Inorg. Chem. **1998,** *37,* 3640−3643

Notes

New Polyether-Substituted Metallacarboranes as Extractants for ^{137}Cs and ^{90}Sr from Nuclear Wastes

Clara Viñas,[†] Sílvia Gomez,[†] Josep Bertran,[†]
Francesc Teixidor,*,[†] Jean-François Dozol,*,[‡] and
Hélène Rouquette[‡]

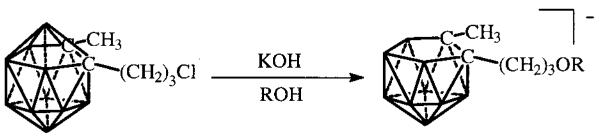
Institut de Ciència de Materials de Barcelona (CSIC),
Campus de la UAB, 08193 Bellaterra, Spain, and
DCC/DESD/SEP, CEA Cadarache,
13108 Saint Paul lez Durance, France

Received November 19, 1997

Introduction

Hawthorne initiated in 1965 the explosion in metallacarborane chemistry.[1] Since that time, due to their interesting properties and applications, metallacarboranes from all areas of the periodic table have been prepared using the dicarbollide ligand $C_2B_9H_{11}^{2-}$.[2] There has been a growing interest in these derivatives with regard to such areas as their solubility,[3] isolation and separation, and characterization of organic bases, radiometal carriers,[4] and electron-acceptor molecules.[5] One of these organometallic complexes, $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$, has attracted the most attention because of its robustness and stability in the presence of strong acid, moderate base, high temperature, or intense radiation.[6] This stability makes it capable of being used in nuclear waste remediation. The large size-to-charge ratio and the hydrophobic nature of $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$ allows the extraction of cesium and strontium ions from an aqueous phase to an organic phase, leaving other alkaline and higher-valent metals behind.[3,6,7] The ions ^{137}Cs and ^{90}Sr are used for fueling thermoelectric generators and sterilizing medical equipment, among other things, making the possibility of recycling them very attractive.[8]

It is known that compounds incorporating oxygen in the molecule have been tested for use in the extraction of radionuclides.[9] This, along with the good ^{137}Cs- and ^{90}Sr-extracting capacity of $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$, led us to combine both components in the same molecule to produce more selective extracting agents and to increase the lipophilic character of the $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$ derivatives. For this purpose, a new family of $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$ derivatives has been synthesized ($[3,3'\text{-Co}(1\text{-}CH_3\text{-}2\text{-}(CH_2)_3OR\text{-}1,2\text{-}C_2B_9H_9)_2]^-$). One of them incorporates two oxygen atoms in a chelating disposition (**6**, R = $-(CH_2)_2OCH_3$). The other two were synthesized with only one oxygen atom in the exocluster chain. The different chain lengths should induce different lipophilic properties, thus distinct extracting properties (**5**, R = $-CH_2CH_3$; **7**, R = $-(CH_2)_3CH_3$).



2 R = CH_2CH_3
3 R = $(CH_2)_2OCH_3$
4 R = $(CH_2)_3CH_3$

Figure 1. Synthetic procedure for the formation of $[7\text{-}CH_3\text{-}8\text{-}(CH_2)_3OR\text{-}7,8\text{-}C_2B_9H_{10}]^-$.

Results and Discussion

For the synthesis of these cobaltabis(dicarbollide) derivatives, it was necessary to have available a suitable starting compound. The closo compound $1\text{-}CH_3\text{-}2\text{-}(CH_2)_3Cl\text{-}1,2\text{-}C_2B_{10}H_{10}$ (**1**)[10] fulfilled our requirements. It provides a route to several polyether carborane derivatives and is obtained in good yield. Reaction of **1** with KOH in ROH leads to the wanted nido $[7\text{-}CH_3\text{-}8\text{-}(CH_2)_3OR\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (**2**, R = $-CH_2CH_3$, **3**, R = $-(CH_2)_2OCH_3$, **4**, R = $-(CH_2)_3CH_3$) compounds in a one-pot reaction. The versatility of **1** with the terminal chloride permitted not only the partial degradation but also the substitution on the C−Cl fragment by the nucleophilic $^-$OR species. Just by changing the solvent, a different organic fragment is introduced into the exocluster chain, permitting a modulation of the lipophilic properties of the compound. The reaction is schematically indicated in Figure 1.

