SYNTHESIS OF NEW POLYMERIC RHODIUM CARBORANE COMPLEXES SERVING AS HOMOGENEOUS CATALYSTS FOR THE HYDROSILYLATION OF 1-HEXENE

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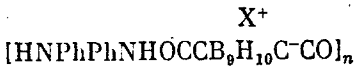
The coordination of $Rh(PPh_3)_3Cl$ on a dicarbaundecaborate polyamide gives a new polymeric rhodium hydride complex with catalytic activity in the hydrosilylation of 1-hexene by triethylsilane. The rhodium derivative of 7,9-dicarba-nido-undecaborate(11)-7,9-dicarboxyanilide was synthesized as a model of the monomeric unit. Co^{III} and Ni^{IV} bis(dicarbollyl) complexes also display catalytic activity in hydrosilylation reactions.

Rhodium carborane hydride complexes and their polymer analogs display high catalytic activity in various reactions [1-3].

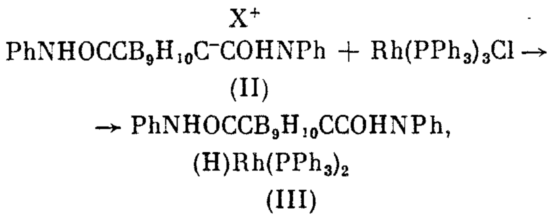
In the present work, we obtained a rhodium carborane hydride polyamide complex. The polyamide with dicarbaundecaborate fragments in the major chain obtained in our previous work [4] was used as the polyligand.



$$\overset{X^+}{[HNPhPhNHOCCB_9H_{10}C^-CO]_n} \qquad (I)$$

where $X^+ - K^+$, $N^+(C_4B_9)_4$.

This ligand was selected intentionally since the open pentagonal plane of the dicarbaundecaborate anion in polymer (I), which is capable of η^3-coordination with transition metals, facilitates direct conversion to metallopolymers. In order to study the possibility of the coordination of transition metal ions with a dicarbaundecaborate anion containing amide substituents at the carbon atoms of the nido polyhedron, we investigated the reaction of $Rh(PPh_3)_3Cl$ and 7,9-dicarba-nido-undecaborata(11)-7,9-dicarboxyanilide (II), which is a model of the monomeric unit in (I).



$$\underset{(II)}{\overset{X^+}{PhNHOCCB_9H_{10}C^-COHNPh}} + Rh(PPh_3)_3Cl \rightarrow$$

$$\rightarrow \underset{(III)}{\underset{(H)Rh(PPh_3)_2}{PhNHOCCB_9H_{10}CCOHNPh,}}$$

where $X^+ - K^+$, C_s^+, $N^+(C_4H_9)_4$.

The reaction of (II) with $Rh(PPh_3)_3Cl$ was carried out in absolute ethanol or THF at reflux and was complete in 3-4 h. The yield of (III) depends on the X^+ counter-ion in (II) and ranges from 25 to 45%. Product (III) was characterized by IR spectroscopy and elemental analysis. Found: C, 61.57; H, 5.14; B, 10.05; P, 6.08%. Calculated for $C_{52}H_{53}B_9N_2O_2P_2Rh$: C, 61.59: H, 5.11; B, 9.75; P, 6.19%. The IR spectrum of the model compound has bands in the vicinity of 2070 cm^{-1} characteristic for M-H hydride bonds [1]. Furthermore, the spectra have a characteristic broad signal at 2580 cm^{-1} related to vibration of the B-H bonds in the polyhedron.

The coordination of polymer (I) with $Rh(PPh_3)_3Cl$ with limited solubility in THF was carried out in DMF in a dry argon stream at ~20°C since decomposition of the polymer occurs

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TABLE 1. Dependence of the Products of the Hydrosilylation of 1-Hexene by Triethylsilane (TES) on the Catalyst and Reaction Conditions

Catalytic system*	T, K	Time, h	Total yield, %	Product composition, % **	
				$CH_3(CH_2)_3CH{=}{=}CHSiEt_3$	$CH_3(CH_2)_5SiEt_3$
(III)	313	3	31	48	52
	413	2	35	8	92
(IV)	318	3	48	80	20
	413	2	45	43	57
(IV)+ $(C_2B_9H_{11})_2Ni$ ***	318	3	90	35	65
	413	2	95	18	82
(IV)+ $(C_2B_9H_{11})_2Co^-$	318	3	72	85	15
	413	2	91	87	13
$(C_2B_9H_{11})_2Ni$	318	3	0	0	0
	413	2	92	5	95
$(C_2B_9H_{11})_2Co^-$	318	3	0	0	0
	413	2	0	0	0

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*The 1-hexene/TES ratio was 5:1. N-Methylpyrrolidine was the solvent.

