

## PARTITIONING ANIONIC AGENTS BASED ON 7,8-DICARBA-NIDO-UNDECABORATE FOR THE REMEDIATION OF NUCLEAR WASTES

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### Abstract

$[3,3'-M(1,2-C_2B_9H_{11})_2]^-$  ( $M = Co^{3+}, Fe^{3+}, Ni^{3+}$ ) anionic compounds perform similarly in PVC membranes as  $Cs^+$  sensors in ion selective electrodes. Their behaviour is very similar, but the higher stability of  $[3,3'-Co(1,2-C_2B_9H_{11})_2]^-$  makes it the more interesting for extraction at low pH's. Species  $[1,1'-(PPh_2)_2-3,3'-Co(1,2-C_2B_9H_{11})_2]^-$ , **[2]**,  $[1,1'-(OPPh_2)_2-3,3'-Co(1,2-C_2B_9H_{11})_2]^-$  **[3]**,  $[3,3'-Co(1-CH_3-2-(CH_2)_nOR-1,2-C_2B_9H_9)_2]^-$  (**[4]**:  $n = 3$ ,  $R = -CH_2CH_3$ ; **[5]**:  $n = 3$ ,  $R = -(CH_2)_2OCH_3$ ; **[6]**:  $n = 3$ ,  $R = -(CH_2)_3CH_3$ ; and **[7]**:  $n = 6$ ,  $R = -(CH_2)_3CH_3$ ), were tested for  $^{137}Cs$ ,  $^{90}Sr$  and  $^{152}Eu$  in extraction. Permeability tests on Supported Liquid Membranes with H**[6]**, and H**[7]** have shown that these compounds present the highest values reported so far for this sort of radionuclides transport experiments.

## 1. Introduction

Nuclear waste reprocessing operations produce both high level and medium level activity liquid wastes (HLW/MLW). The major nuclides in these radioactive wastes are those with long half-lives, mainly  $\beta/\gamma$  emitters or  $\alpha$  emitters such as transuranium elements. This is why great efforts have been devoted throughout the world to propose harmless storage of these wastes. The burial of vitrified reprocessed HLWs (containing fission products and  $\alpha$  emitters) has been considered as the safest method for their permanent disposal, whereas MLWs are treated by evaporation in order to concentrate their radioactivity into the smallest possible volume. This treatment nevertheless leads to large volumes of concentrates composed of active and inactive salts (mainly:  $\text{NaNO}_3$ ,  $4 \text{ mol.l}^{-1}$  and  $\text{HNO}_3$ ,  $1 \text{ mol.l}^{-1}$  as the matrix). The greater part of these concentrates has to be disposed off in geological formations after embedding due to their activity in long-lived radionuclides (actinides, strontium, caesium, etc.). Therefore it would be desirable to remove these long-lived radionuclides from the contaminated liquid wastes before embedding. These would allow a large part of these wastes to be directed to a subsurface repository, and a very small part containing most of the long-lived radionuclides to be disposed off, after conditioning, in geological formation [1].

The field of metallocarborane chemistry was initiated by Hawthorne in 1965 [2]. Since that time, metallocarboranes from all areas of the periodic table have been prepared using the dicarbollide ligand [3]  $[\text{C}_2\text{B}_9\text{H}_{11}]^{2-}$  (Figure 1). These derivatives have become of increasing interest with regard to their solubility [4], isolation, separation and characterisation of organic bases, radiometal carriers [5], electron acceptor molecules [6], among other areas. One of these organometallic complexes,  $[\text{3,3}'\text{-Co}(\text{1,2-}\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  (**1**), has attracted the most attention because of its robustness, its stability in the presence of strong acid ( $\text{HNO}_3$ ), at relatively high temperatures and under a very high radiation [7]. This stability allows it to be considered for nuclear waste remediation. Its hexachloro protected analogue,  $[\text{1-Cl}_6]^-$ , is remarkable as an extractant (Figure 2). The large size to charge ratio and the hydrophobic nature of **1** and  $[\text{1-Cl}_6]^-$  allows extraction of caesium and strontium ions from an aqueous phase to an organic phase, leaving other alkaline and higher-valent metals behind [4,7,8]. The ions  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  are used for thermoelectric generators and sterilisation of medical equipment, among other areas, making the possibility of recycling them very attractive [9].