To synthesize the corresponding cobaltabis(dicarbollide) derivatives, we used a method previously developed in our group.[11] The nido species **2**, **3**, and **4** reacted with K*t*BuO and $CoCl_2$ in 1,2-dimethoxyethane (dme) as the solvent. A mixture of two geometric isomers, which we were not able to separate (racemic mixture and meso form) due to their extremely similar properties, were produced in these syntheses. Peak intensity analysis of the ^{11}B NMR spectra confirms, however, the existence of geometric isomers. After purification with AcOEt/

[†] Institut de Ciència de Materials de Barcelona (CSIC).

[‡] CEA Cadarache.

(1) (a) Hawthorne, M. F.; Young, D. C.; Wegner, P. A. *J. Am. Chem. Soc*. **1965**, *87*, 1818. (b) Hawthorne, M. F.; Andrews, T. D. *J. Chem. Soc., Chem. Commun.* **1965**, 443.

(2) Saxena, A. K.; Maguire, J. A.; Hosmane, N. S. *Chem. Rev.* **1997**, *97*, 2421.

(3) Plesek, J. *Chem. Rev.* **1992**, *92*, 269.

(4) (a) Shelly, K.; Knobler, C. B.; Hawthorne, M. F. *New J. Chem*. **1988**, *12*, 317. (b) Hawthorne, M. F. *Pure Appl. Chem*. **1991**, *63*, 327.

(5) Chetcuti, P. A.; Hofherr, W.; Liégard, A.; Rihs, G.; Rist, G.; Keller, H.; Zech, D. *Organometallics* **1995**, *14*, 666.

(6) Rais, J.; Selucky, P. *Nucleon* **1992**, *1*, 17.

(7) Reilly, S. D.; Mason, C. F. V.; Smith, P. H. *Cobalt(III) Dicarbollide: A Potential ^{137}Cs and ^{90}Sr Waste Extraction Agent*. Report LA-11695, Los Alamos National Laboratory: Los Alamos, NM, 1990.

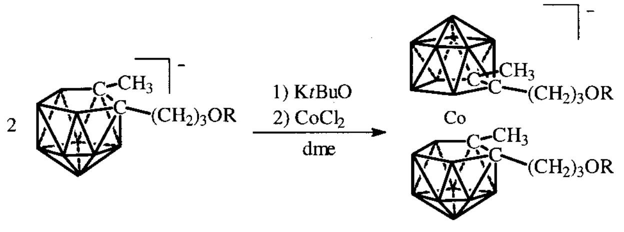
(8) Hurlburt, P. K.; Miller, R. L.; Abney, K. D.; Foreman, T. M.; Butcher, R. J.; Kinkead, S. A. *Inorg. Chem*. **1995**, *34*, 5215.

(9) (a) Dozol, J. F.; Böhmer, V.; McKervey, A.; Lopez Calahorra, F.; Reinhoudt, D.; Schwing, M. J.; Ungaro, R.; Wipf, G. *New macrocyclic extractants for radioactive waste treatment: ionizable crown ethers and functionalized calixarenes.* EU Report EUR 17615 EN; Luxembourg, 1997; (b) Ungaro, R.; Casnati, F.; Ugozzoli, F.; Pochini, A.; Dozol, J. F.; Hill, C.; Rouquette, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1506. (c) Casnati, A.; Pochini, A.; Ungaro, R.; Ugozzoli, F.; Arnaud, F.; Fanni, S.; Schwing, M. J.; Egberink, R. J. M.; Jong, F.; Reinhoudt, N. D. *J. Am. Chem. Soc.* **1995**, *117*, 2767.

(10) Teixidor, F.; Gomez, S.; Lamrani, M.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *Organometallics* **1997**, *16*, 1278.

(11) Viñas, C.; Pedrajas, J.; Bertran, J.; Teixidor, F.; Kivekäs, R.; Sillanpää, R. *Inorg. Chem.* **1997**, *36*, 2482.

S0020-1669(97)01467-5 CCC: $15.00



5 R = CH_2CH_3
6 R = $(CH_2)_2OCH_3$
7 R = $(CH_2)_3CH_3$

Figure 2. Schematic synthesis of $[3,3'\text{-Co}(1\text{-CH}_3\text{-2-(CH}_2)_3\text{OR-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$.

