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Synthesis of *closo*-3,3-(η^3,η^2-tricyclo[5.2.1.0^{2,6}]deca-4,8-diene-3-yl)-1-(hydroxymethyl)-3,2,1-dicarbollylrhodium and the crystal structure of its dimer with the O—H...Rh bond

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Protonation of the [*closo*-3,3-(η^4-$C_{10}H_{12}$)-1-(CH_2OH)-3,1,2-$RhC_2B_9H_{10}$]$^-$ PPN^+ ($C_{10}H_{12}$ — dicyclopentadiene, PPN^+ — bis(triphenylphosphine)iminium cation) at the ethylene bond of the norbornene moiety yields the neutral *closo*-3,3,3-(η-$C_{10}H_{13}$)-1-(CH_2OH)-3,1,2-$RhC_2B_9H_{10}$ with an agostic C—H...Rh bond. On prolonged storage in EtOH, the latter complex is converted into *closo*-3,3-($\eta^{3,2}$-$C_{10}H_{11}$)-1-(CH_2OH)-3,1,2-$RhC_2B_9H_{10}$ with π-allylolefinic type coordination. Its crystal structure as dimeric aggregates with O—H...O and O—H...Rh bonds was determined by X-ray diffraction.

Key words: rhodacarboranes, dicyclopentadiene, O—H...Rh bond, X-ray structure analysis.

The majority of metallacarboranes of transition metals with five-electron ligands belong to the group of η^5-alkylcyclopentadienyl[1] and η^5-indenyl[2] π-complexes. Known examples of (π-dienyl)metallacarboranes with η^3,η^2-allylolefinic type bonds are ruther scanty so far and limited to complexes with either endocyclic η^3-allylic and exocyclic η^2-olefinic[3] or, *vice versa*, endocyclic η^2-olefinic and exocyclic η^3-allylic metal—hydrocarbon ligand coordination.[4] In the present work, we report the first example of *closo*-rhodacarborane, in which the rhodium atom is coordinated by the tricyclic dienyl ligand *via* endocyclic η^3,η^2-allylolefinic binding.

We have found that the anionic complex [*closo*-3,3-(η^4-$C_{10}H_{12}$)-1-(CH_2OH)-3,1,2-$RhC_2B_9H_{10}$]$^-$$PPN^+$ [**1**, $C_{10}H_{12}$ — dicyclopentadiene, PPN^+ — bis(triphenylphosphine)iminium cation] obtained from the dicarbollide-dianion [*nido*-7-(CH_2OH)-7,8-$C_2B_9H_{10}$]$^{2-}$ and the [(η^4-$C_{10}H_{12}$)RhCl]$_2$ dimer under the conditions