Figure 1

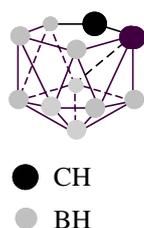
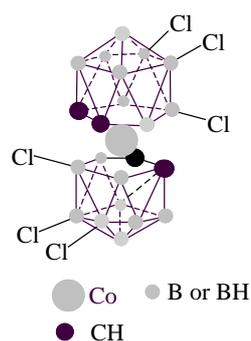


Figure 2.  $[\text{1-Cl}_6]^-$



The  $[\text{3,3}'\text{-Co}(\text{1,2-}\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ , **1** anion, has been used as a highly selective  $^{137}\text{Cs}$  sequestering agent in extraction processes, in the presence of  $\text{Na}^+$ , with nitrobenzene [4] as the receiving phase. However, nitrobenzene is an ecologically unacceptable solvent, so that other receiving phases are required for environmental applications. Thus, other solvents are needed. On the other hand, additional metallocarboranes similar to **1** are available, namely these with  $\text{Fe}^{3+}$ , and  $\text{Ni}^{3+}$ . In an effort to decide

which of these, the  $\text{Co}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ni}^{3+}$  metallacarboranes was the most adequate, their  $\text{Cs}^+$  salts were implemented in ion selective electrodes (ISE's). As the potentiometric performance of an ISE can be viewed to be similar to the transport process in one membrane their study as  $\text{Cs}^+$  sensors would provide reliable and important information on the stability and extracting capacity of these metallacarboranes, hence permitting to decide which one was more adequate. The study was also intended to discern which of the three anions was more selective towards  $\text{Cs}^+$ , in order to choose one for the subsequent studies. The results obtained, however, indicated that the three anions  $[\text{3,3}'\text{-Co(1,2-C}_2\text{B}_9\text{H}_{11})_2]^-$ ,  $[\text{3,3}'\text{-Fe(1,2-C}_2\text{B}_9\text{H}_{11})_2]^-$ , and  $[\text{3,3}'\text{-Ni(1,2-C}_2\text{B}_9\text{H}_{11})_2]^-$  were comparable in their behaviour in ISE's [10]. Since the  $\text{Co}^{3+}$  complex provides easier synthetic routes, higher yield and higher stability, it was chosen for the studies on the extraction of radionuclides.

Organic compounds incorporating oxygen in the molecule mainly as ethers, and phosphine oxide derivatives have been also tested for this kind of radionuclides waste removal [11]. Accordingly several ether C-substituted cobaltacarboranes [12,13] were prepared and great effort has been dedicated more recently to phosphine oxides, and fluorinated compounds in order to improve the efficiency showed by  $[\mathbf{1}]^-$  and  $[\mathbf{1-Cl}_6]^-$ .

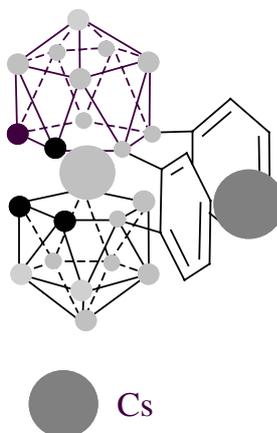
In this paper we report on the synthesis and extracting possibilities offered by these C-substituted cobaltabisdicarbollide species, along with some comments on the B-substitution.

## 2. Discussion

### 2.1 *What benefits can be expected from the polyhedral anions?*

Anions with low nucleophilicity, good solubility and weak coordination capacity have recently experienced great interest in areas of major commercial importance such as olefin polymerization [14], lithium battery technology [15], and the radionuclides extraction mentioned above. In 1986 the carborane anion  $\text{CB}_{11}\text{H}_{12}^-$  was introduced as a candidate for the least co-ordinating anion [16]. Paradoxically, carboranes combine a versatile functionalization chemistry with unparalleled inertness. One of their main characteristics, which is relevant to this work, is the delocalization of the anionic charge throughout its volume, thus producing the anions with lowest charge density. It has been demonstrated [17] that the delocalized charge on these large anions tends to make them nearly ideal spectator ions with little opportunity to perturb the structure of the cation. In addition to the 12-vertex ions,  $\text{CB}_{11}\text{H}_{12}^-$  and  $\text{B}_{12}\text{H}_{12}^{2-}$  there are related classes of anions based on the 10-vertex  $\text{B}_{10}\text{H}_{10}^{2-}$  and  $\text{CB}_9\text{H}_{10}^-$  ion, as well as the above mentioned  $\text{M}^{3+}$  bisdicarbollides. The cobaltabisdicarbollide anion, whose hexachloroderivative molecular structure is depicted in Figure 2 consists of a  $\text{Co(III)}$  ion sandwiched by two dicarbollide moieties. Each dicarbollide  $(\text{C}_2\text{B}_9\text{H}_{11})^{2-}$  bears two negative charges, overall producing a mononegative species. This anion presents a great chemical resistance, e.g. it withstands in  $\text{HNO}_3$  2M and in concentrated HCl for several days without apparent decomposition. Thus, these anions do not encounter a parallel in current inorganic or organic areas of chemistry. They are very relevant and can hardly be replaced by other anions. They offer other possibilities derived from their elemental nature as neutron scavengers or glass forming elements, both important for nuclear waste remediation.

