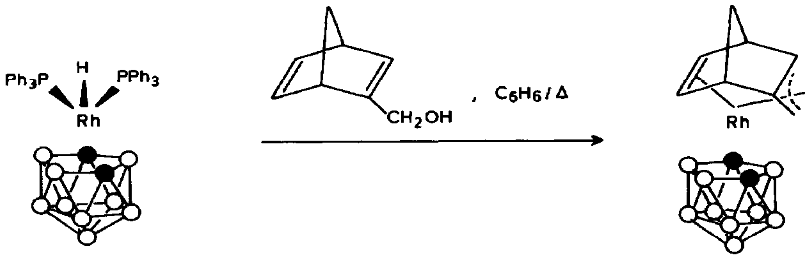
It was found that the reaction of the complexes IVa or IVb with the dicarbollide anions IIa, IIb gives the rhodacarboranes IIIa, IIIb under conditions similar to those for the acetylacetonatorhodium complex I, but in higher yield. Naturally one may suppose that the reaction of the carbinols I and IVa with the dicarbollide anions in the first stage yields the anionic (η^4-diene)rhodacarboranes, [closo-3,3-(η^4-C_7H_7-2-CH_2OH)-1,2-R^1R^2-3,1,2-$RhC_2B_9H_9]^-$.

Complexes of this type in the form of PPN-salts [closo-3,3-(η^4-C_7H_7-2-R)-1,2-Me_2-3,1,2-$RhC_2B_9H_9]^-$ PPN^+ (Va, Vb, R = CH_2OH, CHO) were prepared by



(VIIa, VIIb)

(IIIa : $R^1 = R^2 = H$;
IIIc : $R^{1(2)} = Me$, $R^{2(1)} = H$)



(VIII)

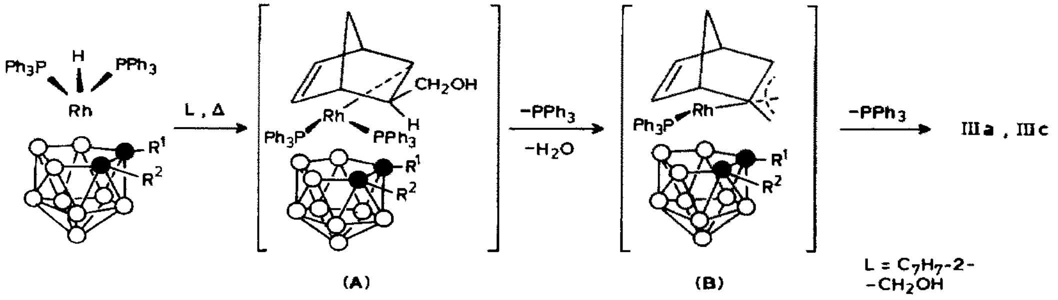
reaction of the dimer IVb, and (η^4-C_7H_7-2-CHO)Rh(acac) (VI), and dicarbollide anions IIb and the product was identified by ^1H NMR spectroscopy. ^1H NMR data (in CD_2Cl_2) for Va: 8.69 (s,1,CHO), 7.39–7.74 (m,15,Ph), 3.9 (m,1,H5(6)), 3.83 (m,1,H1(4)), 3.74 (m,1,H6(5)), 3.66 (m,1H4(1)), 3.28 (m,1,H(3)), 2.08 (s,Me), 1.70 (s,3,Me), 1.17 (m,2,H($7_{\alpha,\beta}$)); for (Vb): 4.51 (d.br.1, J_{AB} 11.0 Hz,H(8_A)), 3.66 (d.br.1, J_{BA} 10.9 Hz,H(8_B)), 3.46 (m + impur.,2,H5(6)), 3.38 (m,1,H6(5)), 3.30 (m,1,H1(4)), 3.17 (m,1,H(3)), 3.06 (m,1,H4(1)), 1.99 (s.br.,3,Me), 1.79(s.br.,3,Me), 1.26 (m + impur.,3,H($7_{\alpha,\beta}$)). In addition, the i-Pr group signals appear in the spectrum of Vb: 3.67 (septet. J 6.2 Hz,CH), 1.07 (d, J 6.2 Hz,Me). The formation of complex Va from IVb may occur as a result of hydrolysis of the appropriate 2-(acetyloxymethyl) derivative under the strong alcoholic conditions required for this reaction. Special experiments have shown that treatment of complex Va with HPF_6 in ether yields allylolefin rhodacarborane (IIIb) and the PPN^+ PF_6^- salt.

We have also developed a principally new one-step synthesis of allylolefin rhodacarboranes of type VII on the basis of available closo-bis(triphenylphosphine)-hydridorhodacarboranes.