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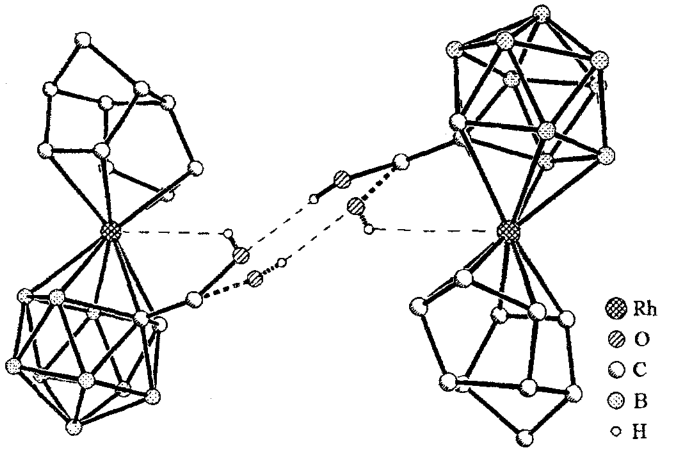
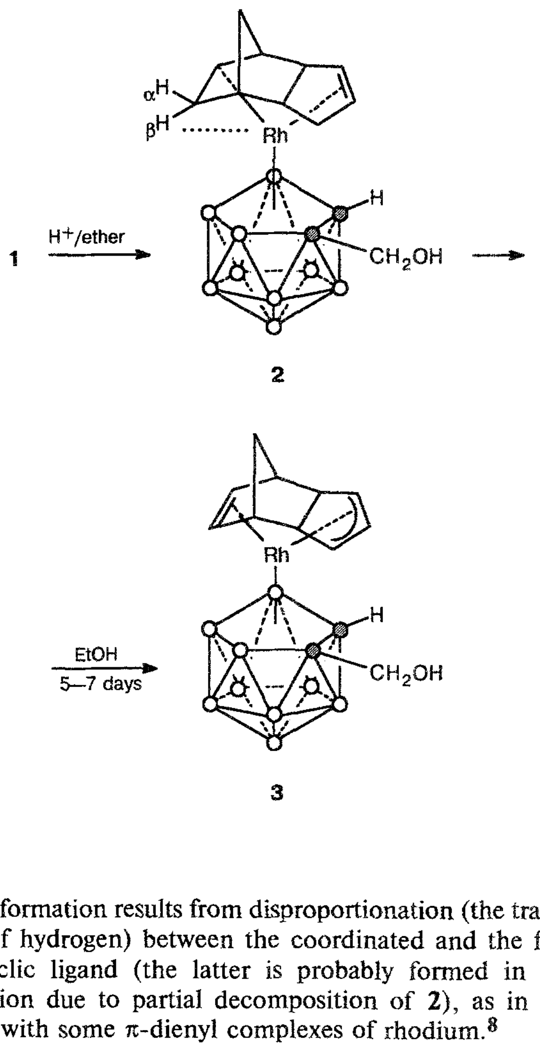


Fig. 1. Structure of the dimeric H-bonded associate in the crystal of 3.

Scheme 1



described earlier,[5] was protonated in ether at the double bond of the norbornene moiety of the dicyclopentadienyl ligand by the action of acids (70% HPF_6 or MeCOOH) to form neutral *closo*-3,3,3-(η-$C_{10}H_{13}$)-1-(CH_2OH)-3,1,2-$RhC_2B_9H_{10}$ (**2**) in a 62 % yield (Scheme 1). In complex **2**, there is an agostic C—H···Rh bond, according to the ^1H NMR (in CD_2Cl_2) data [δ: 0.62 (qm, α-H); −2.8 (br.d, β-H, J_{gem}=19.6 Hz)] and the X-ray analysis.* It is noteworthy, that under much milder conditions, *viz.*, by treatment of **1** with methylene chloride on a silica gel column, **2** is also formed in 82% yield. Although zwitter-ionic metallacarboranes of the *closo*-3,3-(η^4-diene)-1-CH_2^+-3,1,2-$RhC_2B_9H_{10}$ type are known,[6] the reaction conditions used do not cause the protonation at the CH_2OH moiety of the π-dicarbollylic ligand in complex **1** [for **2**: ν(OH) 3491 and 3417cm^{-1} (KBr); δ(CD_2Cl_2): 3.91 (br.t, OH)], which points to the high regioselectivity of the process.

It was found that when an ethanolic solution ($2 \cdot 10^{-3}$*M*) of **2** was storaged at 22°C for 5—7 days a new metallacarborane complex with an allyl-olefinic metal—ligand bond, *closo*-3,3-$\eta^{3,2}$-$C_{10}H_{11}$)-1-(CH_2OH)-3,1,2-$RhC_2B_9H_{10}$](**3**), was formed in 34% yield. In the ^1H NMR spectrum of complex **3** (in CD_2Cl_2) the signals of olefinic and allylic fragments typical of this type π-complexes[7] are present. Because of the absence of symmetry in the monosubstituted π-dicarbollyl ligand, these signals are displayed as distinct multiplets at δ 6.97 and 6.86 [H(8) and H(9)] and 6.45, 6.36, and 5.35 [H(3), H(5), and H(4), respectively].