Figure 3



## 2.2 Possibilities of modification

As can be seen from Figure 2, two different sort of reacting points are possible in  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ , the BH's and the CH's. Not all BH's sites are equally reactive, those that have permitted substitution by Cl are the more reactive. This matter has been developed by the Boron Chemistry group at Rez near Prague, and their results shall be attributed to S. Hermaneck, J. Plesek and B. Grüner [18]. One excellent example for extraction of  $\text{Cs}^+$  is given by bisphecosan represented in Figure 3. Excellent recent results derive from the dioxane substituted  $\text{Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2^-$  complex,  $8\text{-C}_4\text{H}_8\text{O}_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})$  ( $1',2'\text{-C}_2\text{B}_9\text{H}_{11}$ ). This is neutral and strongly susceptible to nucleophilic attack by anionic nucleophiles, being a precious and highly versatile starting material to produce a rich variety of anionic extracting agents for actinides, the result being only limited to the availability of anionic nucleophiles. These results have been produced in the frame of contract IC15-CT98-0221 and shall be attributed to the same authors from Rez plus Dr. J. Baca.

## 2.3 Synthesis of C-substituted derivatives of $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$

A general approach to the synthesis of C-substituted derivatives of cobalt bis(1,2-dicarbollide) consists in the preparation of the corresponding substituted *o*-carboranes, their degradation into the nido-7,8-dicarborenes, followed by deprotonation and reaction with cobalt(II) chloride [19]. This synthesis is extremely time consuming and always shall produce  $[3,3'\text{-Co}(1\text{-R-}1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^-$  derivatives with identical substituents in each dicarbollide moiety.

However, a more versatile method starting from  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$  was needed as it would permit a more rapid way to produce derivatives at carbon. A recent approach by Chamberlain *et al.*, to  $[3,3'\text{-Co}(1\text{-R-}1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$  ( $1,2\text{-C}_2\text{B}_9\text{H}_{10}$ ) anionic mono-derivatives consists in the treatment of  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$  with *n*-butyllithium followed by the reaction with alkyl halides [20].

This procedure was a good alternative as  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$  was a readily available starting material. Some years before we had attempted the same procedure but we had got no conclusive results [21]. According to Chamberlain *et al.* the synthetic procedure is straightforward. A violet colour due to the deprotonated  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})_2]^{2-}$  dianion is produced upon the addition of 1 equivalent of BuLi to the orange initial solution of  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ , in THF.

This dianionic species must be extremely basic, thus very reactive towards weak acids. We had abandoned this reaction in 1994 since following an equal procedure, the product always reverted to the orange colour of the cobalt bis(1,2-dicarbollide). However, the interesting report [20] from Los Alamos National Laboratory, brought back the possibility of this, otherwise, extremely interesting reaction.