Table 1. Distribution Coefficients (*D*) of the Different Radionuclides Extracted by the Protonated Form of Cobaltabis(dicarbollide) Derivatives

	D_{Cs}		D_{Sr}		D_{Eu}	
compd	pH 3	pH 1	pH 3	pH 1	pH 3	pH 1
H[**5**]	>100	3	13	<0.01	90	0.01
H[**6**]	>100		2		28	
H[**7**]	>100	>100	55	0.3	40	4.8

CH_3CN (10:2) the anions **5** ($[3,3'\text{-Co}(1\text{-CH}_3\text{-2-(CH}_2)_3\text{OCH}_2\text{-CH}_3\text{-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$), **6** ($[3,3'\text{-Co}(1\text{-CH}_3\text{-2-(CH}_2)_3\text{O(CH}_2)_2\text{-OCH}_3\text{-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$) and **7** ($[3,3'\text{-Co}(1\text{-CH}_3\text{-2-(CH}_2)_3\text{O-(CH}_2)_3\text{CH}_3\text{-1,2-C}_2\text{B}_9\text{H}_9)_2]^-$) were obtained. See Figure 2. Depending on the nature of the exocluster chain, distinct ratios of ligand to K*t*BuO were applied (1:3 (**5**), 1:7 (**6**), 1:8 (**7**)). The R_f's in silica gel for each compound are related to the polarity of the organic chain. Anion **6** has the highest polarity due to the presence of the two oxygen atoms, displaying the lowest R_f. Anion **7** has the most lipophilic chain. Consequently, its corresponding band in TLC appears at a position higher than the other in the same purification conditions.

Extraction Experiments

The bis(dicarbollide) derivatives **5**, **6**, and **7** have been tested in the liquid–liquid extraction of ^{137}Cs, ^{90}Sr, and ^{152}Eu. Table 1 presents the distribution coefficient (*D*) of the different radionuclides for each complex. The *D* term is defined as the equilibrium distribution ratio of the radionuclide between the organic and the aqueous phases.

Distribution coefficients of the metals decrease with pH in the feeding solution. This phenomenon is due to the equilibrium of the cation M^{n+}, which is governed in acidic medium for a basic cobaltabis(dicarbollide) by[7]

$$n\mathrm{H_{org}}^{+} + \mathrm{M_{aq}}^{n+} \Leftrightarrow n\mathrm{H_{aq}}^{+} + \mathrm{M_{org}}^{n+} \tag{1}$$

The proton in the organic phase is provided by the cobaltabis(dicarbollide), with an extraction constant K_{ex}

$$\frac{[\mathrm{H_{aq}}^{+}]^n[\mathrm{M_{org}}^{n+}]}{[\mathrm{H_{org}}^{+}]^n[\mathrm{M_{aq}}^{n+}]} = K_{ex} \tag{2}$$

In a first approach, for the extraction of trace level radioactive cations producing a small change in the nitric acid concentration, the distribution coefficients can be linked to the extraction constant by the following relationship

$$D_{\mathrm{M}^{n+}} = \frac{\mathrm{M_{org}}^{n+}}{\mathrm{M_{aq}}^{n+}} = K_{ex}\frac{[\mathrm{H^{+}CoB_2}^{-}]}{[\mathrm{HNO_3}]} \tag{3}$$

Table 2. Percentage of Extracted ^{137}Cs for H[**7**] vs Time and the Corresponding $-\ln(C/C^0)$ Value

time (h)	% ext Cs	$-\ln(C/C^0)$	time (h)	% ext Cs	$-\ln(C/C^0)$
0.00	0.0	0.000	0.42	80.3	1.625
0.08	33.6	0.409	0.50	82.5	1.741
0.16	51.7	0.708	0.66	88.3	2.143
0.25	63.6	1.011	0.83	92.1	2.541
0.33	74.1	1.351	1.00	92.8	2.628

where $[\mathrm{H^{+}CoB_2}^{-}]$ corresponds to the concentration of the protonated cobaltabis(dicarbollide) species. The higher the nitric acid concentration, the lower will be the distribution coefficient.