Although the mechanism of the dehydrogenation of compound **2** into **3** is not established, we suggest the transformation results from disproportionation (the transfer of hydrogen) between the coordinated and the free tricyclic ligand (the latter is probably formed in the solution due to partial decomposition of **2**), as in the case with some π-dienyl complexes of rhodium.[8]

The X-ray analysis [Mo-Kα irradiation, $P\bar{1}$ space group, a=7.519(1), b=9.160(1), c=12.850(1) Å, α=93.68(1), β=98.66(1), γ=104.06(1)°, Z=2 ($C_{13}H_{24}B_9ORh$), R=0.0214 of 3652 reflexes with $F^2 \geq 3\sigma(F^2)$] demonstrates that the crystals of **3** are constructed of H-bonded centrosymmetrical dimeric associates (Fig. 1). An interesting example of disorder of the OH-group over two possible positions was found in this crystal. It is caused by the necessity of the distribution of the two active hydrogen atoms between three possible H-bonds: two OH···Rh type [O—H 0.54(5), H···Rh 2.98(5), O···Rh 3.315(2) Å, O—H···Rh angle equal to 125(3)°], and one O—H···O type. The study of the mechanisms of the formation of complex **3** and the H-bonds in complexes **2** and **3** using IR spectroscopy is under investigation.

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* X-Ray analysis data for complex **2** will be published in a full report in cooperation with Dr. C. B. Knobler and Prof. M. F. Hawthorne (California University, USA).

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Synthesis of bis(2-cyanoacrylates) from 2-cyanoacryloyl chloride and 2-butene- and 2-butyne-1,4-diols

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The interaction of 2-cyanoacryloyl chloride with unsaturated 1,4-diols leads to bis(2-cyanoacrylates) with a double or triple C—C bond.

Key words: bis(2-cyanoacrylates), 2-cyanoacryloyl chloride, unsaturated diols.

Bis(2-cyanoacrylates) (BCAs) used as cross-linking agents for cold-setting glues[1] are now synthesized by two main methods, *viz.*, by a laborious five-step synthesis[1] or by the direct esterification of 2-cyanoacrylic acid with alkane-1,6- or alkane-1,8-diols in the presence of hydroquinone and *p*-toluenesulfonic acid with continious azeotropic distillation with benzene of the water thus formed.[2] The latter of these methods was later found to be inefficient for the synthesis of BCAs of unsaturated 1,4-diols. A far more useful route for the preparative synthesis of BCAs appeared to be the method that we developed earlier for the preparation of thiolic and oxygen esters of 2-cyanoacrylic acid. This method was based on the interaction of 2-cyanoacryloyl chloride[3] with lead thiolates[4] or alcohols,[5] respectively. Using this approach with somewhat modified reaction conditions, we obtained the BCAs of 2-butene- and 2-butyne-1,4-diols in moderate yields (Scheme 1).

Under the experimental conditions described earlier,[2] the BCAs obtained from unsaturated diols undergo considerable polymerization. The structures of the BCAs in question follow from their NMR spectra as well as from the identity of their melting points with those present in the literature[1] for the respective compounds.

Experimental

2-Butene-1,4-diol bis(2-cyanoacrylate) (1a). 2-Butene-1,4-diol (1.5 g, 0.017 mol) and toluene (50 mL) were added to a solution of 2-cyanoacryloyl chloride obtained from 2-cyanoacrylic acid (4.2 g, 0.04 mol) by the known method.[3] The mixture was stirred for 3—4 h at 20 °C, two thirds of the solvent was removed *in vacuo*, and the residue was poured into hot heptane (300 mL) saturated with SO_2. The solution was allowed to stay in a freezer overnight, then the precipitate was filtered off and recrystallized from octane to afford **1a** in 42 % yield. M.p. 105—107 °C (*cf.* Ref. 1: m.p. 106—108 °C).

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