It has been found that equimolar amounts of 2-(hydroxymethyl)norbornadiene and closo-3,3-$(PPh_3)_2$-3-H-1(2)-R-3,1,2-$RhC_2B_9H_{10}$ (VIIa, VIIb, R = H(a), Me(b)) yield the complexes IIIa, IIIc on heating in benzene. Closo-2,2-$(PPh_3)_2$-2-H-2,1,7-$RhC_2B_9H_{11}$ can also be used as the carboranyl component in the reaction. In this case closo-2,2-(η^2,η^3-$C_7H_7CH_2$)-2,1,7-$RhC_2B_9H_{11}$ (VIII) is formed in high yield.

At present the detailed mechanism of this reaction is not clear. Since the reaction proceeds only on heating it proved impossible to monitor the course of the process under milder conditions by ^1H NMR or ^{31}P NMR spectroscopy.

In the initial stage, the insertion of the norbornadiene C(2)=C(3) double bond into the metal-hydride bond may occur to form a σ-complex (**A**), which by elimination of H_2O and PPh_3 molecules gives the intermediate η^3-allylmonophosphine complex (**B**).On heating, **B** undergoes intramolecular substitution of the triphenylphosphine by the norbornadiene cycloolefin ligand and thus forms the products IIIa, IIIc or VIII.



On the other hand, taking into account the acidic character of the hydride atom of the closo-bis(triphenylphosphine)hydridorhodacarboranes [11] and the ability of these complexes to undergo facile elimination of the triphenylphosphine ligand in solution [12], we should consider the possibility of the formation of **B** also by nucleophilic substitution with prior protonation of the hydroxy group oxygen atom. In this case we envisage the formation of the σ-complex C in which the metal atom is bonded to the exocylic methylene group. The transition of σ-complex C to complex **B** involves the allylic $\eta^1 \rightarrow \eta^3$ rearrangement with the simultaneous elimina-

Table 1

^{1}H NMR spectra of rhodacarboranes IIIa–IIId and VIII in CD_2Cl_2 solution

Compound	^{1}H chemical shifts δ (ppm) (multiplicity [a], relative intensity, coupling constant (Hz), assignment)
IIIa	5.41 (s,br, 1, H(8)-*syn*); 4.70 (m*, 1, H(6)); 4.55 (m, 1, H(5)), 4.50 (m, 1, H(3)); 3.81 (m, 1, H1(4)); 3.70 (s,br, 1, H(8)-*anti*); 3.51 (m, 1, CH_{carb}); 3.47 (m, 1, H4(1)), 3.28 (m, 1, CH_{carb}); 2.01 (d_q, 1, J_{AB} 10.1, J_q 1.5, H($7_{\alpha,\beta}$)); 1.86 (d_t, 1, J_{BA} 10.1, J_t 1.7, H($7_{\beta(\alpha)}$))
IIIb	5.43 (s,br, 1, H(8)-*syn*); 4.90 (m*, 1, H(6)); 4.32 (m, 1, H(3)); 4.04 (s,br, + m*, 2, H(5), H(8)-*anti*), 3.74 (m, 1, H1(4)); 3.41 (m, 1, H4(1)); 3.29 (s, 3, Me), 1.99 (s, 3, Me); 1.89 (d,br, 1, J_{AB} 9.6, H($7_{\alpha(\beta)}$)); 1.77 (d_t, 1, J_{BA} 10.0, J_t 1.7, H($7_{\beta(\alpha)}$)
IIIc [b,c]	5.34 (s,br, H(8), H′(8)-*syn*); 4.93 (m*, H(5,6)); 4.42 (m, ?), 4.25 (m*, H′(5,6)); 4.13 (s,br, H(8)-*anti*); 3.91 (m, H(3)); 3.86 (s,br, H′(8)-*anti*); 3.83 (m, ?); 3.77 (m, ?), 3.59 (m, ?); 3.48 (m, ?); 2.20 (s, Me); 1.98 (d_t, J_{AB} 9.9, H($7_{\alpha(\beta)}$)); 1.89 (m + s, H($7_{\alpha,\beta}$) + Me′); 1.86 (d_q, J_{AB} 9.9, J_q 1.7, H($7_{\beta(\alpha)}$))
IIId [b]	7.52–6.93 (m, 5×2, Ph + Ph′); 5.13 (s,br, 1, H(8) – *syn*); 4.94 (m*, 1, H(6)); 4.83 (s,br, 1, H′(8)-*syn*); 4.80 (m, 1 2, H(5) + H′(6)); 4.14 (m, 1,2, H′(5) + H(4(1)); 4.09 (s,br, 1, H(8)-*anti*); 3.95 (s.br, 1, H′(8)-*anti*); 3.80 (m, 1, H′4(1)); 3.71 (m, 1,2, H1(4) + H′1(4)); 3.46 (m, 1, H(3)); 3.32 (m,1, CH'_{carb}); 3.21 (m, 1, CH'_{carb}); 2.93 (m, 1, H′(3)); 1.85 (d,br, 1, J_{AB} 10.0, H($7_{\alpha(\beta)}$); 1.74 (m, 2, H′($7_{\alpha,\beta}$)); 1.73 (d_t, 1, J_{BA} 10.0, J_t 1.6, H($7_{\beta(\alpha)}$)
VIII	5.58 (s,br, 1, H(8)-*syn*); 4.94 (m*, 1, H(6)); 4.34 (m*, 1, H(5)); 4.13 (s,br, 1, H(8)-*anti*); 3.77 (m, 1, H(3)); 3.68 (m,1, H1(4)); 3.52 (m, 1, H4(1)); 2.40 (m, 1, CH_{carb}); 2.15 (m, 1, CH_{carb}); 2.00 (d,br, 1, J_{AB} 9.8, H($7_{\alpha(\beta)}$)); 1.85 (d_t, 1, J_{BA} 9.8, J_t 1.9, H($7_{\beta(\alpha)}$))

