Brief Communications

Synthesis of binuclear rhodacarboranes from 1,4- and 1,3-$C_6H_4(CH_2$-9-$C_2H_2B_9H_9$-7,8-*nido*$]_2^{2-}$ dianions and $(Ph_3P)_3RhCl$

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1,4- and 1,3-$C_6H_4(CH_2$-9-$C_2H_2B_9H_9$-7,8-*nido*$]_2^{2-}$ dianions obtained from *nido*-7,8-dicarbollide ion and 1,4-bis(bromomethyl)- and 1,3-bis(bromomethyl)benzenes react with $(Ph_3P)_3RhCl$ to give binuclear rhodacarboranes, 1,4- and 1,3-[3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{10}$-4-$CH_2]_2C_6H_4$.

Key words: *nido*-7,8-dicarbollide ion, 1,4- and 1,3-bis(bromomethyl)benzenes, binuclear rhodacarboranes.

Binuclear complexes of transition metals are attracting much attention as effective catalysts of organic reactions.[1] Effective catalysts of hydrosilylation of olefins, acetylenes, and ketones, of isomerization and hydrogenation of olefins, and dehydrochlorination of alkanes were found in the series of mononuclear rhodacarboranes of the $(Ph_3P)_2RhHC_2RR'B_9H_9$ type, both free and immobilized on polymeric supports.[2]

Studies on binuclear rhodacarboranes, which contain two π-dicarbollyl ligands linked by C—C or C—B σ-bonds, are virtually nonexistent. A short communication deals with the synthesis of binuclear rhodacarborane $[(Et_3P)RhC_2B_9H_{10}]_2$[3] from 1,1-bisdicarbollide ion and $Rh(cod)(PEt_3)Cl$. Two π-dicarbollyl ligands in this structure are linked through the carbon atoms of the pentagonal plane of the ligand.

In the present work, we describe the synthesis of two other binuclear rhodacarboranes, in which two π-dicarbollyl ligands are linked through the boron atoms of the pentagonal plane of the ligand by *para*- and *meta*-xylyl groups.

The binuclear rhodacarboranes were obtained by a two-stage method. In the first stage, cesium 1,4-phenylene-bis(9-methylene-*nido*-7,8-dicarbaundecaborate) (**4**) and 1,3-phenylene-bis(9-methylene-*nido*-7,8-dicarbaundecaborate) (**5**) were synthesized from *nido*-7,8-dicarbollide ion (**3**) and 1,4-$(CH_2Br)_2C_6H_4$ (**1**) and 1,3-$(CH_2Br)_2C_6H_4$ (**2**), respectively (Scheme 1).

The reaction of the *nido*-7,8-dicarbollide ion with organic halides, depending on conditions, can lead either to a "normal" product of alkylation at the B(9) atom localized in the pentagonal plane of the *nido*-7,8-dicarbaundecaborate anion or is accompanied by a multistep rearrangement resulting in the *nido*-7,9-dicarbaundecaborate anion, and the alkylation proceeds at the B(8) atom, which is also localized in the pentagonal plane, or a mixture of both the isomeric products is formed.[4,5]

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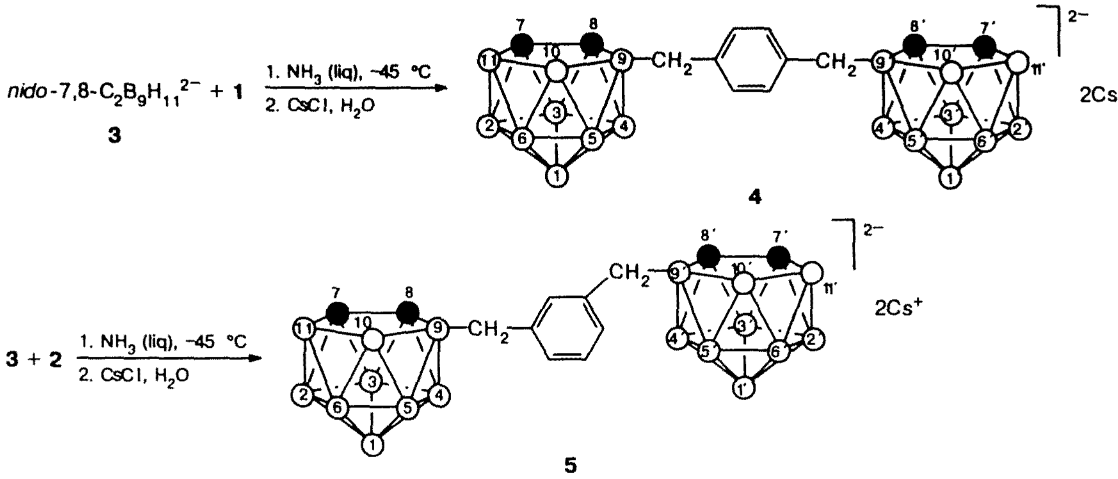
Scheme 1