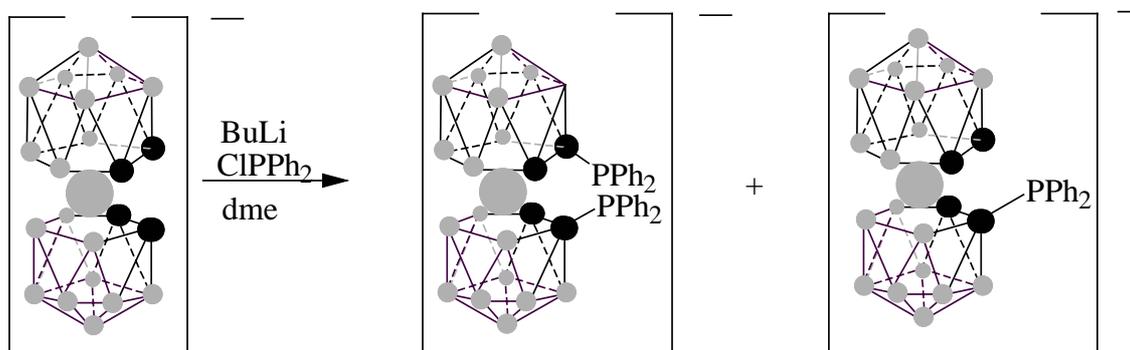
The reaction is very tricky and does not proceed precisely, in our hands, as the authors say. By using the same reagents as they did we were able to get partial conversion, usually of the order of 30-40%. The rest was unreacted  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ . Now, after having reinvestigated this reaction we believe that this “unreacted  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ ” is in fact a “reverted  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ ”.

### 3. Preliminary results

The solvent initially used was dimethoxyethane,  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$ , however after noticing the strong basicity of the deprotonated  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1,2\text{-C}_2\text{B}_9\text{H}_{11})]^{2-}$ , this was replaced by THF. The initial reagents used were  $\text{Cl}(\text{CH}_2)_3\text{Br}$  and  $\text{ClPPh}_2$ . For this last one, a minor product was obtained which suggested that some reaction, although in very low extension, had taken place. The rest was  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ . This led us to think that  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1,2\text{-C}_2\text{B}_9\text{H}_{11})]^{2-}$  was a strong base but a weak nucleophile. Thus, TMDA was added to the reaction pot, (TMDA =  $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ ), as it is known that butyllithium aggregates show a marked increase in the reactivity when co-ordinating solvents or reagents are added. This explains the initial use of dimethoxyethane. However, neither at room temperature nor under refluxing conditions the result did improve.

Other reagents were  $\text{BrCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$ , alone or in the presence of  $\text{AgBF}_4$ . The result was unsuccessful as previously. The low nucleophilicity of  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1,2\text{-C}_2\text{B}_9\text{H}_{11})]^{2-}$  had to be overcome by a good leaving group on the second reagent, as was obvious when using  $\text{Cl}(\text{CH}_2)_6\text{I}$ . In this case the  $^{11}\text{B}\{^1\text{H}\}$  NMR of the reaction crude indicated that there was something else besides  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ , but this ended up to be a mixture of several compounds with very similar properties which did not permit an adequate separation, but the interesting point was that it seemed to be necessary the existence of a good leaving group in the reagent.

Figure 4



Although results seemed to be improving the method was not convenient as cumbersome separation procedures were needed. However from the data we had gathered the following conclusions could be inferred: 1) The existence of weakly acidic hydrogens in the reagent was responsible for the

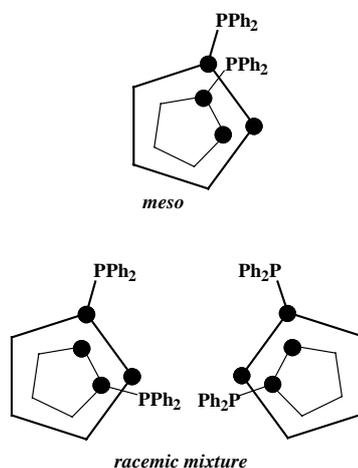
protonation of  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1,2\text{-C}_2\text{B}_9\text{H}_{11})]^{2-}$ , thus reverting to  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ ; 2) Good leaving groups are necessary to facilitate attack by  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{10})(1,2\text{-C}_2\text{B}_9\text{H}_{11})]^{2-}$ ; and 3) A high excess of reagent is convenient to lower the ratio of reverted  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ .

Considering these points it was initially decided that  $\text{I}_2$  was a very good candidate. It did not carry any hydrogen, is susceptible to nucleophilic attack and it can be removed from the flask reaction by sublimation at room temperature. As it was described in the introduction,  $\text{I}_2$  has been adequate to produce electrophilic substitution on boron atoms in  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ . Contrarily, in this project, the formation of a C-I bond is sought as a versatile candidate for C-C bond formation, by using appropriate Grignard reagents for coupling reactions.