[a] s, singlet; d, doublet; t, triplet; m, multiplet, q, quartet, d_t, doublet of triplets; m*, signal is quadruplet-like. [b] It was studied as a mixture of isomers. [c] (?), the signals were not assigned.

tion of one PPh_3 ligand. In our opinion the protonation stage preceding the formation of complex **C** could be facilitated by the preliminary coordination of the diene ligand to the rhodium atom via the C(2)=C(3) double bond, which should increase the basicity of the oxygen atom of the carbinol OH group [13].

Recently, the nucleophilic substitution reaction between $CH_2{=}CHCH_2X$ (X = Cl or AcO) and anionic complex $[closo\text{-}3,3\text{-}(PPh_3)_2\text{-}3,1,2\text{-}RhC_2B_9H_{11}]^-$ gave the 18-electron neutral complex (η^3-allyl)rhodacarborane. Its structure [14] is quite similar to that attributed by us to complex **B**. This fact may be seen as indirect evidence of the possibility that complexes **B** may indeed represent the key intermediates in the reactions of hydridorhodacarborane with 2-(hydroxymethyl)norbornadiene.

The structures of complexes IIIa–IIId and VIII are confirmed by ^{1}H and ^{13}C NMR data (Table 1 and 2), and by mass spectroscopy (see Experimental). In the ^{1}H NMR spectra of the rhodacarboranes all norbornadienyl ligand signals appear as separate multiplets, whereas the proton signals of the unsubstituted or monosubstituted carborane moieties are, in fact, broad and unresolved.

It is noteworthy that in the ^{1}H NMR spectra of all the allylolefin complexes the proton signals of the exocyclic methylene group of the dienyl ligand have quite different chemical shifts ($\Delta\delta \sim 1.5$ ppm) while the *J*(H–H) coupling constant is not larger than 1–1.2 Hz (as estimated from the halfwidths of the signals). Such a difference in chemical shifts of geminal protons with an extremely small coupling constant is typical of *syn–anti* protons in η^3-allylmetal complexes [15].

Table 2

^{13}C NMR spectra of rhodacarboranes IIIa–IIId and VIII

Compound (Solvent)	^{13}C chemical shifts (ppm downfield from TMS and $J(^{13}C-^{103}Rh)$ (Hz) in parentheses)									C_{carb}
	C(1)(4)	C(2)	C(3)	C(4)(1)	C(5)(6)	C(6)(5)	C(7)	C(8)	R	
IIIa	46.4	102.6	42.6	43.7	60.6	64.5	55.9	80.3	–	44.0 46.0
(Me_2CO)	(s)	(2.9)	(8.4)	(s)	(5.5)	(5.2)	(2.2)	(5.1)		(m,br)(m,br)
IIIb	45.6	104.2	46.9	44.0	66.6	73.3	55.9	84.8	28.5 31.9	68.7 72.8
(Me_2CO)	(s)	(s,br)	(8.0)	(s)	(5.3)	(5.3)	(2.7)	(6.6)	(s) (s)	(m,br)(m,br)
IIIc [a]	46.9	104.3	43.7	44.4	70.3	77.0	65.7	87.3	33.2	62.0 (?)
(Me_2CO)	(s)	(s,br)	(8.9)	(s)	(4.4)	(4.4)	(s,br)	(3.0)	(s)	(m,br)
	46.4	100.8	38.5	43.5	64.0	64.3		76.5	31.7	58.7 (?)
	(s)	(s,br)	(8.7)	(s)	(5.8)	(5.8)		(7.3)	(s)	(m,br)
IIId [a]	46.4	104.0	47.0	44.0	70.7 [b]	72.4 [b]	55.3	86.5	[c]	50.9 (?)
(CH_2Cl_2)	(s)	(s,br)	(8.1)	(s)	(4.1)	(5.4)	(2.7)	(4.1)		(m,br)
	46.3	101.2	40.2	43.4	64.5 [b]	67.2 [b]	55.1	77.9 [b]		50.7 (?)
	(2.7)	(s,br)	(8.1)	(s)	(6.8)	(5.4)	(2.2)	(6.8)		(m,br)
VIII	45.1	100.1	42.0	43.4	60.2	60.7	56.1	81.5	–	46.4 49.7
	(s)	(s,br)	(8.5)	(s)	(5.7)	(7.1)	(2.8)	(4.4)		(m,br)(m,br)

[a] Mixture of isomers. [b] The assignment of signal requires additional confirmation. [c] C_i 142.9(s), 143.6(s); C_o, C_m 123.7(s), 128.6(s), C_p 126.6(s).