For the extraction of ^{137}Cs, all the compounds tested show a very high extraction efficiency at pH 3 ($D > 100$), regardless of the nature of the exocluster chain. This efficiency is expected to decrease as the acidity of the medium increases. This is the behavior displayed by **5**, whose *D* value decreases from >100 to 3, just by varying the pH value from 3 to 1. However, **7**, which is very similar to **5** but has the longest alkylic chain next to the oxygen atom, maintains an excellent efficiency for the extraction of ^{137}Cs even at pH 1. Anion **7** shows again the best performance for the extraction of ^{90}Sr, but the *D* value decreases strongly with decreasing pH. For the extraction of ^{152}Eu, it seems that a lower number of carbon atoms is required next to the oxygen atom of the chain. Therefore, **5** shows the best performance in the extraction of ^{152}Eu. The lower efficiency in the extraction of ^{90}Sr and ^{152}Eu shown by these compounds and the excellent results obtained in the extraction of ^{137}Cs should permit a selective extraction of the last one from a mixture containing all there radionuclides in solution. This result led us to perform some transport experiments by using supported liquid membranes (SLM) with nitrophenylhexyl ether (NPHE) as the membrane solvent. Preliminary results carried out with compounds H[**5**], H[**6**], and H[**7**] showed that the best transport performance was for compound H[**7**]. As a consequence, testing with the other two compounds was not continued.

The transport of radionuclides from aqueous HNO_3 solutions was followed by regular measurement of the decrease of radioactivity in the feed solution by γ spectrometry analysis. This allowed graphical determination of the constant permeabilities *P* (cm/h) of ^{137}Cs permeation through the SLM for 24 h, by plotting the logarithm of the ratio C/C^0 vs time, as described in the model of mass transfer proposed by Danesi[12]

$$\ln\left(\frac{C}{C^0}\right) = -\varepsilon\frac{S}{V}Pt \tag{4}$$

where *C* is the concentration of the cation in the feed solution at time *t* (mol/L); C^0 is the initial concentration of the cation in the feed solution (mol/L); ε is volumic porosity of the SLM (%); *S* is membrane surface area (cm^2); *V* is volume of feed and stripping solutions (cm^3); and *t* is time (h).

Table 2 presents the percentage of extracted cesium and the corresponding $-\ln(C/C^0)$ calculated values at different times during 1 h. Figure 3 shows the graph of $-\ln(C/C^0)$ vs time which leads to the determination of the constant permeability *P*.

Under these conditions, at pH 3, transport of ^{137}Cs was very efficient, and a permeability of 30.6 cm/h was obtained. An extraction of 93% of ^{137}Cs in 1 h was achieved. As a comparison, permeabilities ranging from 1 to 4 cm/h have been measured for several "carriers" such as calix[4]arenes crown

---

(12) Danesi, P. R. *Sep. Sci. Technol.* **1983–1985**, *19*, 857–894.

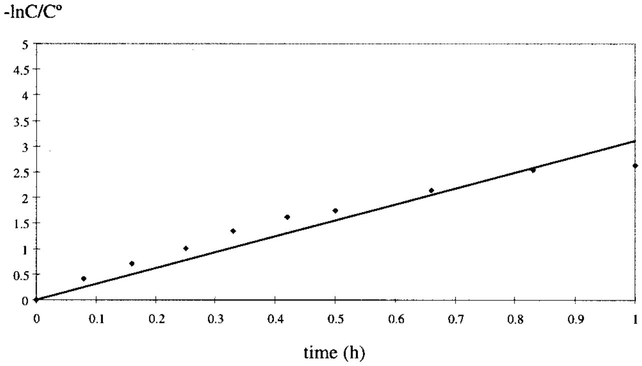


Figure 3. Graphical determination of the constant permeability *P* (cm/h) of ^{137}Cs permeation through SLM for H[**7**].

6, carbamoylmethylphosphine oxides (CMPO), or diphosphine dioxides under comparable conditions. Improved permeabilities were achieved with calixarenes incorporating CMPO moieties (4−7 cm/h). Although these results are very promising, fine modifications on **5**, **6**, and **7** are still needed to improve their extraction capacity at lower pH.[13]

Conclusion

Cobaltabis(dicarbollide) derivatives are monoanionic compounds suitable for the extraction of radionuclides. This, along with their low charge density and resistance to radiation, makes them suitable for the removal of cationic radionuclides from nuclear wastes. The modification of the nature of the compounds through the introduction of ether chains of different sizes in the C atom of the cluster permits the modulation of the extracting properties of the compound. The introduction of a dioxygen chelating chain does not represent an enhancement of the extractive properties. On the contrary, modifications of the length of the monooxygen alkylic chain led to the best performance at pH = 3 for the extraction of ^{90}Sr with H[**7**] and for the extraction of ^{152}Eu with H[**5**]. At pH = 1, compound H[**7**] displays the best performance for ^{137}Cs. Transport experiments confirmed the interest of implementing cobaltabis(dicarbollide) derivatives such as **7** on SLM to separate ^{137}Cs from nuclear wastes. Further studies are being performed in our group with compounds incorporating a C6 spacer instead of a C3 spacer attached to the carbon atom of the cluster.