#### 4. Synthesis of diphenylphosphine cobaltabisdicarbollide derivatives

The reaction is schematised in Figure 4. Reaction of  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  with BuLi in dimethoxyethane followed by chlorodiphenylphosphine yields the disubstituted species  $[2]^-$  and only minor amounts of the monophosphine. Concerning the disubstituted species, a mixture of isomers could be possible: the *meso* form ( $\text{C}_s$  symmetry) and a *racemic* mixture ( $\text{C}_2$  symmetry). The first contains a mirror plane ( $\sigma_h$ ) while the second contains a  $\text{C}_2$  axis. These possible species are schematically represented in Figure 5. The  $^{13}\text{C}$ -, and  $^1\text{H}$ -NMR confirms the existence of only one of the two possible species. To determine which one of the two had been obtained, crystals suitable for X-ray diffraction were grown [22]. The structure demonstrated that the racemic form was the one produced. These phosphine compounds are basic as a consequence of the negative charge, and of the phosphines themselves. These should not be compatible with the strong acid conditions found in the radioactive waste. The phosphine oxides would be more convenient for the purposes of this project.

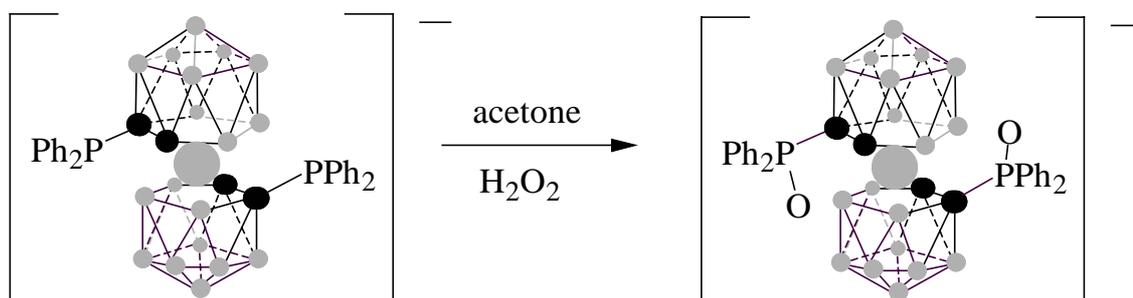
Figure 5



#### 5. Synthesis of diphenylphosphine oxide cobaltabisdicarbollide derivatives

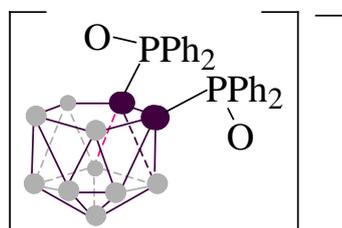
The reaction is schematised in Figure 6. Reaction of  $[1,1'-(\text{PPh}_2)_2\text{-}3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ ,  $[2]^-$  with  $\text{H}_2\text{O}_2$  in acetone yields the expected phosphine oxide.

Figure 6



As the initial diphosphine was in the racemic form, upon oxidation, it was required that the resulting phosphine oxide maintained this isomerism. Indeed this is what happened. This was fully confirmed by the X-ray structural determination of suitable crystals. The acid stability of both  $[1,1'-(\text{PPh}_2)_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  and  $[1,1'-(\text{OPPh}_2)_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  [**3**] was studied by dissolving the  $\text{Cs}^+$  salts of these two species in 3M  $\text{HNO}_3$  and  $\text{HCl}$ . The resulting solutions were then neutralized with 3M  $\text{NaOH}$ . The possible modifications were then followed by  $^{31}\text{P}$ -NMR. It was found that the oxide was recovered fully, while the initial phosphine could be recovered in a 80%. These results demonstrated the stability of the phosphine oxides versus the starting phosphines. The  $[1,1'-(\text{OPPh}_2)_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  oxide is one cluster anion bearing two  $\text{OPPh}_2^-$  units, similar to the anion shown in Figure 7. This would allow to study the role of the cluster. Both are monoanionic species and both contain two  $\text{OPPh}_2^-$  units.