The assignment of the signals to the *syn–anti* protons was based on the well-known phenomenon that the substituents in the *syn*-position in π-allyl systems are less shielded than in the *anti*-position [16]. In the ^1H NMR spectra of complexes IIIc, IIId, the majority of the signals from each of the diastereomers appear as separate multiplets. Some of the isomer signals, especially those from mixture IIIc, are overlapping, which complicates their exact assignment (see Table 1).

The ^{13}C NMR signals of the carbon atoms of the norbornadienyl ligand in complexes IIIa–IIId and VIII have different $J(^{103}Rh-^{13}C)$ coupling constants depending on the position of the carbon atom in the dienyl ligand. Thus the signals of the bridgehead carbon atoms of the norbornadiene framework are singlets; the C(7) carbon atoms signals are doublets with a very small $J(^{103}Rh-^{13}C)$ value, while the carbon signals at the double bonds with the exception of the key atoms C(2) are doublets with $J(^{103}Rh-^{13}C)$ equal to 5–8 Hz. It is noteworthy that the same values of $J(^{103}Rh-^{13}C)$ equal to 5–7 Hz are observed for exocyclic carbon C(8) signals, which indicates that there is a Rh–C(8) bond in these complexes. The fact that the signals of the C(8) carbon in the ^{13}C NMR spectra of rhodacarboranes prepared are noticeably shifted upfield, compared with carbon C(2) signals, is evidently caused by a strong shielding effect of the metal atom.

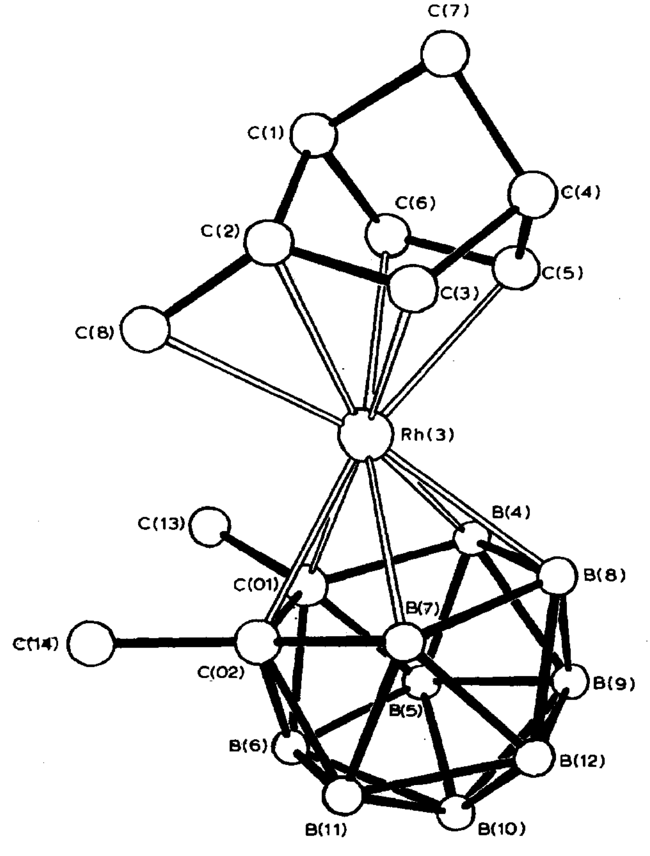


Fig. 1. Molecular structure of complex IIIb.