Alkylation of dianion **3** with α,ω-organyl dihalides has not been hitherto studied. It follows from the abovesaid that the interaction of dianion **3** with 1,4- or 1,3-bis(bromomethyl)benzene (**1** or **2**) can lead to one of three isomeric compounds containing either two *nido*-7,8-dicarbaundecaborate anions or two *nido*-7,9-dicarbaundecaborate anions, or one *nido*-7,8-dicarbaundecaborate and one *nido*-7,9-dicarbaundecaborate anion, or to a mixture of these compounds.

Cesium salts **4** and **5** containing two *nido*-7,8-dicarbaundecaborate groups were obtained in individual form under conditions we found in the reaction of compound **3** with dibromides **1** and **2**. The structure of these dianions was confirmed by ^{11}B NMR spectra. The spectral data are given in Table 1, from which it follows unambiguously that the compounds obtained are the derivatives of the *nido*-7,8-dicarbaundecaborate anion. For comparison, Table 1 also contains the ^{11}B NMR spectral data of the known[5] compound 7,8-Me_2-9-$PhCH_2$-7,8-$C_2B_9H_9^-$. The highfield region, where the B(10) and B(1) atoms resonate, is characteristic of the ^{11}B NMR spectra of compounds **4** and **5**. The chemical shifts of the B(10) and B(1) atoms in the spectra of compounds **4** and **5** virtually do not differ from those in the spectrum of the starting compound **3**. When the proton at the B(9) atom is substituted by the CH_2 group, a signal of the B(9) atom is shifted downfield by 10—11 ppm, other chemical shifts in the spectrum remaining unchanged. Thus, one can conclude that the substitution in compound **3** occurs selectively at the boron atom of the open plane at the B(9) position.

In the second stage, binuclear complexes 1,4- and 1,3-[3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{10}$-4-CH_2]$_2C_6H_4$, **6** and **7**, respectively, are formed in the interaction of cesium salts **4** and **5** with $(Ph_3P)_3RhCl$ (Scheme 2).

Complexes **6** and **7** are yellow crystals, stable in air. According to TLC data, they are individual compounds.

Experimental

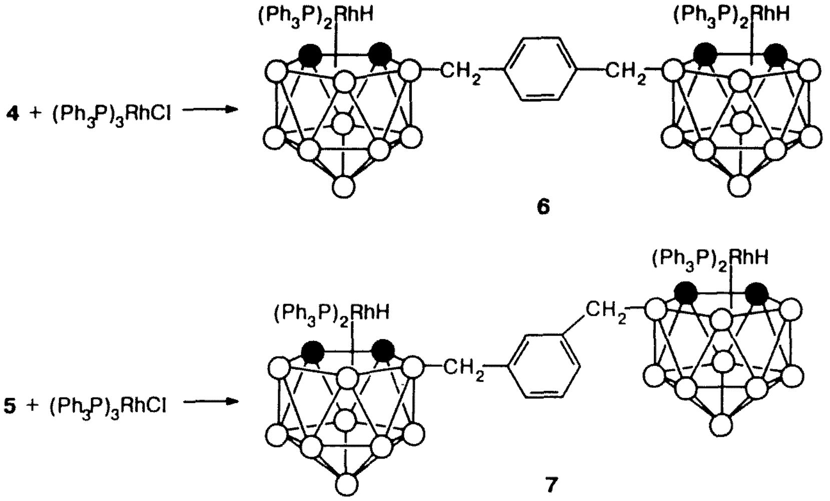
^{11}B NMR spectra were recorded on a Bruker WP-200 SY instrument (64.2 MHz). The starting compounds, namely, potassium 7,8-dicarba-*nido*-undecaborate[6] and 1,4-bis(bromo-

Table 1. The parameters of the ^{11}B NMR spectra of 7,8-Me_2-9-$PhCH_2$-7,8-$C_2B_9H_9^-$ (**8**), 1,4-$C_6H_4(CH_2$-9-$C_2H_2B_9H_9$-7,8-*nido*$)_2^{2-}$ (**4**) and 1,3-$C_6H_4(CH_2$-9-$C_2H_2B_9H_9$-7,8-*nido*$)_2^{2-}$ (**5**) in acetone