Figure 7

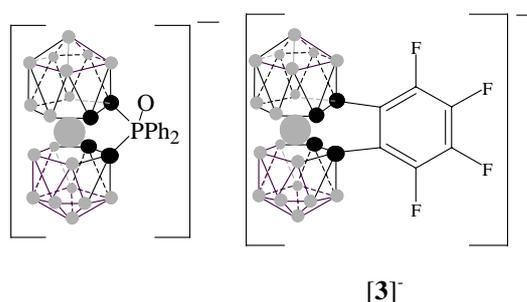


## 6. Introducing bridging fragments

$\text{C},\text{C}'$  bridged species could be relevant as they hinder rotation of the two halves of the molecule. Interestingly, extraction results found in the former project CIPA-CT93-0133 (EUR 18217 EN) by the IIC-, NRI (Rez) and CEA (Cadache) upon derivatives of  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  bridged at the 8,8'- positions, both being boron positions, e.g. PHECOSAN stimulated research on these species. Similarly, bridged  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  on the carbon atoms, have been produced now. Contrarily to those described formerly, the bridge in these cases would be between carbon atoms.

Syntheses have been performed as described in Figure 4.  $\text{Cl}_2\text{PPh}$  and perfluorinated benzene have been used as reagents. The bridging phosphine has been oxidized following the  $\text{H}_2\text{O}_2/\text{acetone}$  procedure shown in Figure 6.

Figure 8



### 6.1 Protecting the cluster with halogen groups

It was long reported that hexachlorinated  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_5\text{Cl}_6)_2]^-$  and dibrominated  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{10}\text{Br}_2)_2]^-$  derivatives of  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  withstand acid conditions better than the parent compound. The fact that the hexachloro and the dibromo protected species had a comparable stability in acid conditions indicated that the crucial point was substitution on 8,8'- as these are the only common protected positions in both compounds. Considering that the low performance of these and other previously reported  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  derivatives at  $[\text{H}^+] > 0.1 \text{ M}$  in Eu, Sr, and actinides had to be due to the reactivity of BH's at the 8,8'- positions, a project leading to protect these positions is under way.

This may be addressed starting from the already protected 8,8'- positions either with halogen or carbon atoms. A second alternative would be to protect the phosphine or phosphine oxide product. Results have shown that starting from the  $[8,8'-\text{Cl}_2-\text{Co}(\text{C}_2\text{B}_9\text{H}_{19})_2]^-$  is better than starting from  $[\text{Cl}_6-\text{Co}(\text{C}_2\text{B}_9\text{H}_8)_2]^-$ . This may have to do with steric hindrance.

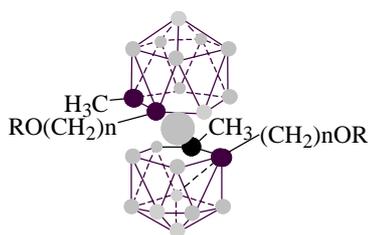
On the other hand, when the protection reaction was performed on the  $[1,1'-(\text{PPh}_2)_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  anion, results concerning halogen substitution at boron atoms were unsuccessful. Reaction with  $\text{Br}_2$  in glacial acetic acid led to borates.

More encouraging seem to be the results obtained from the phosphine oxide  $[1,1'-(\text{OPPh}_2)_2-3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ . Reactions have been directed to get 8,8'- disubstitution (protection) as these seem to be sufficient to improve the stability of the cluster in acid media.

### 7. Extractants derived from $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$

The series of compounds derivatives of  $[3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  derivatives incorporating ether groups,  $[3,3'-\text{Co}(1-\text{CH}_3-2-(\text{CH}_2)_n\text{OR}-1,2-\text{C}_2\text{B}_9\text{H}_9)_2]^-$ , which are presented graphically in Figure 9 ([4]:  $n = 3$ ,  $\text{R} = -\text{CH}_2\text{CH}_3$ ; [5]:  $n = 3$ ,  $\text{R} = -(\text{CH}_2)_2\text{OCH}_3$ ; [6]:  $n = 3$ ,  $\text{R} = -(\text{CH}_2)_3\text{CH}_3$ ; [7]:  $n = 6$ ,  $\text{R} = -(\text{CH}_2)_3\text{CH}_3$ ) [12,13] have been studied following the general approach indicated in "Synthesis of C-Substituted Derivatives of  $[3,3'-\text{Co}(1,2-\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ ".

Figure 9



- [4]<sup>-</sup> n=3, R= CH<sub>2</sub>CH<sub>3</sub>  
 [5]<sup>-</sup> n=3, R= (CH<sub>2</sub>)<sub>2</sub>OCH<sub>3</sub>  
 [6]<sup>-</sup> n=3, R= (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>  
 [7]<sup>-</sup> n=6, R= (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>

The bis(dicarbollide) derivatives [4]<sup>-</sup>, [5]<sup>-</sup>, [6]<sup>-</sup>, [7]<sup>-</sup>, have been tested in the liquid-liquid extraction of <sup>137</sup>Cs, <sup>90</sup>Sr and <sup>152</sup>Eu from the aqueous HNO<sub>3</sub> phase to the organic nitrophenyl hexyl ether.