Table 3

Bond lengths (Å) in complex IIIb

C(01)–C(02)	1.637(6)	B(5)–B(9)	1.761(8)
C(01)–Rh(3)	2.281(4)	B(5)–B(10)	1.759(9)
C(01)–B(4)	1.723(6)	B(6)–B(10)	1.743(9)
C(01)–B(5)	1.711(7)	B(6)–B(11)	1.759(8)
C(01)–B(6)	1.701(7)	B(7)–B(8)	1.799(8)
C(01)–C(13)	1.521(7)	B(7)–B(11)	1.790(8)
C(02)–Rh(3)	2.256(4)	B(7)–B(12)	1.775(8)
C(02)–B(6)	1.759(7)	B(8)–B(9)	1.778(8)
C(02)–B(7)	1.749(7)	B(8)–B(12)	1.767(7)
C(02)–B(11)	1.698(7)	B(9)–B(10)	1.776(9)
C(02)–C(14)	1.544(7)	B(9)–B(12)	1.796(8)
Rh(3)–B(4)	2.153(5)	B(10)–B(11)	1.774(9)
Rh(3)–B(7)	2.226(6)	B(10)–B(12)	1.757(9)
Rh(3)–B(8)	2.218(5)	B(11)–B(12)	1.753(8)
Rh(3)–C(2)	2.211(5)	C(1)–C(2)	1.513(8)
Rh(3)–C(3)	2.139(5)	C(1)–C(6)	1.516(7)
Rh(3)–C(5)	2.215(5)	C(1)–C(7)	1.519(8)
Rh(3)–C(6)	2.247(5)	C(2)–C(3)	1.437(8)
Rh(3)–C(8)	2.354(6)	C(2)–C(8)	1.349(8)
B(4)–B(5)	1.775(8)	C(3)–C(4)	1.528(8)
B(4)–B(8)	1.855(7)	C(4)–C(5)	1.531(7)
B(4)–B(9)	1.769(7)	C(4)–C(7)	1.530(9)
B(5)–B(6)	1.713(9)	C(5)–C(6)	1.365(7)

The protonation of complex (η^4-C_7H_7-2-CH_2OH)Rh(η^5-C_5H_5) with HPF_6 [17] had been used to give the allylolefin complex [(η^2,η^3-C_7H_7-2-CH_2)Rh(η^5-C_5H_5)]$^+$ PF_6^- (IX), which is regarded as the cationic analogue of the rhodacarboranes IIIa–IIId or VIII described herein. It is quite important to note that a comparison of the ^1H and ^{13}C NMR spectra shows that chemical shifts of the corresponding proton and carbon signals of the norbornadienyl in IX, on one hand, and in IIIa–IIId and VIII, on the other, are quite close to each other, and in some cases in fact identical. Thus the NMR data indicate that the rhodacarboranes IIIa–IIId and VIII, and cation IX may be regarded as having a positive charge that is generated primarily at the exocyclic C(8) atom (at least in the case of the reaction with HPF_6) and stabilized by direct interaction with the Rh atom. From this viewpoint the rhodacarboranes IIIa–IIId or VIII may be formally seen as zwitterionic species, which was also confirmed by an X-ray diffraction study of IIIb ($R^1 = R^2 =$ Me).

The molecular structure of IIIb is shown in Fig. 1; bond lengths and relevant bond angles are listed in Tables 3 and 4.

Structural studies of transition metal complexes with carbocationic centers in the β-position relative to the metal atom are quite important for elucidating the mechanism by which these carbocations are stabilized. The data obtained in the past few decades by X-ray crystallography as well as those from NMR, Mössbauer and other spectroscopic methods [18], have provided evidence such two alternative mechanisms by which carbocationic centers, are stabilized, can be proposed: (i) direct interaction of the metal atom with the β-carbocationic center or (ii) participation of a hydrocarbon π-ligand in the delocalization of the positive charge.

Table 4

Relevant bond angles (°) in complex IIIb

C(2)C(1)C(6)	97.7(4)	C(3)C(4)C(5)	97.9(4)
C(2)C(1)C(7)	101.9(4)	C(3)C(4)C(7)	102.0(5)
C(6)C(1)C(7)	102.7(4)	C(5)C(4)C(7)	100.2(4)
C(1)C(2)C(3)	105.8(4)	C(4)C(5)C(6)	107.5(4)
C(1)C(2)C(8)	125.1(5)	C(1)C(6)C(5)	105.9(4)
C(3)C(2)C(8)	123.4(5)	C(1)C(7)C(4)	94.5(4)
C(2)C(3)C(4)	104.8(4)		

The two possible mechanisms of carbocationic stabilization imply that there are two possible interpretations of the structure of complex IIIb, and of its cyclopentadienyl analogues IX [17] and $\{[\mathrm{Rh}(\eta^5\text{-}\mathrm{C_7H_6}\text{-3-Me-2-CHOH})(\eta^5\text{-}\mathrm{C_5H_5})]_2\mathrm{F_2POO}^-\}$ $\mathrm{PF_6}^-$ (X) studied previously [8].

Complex IIIb may be regarded as a zwitterion with the $\overset{+}{\mathrm{C}}(8)$ carbocationic center stabilized by a direct interaction with the Rh atom (vide supra). On the other hand, it may be regarded as a neutral complex with the Rh atom coordinated by η^2-olefinic and η^3-allyl moieties incorporated into the framework of the methylenenorbornadiene ligand.

The η^3-allyl coordination of the metal atom in IIIb and that in IX and X is distinctly non-symmetrical. The Rh–$\overset{+}{\mathrm{C}}(8)$ distance of 2.354(6) Å, involving the formal carbocationic center, is considerably longer than the two other Rh–C(allyl) bonds, Rh–C(2) 2.211(5) and Rh–C(3) 2.139(5) Å. It is noteworthy that the Rh–C(8) distance is significantly longer than the corresponding bond length of 2.27 Å in the structure of IX [17], which as was mentioned before is quite analogous to IIIb, the only difference being that the Cp ligand has been replaced by a dimethyl-*o*-dicarbollide moiety. At the same time the Rh–C(8) bond in complex IIIb, which is almost the same length as that in X [8], involves the carbocationic center additionally stabilized by the adjacent oxygen atom. It is probable that such peculiarities of the Rh–C distances in IIIb, IX and X are due to the different electronic and steric effects of the Cp and dimethyl-*o*-dicarbollide ligands.