**The reaction mixture was characeterized by gas-liquid chromatography on an LKhM chromatograph using an SE-30 column.

***The concentration of $(C_2B_9H_{11})_2M$ (M = Co, Ni) was 10 mole % relative to TES.

in DMF at elevated temperatures [4]. The reaction time in this case was extended to 12 h. The yield of polymeric rhodium carborane hydride complex (IV) was 80%. Polymer (IV) was characterized similarly to complex (III) by IR spectroscopy and elemental analysis. The IR spectra of this polymer were identical to those of the model compound. Elemental analysis indicated ~2% rhodium content, which corresponds to coordination of the rhodium atom with each fifth unit of the dicarbaundecaborate polymer.

Polymer (IV) has good solubility in organic solvents such as N-methylpyrrolidine and DMF and gradually decomposes in the air. This behavior is apparently related to the instability of the uncoordinated dicarba-nido-undecaborate fragments of the polyamide since the rhodium carborane bond is strong [1]. In an inert atmosphere, (IV) may be stored for a long period. Both complexes (III) and (IV) were checked for catalytic activity in the hydrosilylation of 1-hexene by triethylsilane [5], which proceeds as follows:

$$CH_3(CH_2)_3CH = CH_2 + HSiEt_3 \xrightarrow{[Rh]} CH_2(CH_2)_3CH = \\ = CHSiEt_3 + CH_3(CH_2)_5SiEt_3.$$

Furthermore, Co^{III+} and Ni^{IV+} bis(dicarbollyl) complexes [6] were tested for the first time as catalysts and cocatalysts. The results for the catalytic activity of (III) and (IV) as well as of the cocatalysts are given in Table 1. The catalytic properties of (III) and (IV) differ significantly as seen in the ratio of the saturated and unsaturated reaction products and in the total yield of these products. The amount of unsaturated product in the reaction mixture is greater in the presence of (IV), while the amount of the saturated product is greater in the presence of (III). The total yield is greater in the case of polymer catalyst (IV). An increase in the temperature has a significant effect on the ratio of the hydrosilylation products with an increase in the yield of the saturated product.

The total yield was almost doubled when the nickel bis(dicarbollyl) complex was used as a cocatalyst in conjunction with (IV) and the content of the saturated hydrosilylation product was increased. These effects are especially evident upon raising the reaction temperature to 140°C. The bis(dicarbollyl)cobalt anion does not affect the ratio of the reaction products but enhances their total yield.

We should note that while $[(C_2B_9H_{11})_2Co]^-Cs^+$ does not display independent activity in the hydrosilylation reaction, the reaction proceeds in good yield and enhanced selectivity in the presence of $(C_2B_9H_{11})_2Ni$.

Thus, the newly synthesized rhodium carborane hydride complexes derived from 7,9-dicarba-nido-undecaborate(11)-7,9-dicarboxyanilide and a dicarba-nido-undecarborate polyamide are highly active homogeneous catalysts for the hydrosilylation of 1-hexene by triethylsilane.

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A SIMPLE SYNTHESIS FOR 2-ACETONYLCYCLODODECANONE

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A simple method is proposed for the alkylation of cyclododecanone by propargyl halides under phase transfer catalysis conditions with the formation of 2-propargylcyclododecanone. The hydration of 2-propargylcyclododecanone upon catalysis by mercury compounds leads to either 14-methyl-13-oxabicyclo[10.3.0]-pentadeca-1(12),14-diene or 2-acetonylcyclododecanone depending on the reaction conditions. Both these compounds are also readily obtained from 2-(2-chloropropen-2-yl)cyclododecanone which readily forms upon the alkylation of cyclododecanone by 1,2-dichloropropene under phase transfer catalysis conditions.

2-Acetonylcyclododecanone (I) is an important intermediate in the preparative synthesis of cyclopentadecanone (exaltone) and 3-methylcyclopentadecanone (muscone), which are valuable fragrances [1]. A number of syntheses have been described for (I) from cyclododecanone (II) [1-6]. Ketone (II) was found to be smoothly alkylated by alkyl halides [7] and allyl halides [8] under phase transfer catalysis conditions to give 2-alkyl- or 2-allylcyclododecanones, respectively. In the present work, we showed that ketone (II) is readily alkylated by propargyl bromide or chloride under phase transfer catalysis conditions with solid KOH, toluene, and dibenzo-18-crown-6 to give 2-propargylcyclododecanone (III) in high yield. The hydration of ketone (III) provides a simple approach to diketone (I). McAndrew and Russel [1] have reported unsuccessful attempts to obtain ketone (I) by the hydration of acetylenic ketone (III) upon catalysis by mercury compounds. However, in our view, the conclusion of these authors that only cyclododecanone is formed in significant amounts in this hydration reaction is very strange. We rechecked the hydration of acetylenic ketone (III) upon catalysis by mercury compounds and found that different products are obtained depending on the reaction conditions. The hydration of ketone (III) under the conditions of McAndrew [1] gave 14-methyl-13-oxabicyclo[10.3.0]-pentadeca-1(12),14-diene (IV), while cyclododecanone was not detected at all among the reaction products.

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