For the extraction of <sup>137</sup>Cs, the polyether substituted compounds show a very high extraction efficiency at pH 3 (D>100) regardless of the nature of the exocluster chain. This efficiency is expected to be lower if the acidity of the medium is increased. This behaviour is displayed by [4]<sup>-</sup>, whose D value decreases from >100 to 3, just by varying the pH value from 3 to 1. However, [6]<sup>-</sup>, which is very similar to [4]<sup>-</sup>, but with the longest alkyl chain next to the oxygen atom, maintains an excellent efficiency for the extraction of <sup>137</sup>Cs even at pH 1. Anion [6]<sup>-</sup> shows again the best performance for the extraction of <sup>90</sup>Sr but the D value decreases strongly with decreasing pH. For the extraction of <sup>152</sup>Eu, it seems that the larger the exocluster chain the better the performance of the extracting agent. Therefore, [7]<sup>-</sup> shows the best performance in the extraction of <sup>152</sup>Eu. The lower efficiency in the extraction of <sup>90</sup>Sr and <sup>152</sup>Eu shown by compound [6]<sup>-</sup> and the excellent results obtained in the extraction of <sup>137</sup>Cs, should permit a selective extraction of Cs<sup>+</sup> from a mixture containing all the radionuclides in solution. This result led us to perform some transport experiments at CEA (Cadarahe) by using Supported Liquid Membranes (S.L.M.) with NPHE (nitrophenylhexyl ether) as the membrane solvent. Preliminary results carried out with compounds H[4], H[5], H[6] and H[7] showed that the best transport performance was for compound H[6]. Compound [7]<sup>-</sup>, displaying the best efficiency in the extraction of <sup>152</sup>Eu, was used for its transport studies.

At pH 3, transport of <sup>137</sup>Cs was very efficient with compound [6]<sup>-</sup>, and a permeability of 30.6 cm/h was obtained. An extraction of 93% of Cs<sup>+</sup> in 1 hour was achieved.

In the case of the transport of europium, transport with compound H[7] is very rapid at pH 3, showing a permeability of 8.9 cm/h, i. e. an extraction of 31.2% after 1 hour or 91.3 after 3.5 h. For comparison, permeabilities ranging from 1 to 4 cm/h have been measured for several "carriers" such as calix[4]arenes crown 6, CMPO (carbamoylmethylphosphine oxides) or diphosphine dioxides under comparable conditions. Improved permeabilities were achieved with calixarenes incorporating CMPO moieties (4-7 cm/h) [23]. Thus, generally speaking, the cobalta(dicarbollide) carriers are considerably faster transport agents than others well-recognised as doing this job, such as those indicated above [12,13].

As expected H[2] does not display a good extracting capacity at 3≥pH due to the basicity of the phosphine groups, enhanced by the negative charge of the anion. This extracting capacity is very much improved when the phosphine oxides are utilised, however it diminishes abruptly at pH = 1. It is

remarkable the Sr affinity of the fluorinated bridged species shown in Figure 8. The existence of the bridging monophosphine oxide does not influence favourably the extraction.

## 8. Conclusion

Metallacarborane complexes of formula  $[3,3'\text{-M}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$  (M = Co, Fe, No) have been tested as Cs sensors. The results have demonstrated a similar behavior, however due to the large stability of the Co complex and the better yield this seem to be the anion to be studied.

Synthesis of  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$  derivatives can be made from the *o*-carborane, producing the wanted substitution, removing the boron connected to both carbon atoms, and the proton. The dianion, thus formed, is reacted with anhydrous cobalt chloride. An alternative is to start directly from  $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ . In this paper compounds obtained by both ways are prepared, however the second provides a more accessible route to these extracting agents.

The largest drawback that these anions suffer is the lost of activity at low pH, specially below 1. This will require protection at the boron 8,8'- positions. The phosphine oxide extracting agents seem to be adequate for radioactive waste treatment once the pH dependence problem is solved.

On the other hand the anionic character and low charge density of these extracting agents along with the high boron contents and specially the results already obtained by us and other groups participating in the EU project make them extremely suitable candidates to solve the present problem of partitioning.

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