The C(2)–C(3) bond in the η^3-coordinated allyl moiety 1.437(8) Å is elongated, as is usual [8,17], in comparison with the standard C=C double bond length (1.333 Å [19]). The C(2)–C(8) bond of 1.349(8) Å, however, is much shorter than the standard single $\mathrm{C}(sp^2)$–$\mathrm{C}(sp^2)$ bond 1.476 Å [19] and even shorter than the corresponding bonds in IX and X (1.38 [17] and 1.39 Å [8], respectively). The η^3-coordination of the allyl moiety brings about noticeable distortion of the planar-trigonal configuration of the C(2) atom: the C(8) atom is displaced from the C(1)C(2)C(3)C(4) plane towards the metal atom, with the C(2)–C(8) vector being inclined by 20.4° to this plane.

The η^2-coordinated C(5)=C(6) olefinic moiety of the norbornadiene ligand forms much weaker Rh–C bonds in IIIb than in IX and X. This weakening is reflected both in the longer Rh–C(5) 2.215(5) and Rh–C(6) 2.247(5) Å bonds and in the shorter C(5)=C(6) double bond 1.365(7) Å as compared with the corresponding parameters found in IX and X (both Rh–C 2.18, C=C 1.39 and 1.38 Å in IX and X, respectively).

All other geometric characteristics of methylenenorbornadiene ligand are normal; the C–C bond lengths span the range 1.513–1.531 Å, bond angles in the strained bicyclic framework differ significantly from ideal values. Surprisingly C(sp^3)–C(sp^3) and C(sp^2)–C(sp^3) bond lengths in norbornadienyl ligands in IIIb as well as in IX and X are almost equal.

The geometry of dimethyl-*o*-dicarbollide ligand is normal, the C–C distance is equal to 1.637(6) Å, the C–B and B–B edges are in the ranges 1.698–1.759 and 1.713–1.855 Å, respectively. The C_2B_3 pentagonal face that coordinates the Rh atom has a flattened envelope conformation, the folding angle along the B(4)...B(7) line is 4.5°. The C(01)–C(13) and C(02)–C(14) bonds are inclined to the C_2B_3-plane by 23.1 and 18.4° respectively. The Rh–C 2.256(4), 2.281(4) Å, and Rh–B 2.153(5), 2.218(5) and 2.226(6) Å, distances are close to the corresponding bonds found in other *o*-dicarbollide rhodium complexes, cf. average distances 2.26 Å for Rh–C and 2.20 Å for Rh–B in the structure of [closo-3,3-(η^1,η^2-norbornenyl)-1,2-Me_2-3,1,2-$RhC_2B_9H_9$] with an agostic hydrogen atom [4].

Experimental

^1H NMR spectra were recorded with a Bruker WP-200-SY spectrometer with TMS as internal standard. ^{13}C NMR spectra * were recorded with a Bruker SXP-200 spectrometer. The IR spectra were measured with a UR-20 spectrometer in KBr pellets; the mass spectra were recorded with an AEI-MS-30 spectrometer (ionization energy of 70 eV).

The closo-bis(triphenylphosphine)hydridorhodacarboranes used in this work were prepared by published procedures [20].

Preparation of μ-halide dimeric complexes IVa, IVb

A mixture of freshly distilled 2-(hydroxymethyl)norbornadiene (0.1 g, 0.83 mmol) and $[(C_8H_{14})_2RhCl]_2$ (0.5 g, 0.69 mmol) [21] in 20 ml of hexane was stirred for 1.5 h at room temperature. The pale-yellow residue was filtered, washed with hexane and dried in vacuo to give IVa that was used in the following reactions without further purification. Yield of IVa 0.31 g, 0.59 mmol, 86%; found: C, 37.74; H, 4.14; Cl, 12.9. $C_{16}H_{20}Cl_2O_2Rh_2$ calc.: C, 36.85; H, 3.84; Cl, 13.63%. ^1H NMR (CD_2Cl_2): 4.14–4.00 (m,2,H(5,6)), 4.08(d,1,J_{AB} 14.3 Hz,H(8_A)), 3.80(d,1,J_{BA} 14.1 Hz,H(8_B)); 3.76(m,3,H(1,3,4)), 2.74(s.br,1,OH), 1.29(m,2,H(7α,β)).