Compound	δ(^{11}B)	$J_{^{11}B-^{1}H}$ /Hz	Relative intensity	Attribution
8*	0.8	0	1	B(9)
	−8.5	143	2	B(11), B(3)
	−16.8	150	3	B(5), B(6), B(4)
	−20.4	152	1	B(2)
	−33.9	132	1	B(10)
	−36.9	149	1	B(1)
4	−0.143 s	0	1	B(9), B(9′)
	−10.25 d	136	1	B(11), B(11′)
	−15.60 d	128	4	B(2), B(2′)
	−17.57 d	132		B(3), B(3′)
	−17.57 d	132		B(5), B(5′)
	−19.30 d	150		B(6), B(6′)
	−26.04 d	150	1	B(4), B(4′)
	−33.36 dd	132 and 54	1	B(10), B(10′)
	−37.89 d	136	1	B(1), B(1′)
5	−0.18 s	0	1	B(9), B(9′)
	−11.10 d	138	1	B(11), B(11′)
	−16.42 d	130	4	B(2), B(2′)
	−17.82 d	136		B(3), B(3′)
	−17.82 d	136		B(5), B(5′)
	−20.21 d	150		B(6), B(6′)
	−27.01 d	150	1	B(4), B(4′)
	−33.91 dd	136 and 55	1	B(10), B(10′)
	−37.85 d	148	1	B(1), B(1′)

* See Ref. 5.

Scheme 2



methyl)- and 1,3-bis(bromomethyl)benzenes[7], were obtained according to the known procedures.

Cesium 1,4-phenylene-bis(9-methylene-*nido*-7,8-dicarbaundecaborate) (4). Metallic Na (0.73 g, 0.032 g-at.) was added to a solution of $C_2B_9H_{12}K$ (5 g, 0.03 mol) in 70 mL of liquid NH_3 at −45 °C until a blue color persisted. A solution of compound **1** (4 g, 0.015 mol) in 20 mL of THF was added with stirring to the reaction mixture. Stirring was continued for 2.5 h with simultaneous evaporation of ammonia. Hexane (30 mL), then water (50 mL) were added, the organic layer was separated, and an aqueous solution of CsCl was added to the aqueous layer. The precipitate was filtered off and recrystallized from water. Compound **4** (6.8 g, 80 %) was obtained, m.p. 330—332 °C. Found (%): C, 22.70; H, 4.93; B, 30.69. $C_{12}H_{30}B_{18}Cs_2$. Calculated (%): C, 22.65; H, 4.76; B, 30.67.

Cesium 1,3-phenylene-bis(9-methylene-*nido*-7,8-dicarbaundecaborate) (5). Compound **5** (7.1 g, 82 %) was obtained from $C_2B_9H_{12}K$ (5 g, 0.03 mol), metallic Na (0.73 g, 0.032 g-at.), and compound **2** (4 g, 0.015 mol) as described above. M.p. 236—238 °C. Found (%): C, 22.51; H, 4.78. $C_{12}H_{30}B_{18}Cs_2$. Calculated (%): C, 22.65; H, 4.76.

The spectral data of compounds **4** and **5** are summarized in Table 1.

1,4-Phenylene-bis[3,3-bis(triphenylphosphine)-3-hydride-4-methylene-3,1,2-rhodacarborane] (6). $(Ph_3P)_3RhCl$ (5.8 g, 6.2 mmol) was added to a solution of compound **4** (1.9 g, 0.003 mol) in 10 mL of EtOH, and the mixture was refluxed for 3 h. The color of the solution changed from dark red to light yellow. A yellow precipitate formed was filtered off, washed with water and alcohol, and recrystallized from CH_2Cl_2. Compound **6** (4.0 g, 85 %) was obtained, decomp. temp. 240 °C. Found (%): C, 62.07; H, 6.12; B, 11.75; Rh, 13.37. $C_{84}H_{90}B_{18}P_4Rh_2$. Calculated (%): C, 62.10; H, 5.59; B, 11.88; Rh, 12.66.

1,3-Phenylene-bis[3,3-bis(triphenylphosphine)-3-hydride-4-methylene-3,1,2-rhodacarborane] (7). Compound **7** (4.1 g, 87 %) was obtained from compound **5** (1.9 g, 3 mmol) and $(Ph_3P)_3RhCl$ (5.8 g, 6.2 mmol) in 10 mL of anhydrous EtOH analogously. Found (%): C, 61.18; H, 5.64; B, 11.98; Rh, 12.46. $C_{84}H_{90}B_{18}P_4Rh_2$. Calculated (%): C, 62.10; H, 5.59; B, 11.88; Rh, 12.66.

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