The same procedure was used to make complex IVb. Yield 92%; found: C, 39.77; H, 4.07; Cl, 11.71. $C_{20}H_{24}Cl_2O_4Rh_2$ calc.: C, 39.67; H, 3.97; Cl, 11.7%. ^1H NMR (CD_2Cl_2): 4.83 (d,1,J_{AB} 12.3 Hz,H(8_A), 4.08(d,1,J_{BA} 12.2 Hz,H(8_B)), 4.07(m,2,H(5,6)), 3.83(m,1,H(I(4))), 3.81(m,1,H(3)), 3.75(m,1,H(4(1))), 2.07(s,3,Me), 1.25(m,2,H($7_{\alpha,\beta}$)).

General method for synthesis of closo-rhodacarboranes IIIa–IIId by ligand exchange reactions

A. [Nido-7-Me-7,8-$C_2B_9H_{11}$]K (0.19 g, 1.0 mmol) was added to a suspension of i-PrONa prepared from 0.192 g (8 mmol) NaH (50% dispersion in Nujol mull) and 4

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Table 5

Atomic coordinates ($\times 10^4$, for Rh$\times 10^5$, for H$\times 10^3$) and temperature factors (isotropic for H atoms, equivalent isotropic for non-hydrogen atoms)

Atom	x	y	z	B(Å^2)	Atom	x	y	z	B(Å^2)
C(01)	4117(3)	2881(3)	3052(3)	2.7(1)	H(5)	465(3)	435(3)	356(3)	4(1)
C(02)	4658(3)	2041(3)	2572(3)	3.0(1)	H(6)	485(3)	341(3)	178(3)	5(1)
Rh(3)	38523(2)	15019(2)	37186(2)	2.651(7)	H(7)	544(3)	75(3)	316(3)	5(1)
B(4)	4309(3)	2824(3)	4170(3)	2.6(1)	H(8)	520(3)	157(3)	531(3)	4(1)
B(5)	4852(4)	3654(4)	3498(4)	3.9(2)	H(9)	573(3)	335(3)	477(3)	2.9(9)
B(6)	5058(4)	3175(4)	2487(4)	3.8(1)	H(10)	655(3)	378(3)	316(3)	5(1)
B(7)	5278(4)	1373(3)	3312(4)	3.5(1)	H(11)	614(3)	202(3)	208(3)	3.3(9)
B(8)	5122(3)	1885(4)	4380(3)	3.1(1)	H(12)	667(3)	197(3)	391(3)	4(1)
B(9)	5464(4)	3053(4)	4305(3)	3.4(1)	H(131)	286(8)	344(6)	339(8)	17(4)
B(10)	5930(4)	3249(4)	3245(5)	4.3(2)	H(132)	333(3)	370(3)	230(3)	4(1)
B(11)	5778(4)	2229(4)	2622(4)	3.9(1)	H(133)	291(3)	286(3)	231(3)	5(3)
B(12)	6070(3)	2165(4)	3739(4)	3.8(1)	H(141)	469(3)	201(3)	127(3)	5(1)
C(13)	3248(3)	3263(4)	2679(4)	4.2(1)	H(142)	379(3)	165(3)	175(4)	5(1)
C(14)	4347(4)	1695(4)	1660(4)	5.1(2)	H(143)	442(4)	119(4)	152(4)	6(1)
C(1)	2204(3)	570(4)	4219(4)	4.5(1)	H(1)	162(4)	61(4)	401(4)	7(1)
C(2)	2966(4)	289(3)	3620(3)	4.3(1)	H(3)	424(3)	−29(3)	399(3)	4(1)
C(3)	3718(4)	123(3)	4188(4)	4.6(2)	H(4)	373(3)	13(4)	549(3)	6(1)
C(4)	3363(4)	298(4)	5118(4)	5.1(2)	H(5)	364(3)	183(3)	539(3)	5(1)
C(5)	3253(4)	1342(3)	5045(3)	4.2(1)	H(6)	234(3)	219(3)	441(2)	2.6(8)
C(6)	2562(3)	1506(3)	4479(3)	3.8(1)	H(71)	238(3)	−68(4)	494(3)	5(1)
C(7)	2386(4)	−5(4)	5036(4)	5.2(2)	H(72)	206(2)	13(3)	546(2)	2.8(9)
C(8)	3048(4)	530(4)	2765(4)	5.8(2)	H(81)	361	38	239	–
H(4)	382(3)	316(4)	460(3)	4(1)	H(82)	247	57	137	–

ml of absolute i-PrOH under Ar. The mixture was stirred for 1 h at room temperature, then 0.3 g (0.93 mmol) of complex I was added to the mixture, and it was stirred for another 0.5 h. The solvent was evaporated in vacuo, 10 ml of absolute ether and several drops of 70% HPF_6 were added to the residue. The ether layer was removed, the residue was again extracted with acidified ether (2 × 10 ml). The ether extracts were combined, washed with a small amount of water, dried and evaporated. The crude product was purified by chromatography on a silica gel column using ether as eluent. The resulting complex IIIc was recrystallized pure from CH_2Cl_2 hexane mixture as red crystals. Yield of IIIc 0.23 g (0.63 mmol, 66%); found: C, 37.19; H, 6.04; B, 27.47. $C_{11}H_{22}B_9Rh$ calc.: C, 37.26; H, 6.25; B, 27.47%. IR spectrum: ν(B–H) 2542 cm^{-1}. Mass-spectrum: M^+ (for ^{11}B): 356.

The rhodacarborane IIIa was obtained as pale-orange crystals from complex I and IIa in the same manner (58% yield). Found: C, 35.31; H, 6.03. $C_{10}H_{20}B_9Rh$ calc.: C, 35.78; H, 5.92%. IR spectrum: ν(B–H) 2516–2560 cm^{-1}. Mass spectrum: M^+ (for ^{11}B) 342. Complex I and IIb gave IIIb as dark red crystals, in 45% yield. Found: C, 39.27; H, 6.31. $C_{12}H_{24}B_9Rh$ calc.: C, 39.10; H, 6.56%. IR spectrum: ν(B–H) 2512–2556 cm^{-1}. Mass spectrum: M^+ (for ^{11}B) 370. Complex I and IId gave rhodacarborane IIId as orange-dark red crystals in 62% yield. Found: C, 46.34; H, 6.00; B, 23.23. $C_{16}H_{24}B_9Rh$ calc.: C, 46.12; H, 5.80; B, 23.37%. IR spectrum: ν(B–H) 2330–2540 cm^{-1}. Mass spectrum: M^+ (for ^{11}B) 418.

B. [Nido-7,8-$C_2B_9H_{12}$]K (0.165 g, 0.96 mmol) was added to a suspension of i-PrONa prepared from 50% NaH (0.18 g, 7.7 mmol) dispersed in Nujol mull and 3.5 ml i-PrOH under Ar. The mixture was stirred for 1 h at room temperature. Complex IVa (0.25 g, 0.48 mmol) was then added, the mixture was stirred for another 0.5 h, and then evaporated to dryness in vacuo. An acidified ether was added to the residue and rhodacarborane IIIa was isolated after treatment according to procedure A. Yield of IIIa 0.14 g, (0.41 mmol, 86%). ^1H NMR and IR spectra of the complex are similar with those of IIIa which was prepared by method A. The same procedure was employed for making IIIb from complex IVb and IIb. Yield of (IIIb) 94%. Reaction of complex IVa with IIb also gives IIIb in 83% yield.

General procedure for preparation of closo-rhodacarboranes (IIIa, IIIc) and VIII from the closo-bis(triphenylphosphine)hydridorhodacarboranes and 2-(hydroxymethyl)-norbornadiene

A mixture of complex VIIa (0.3 g, 0.46 mmol) and freshly distilled 2-(hydroxymethyl)norbornadiene (0.06 g, 0.49 mmol) in 30 ml absolute benzene was heated at 65–70 °C with stirring for 5 h. The solvent was evaporated off, and the residue was chromatographed on a silicagel column using an ether/hexane mixture (5/1) as eluent. Yield of IIIa 0.13 g (0.39 mmol, 85%). Found: C, 35.46; H, 5.81%. The IR and mass spectral data are the same as those of the IIIa made by methods A and B. Complex IIIc (yield 80%) is synthesized from VIIb by the same procedure. Complex VIII (yield 69%) was obtained similarly from closo-2,2-$(PPh_3)_2$-2-H-2,1,7-$RhC_2B_9H_{11}$ and 2-(hydroxymethyl)norbornadiene. Found: C, 5.83; H, 35.17. $C_{10}H_{20}B_9Rh$ calc.: C, 5.92; H, 35.28%. IR spectrum: ν(B–H) 2520 cm^{-1}.

X-ray diffraction study

Crystals of IIIb are orthorhombic; at +20 °C *a* 14.945(1) *b* 14.547(1), *c* 15.169(1) Å, $V = 3297.8$ Å^3, $D_{calc.}$ 1.485 g cm^{-3}, $Z = 8$, space group *Pbca*. Unit cell parameters and intensities of 2351 unique reflections, with $F^2 \geqslant 3\sigma$ were measured with a Hilger & Watts four-circle automatic diffractometer (+20 °C, λ Mo-K_α, graphite monochromator, $\theta/2\theta$-scan, $\theta \leqslant 30°$).

The structure was solved by direct methods and refined first isotropically, then anisotropically by means of the full-matrix least squares. All H atoms were directly located in the difference Fourier synthesis and included in the final refinement in the isotropic approximation (with the exception of H(81) and H(82) atoms which rendered the refinement unstable and therefore were taken to be fixed contributions with B_{iso} 5 Å^2). The final R-factor is 0.035, weighted R_w-factor is 0.047. All calculations were carried out with an Eclipse S/200 computer using the INEXTL programmes [22]. Atomic coordinates and their temperature factors are listed in Table 5.

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