Experimental Section

Synthesis of Extractants. All experimental manipulations were carried out using standard high-vacuum or inert atmosphere techniques.

Materials. Commercial methyl-*o*-carborane was purified by sublimation at 0.01 mmHg. A 1.6 M solution of *n*-butyllithium in hexane was used as received. The preparation of 1-Cl$(CH_2)_3$-2-CH_3-1,2-$C_2B_{10}H_{10}$ was described in a preceding paper.[10] Degassed dme was stored over sodium benzophenone before use. All organic and inorganic salts were analytical reagent grade and were used as received. Solvents were reagent grade.

Physical Measurements. ^{11}B NMR spectra (96.29 MHz), ^{13}C{^{1}H} NMR spectra (75.47 MHz) and ^{1}H{^{11}B} NMR (300.13 MHz) were recorded on a Bruker ARX-300 spectrometer equipped with the appropriate decoupling accessories. All NMR spectroscopic data were obtained in d_6-acetone at 22 °C. Chemical shift values for ^{11}B NMR spectra were referenced to external $BF_3{\cdot}O(C_2H_5)_2$. Chemical shift values for ^{1}H{^{11}B} and ^{13}C{^{1}H} NMR spectra were referenced to $Si(CH_3)_4$. Elemental analyses were carried out on a Perkin-Elmer 240B analyzer. Analytical thin-layer chromatography was performed on 0.25 mm (20 × 20) silica gel F-254 plates (Tracer).

Preparation of Cs[7-$(CH_2)_3OCH_2CH_3$-8-CH_3-7,8-$C_2B_9H_{10}$], Cs[2]. In a two-necked flask, 2.53 g (45.18 mmol) of KOH is dissolved in ethanol (50 mL approximately) under stirring. Then, 1.50 g (6.39 mmol) of 1-Cl$(CH_2)_3$-2-CH_3-1,2-$C_2B_{10}H_{10}$ is added. The reaction mixture is refluxed for 14 h. After being cooled down, the solvent is evaporated in vacuo, and the residue is diluted by 20 mL of water and acidified with HCl (35%) until the pH is slightly acidic. The resulting aqueous solution is then treated with a solution of CsCl in 10 mL of water, and the precipitate is filtered off and washed with diethyl ether to produce 1.98 g (5.41 mmol) of Cs[**2**] (yield 85%). IR (KBr): ν (cm^{-1}) = 2969, 2950, 2931, 2902, 2870, 2847 (C−H), 2501 (B−H), 1453 (C−H), 1100, 1026 (C−O). ^{11}B NMR: δ = −8.95 (d, ^{1}J(B,H) = 137.57 Hz, 1B), −10.50 (d, ^{1}J(B,H) = 137.57 Hz, 2B), −17.76 (d, ^{1}J(B,H) = 137.57 Hz, 4B), −34.17 (d, ^{1}J(B,H) = 123.80 Hz, 1B), −36.64 (d, ^{1}J(B,H) = 137.57 Hz, 1B). ^{1}H{^{11}B} NMR: δ = 1.09 (t, ^{3}J(H,H) = 7.14 Hz, 3H, −CH_2−CH_3), 1.39 (s, 3H, Cc−CH_3), 1.74 (m, 4H, Cc−CH_2, Cc−CH_2−CH_2), 3.30 (m, 2H, −CH_2−O−CH_2−CH_3), 3.39 (q, ^{3}J(H,H) = 7.14 Hz, 2H, −O−CH_2−CH_3). ^{13}C{^{1}H} NMR: δ = 13.62 (−CH_2−CH_3), 20.28 (Cc−CH_3), 29.98 (Cc−CH_2−), 31.15 (Cc−CH_2−CH_2), 64.23 (−O-CH_2−CH_3), 69.58 (−CH_2−O−CH_2−CH_3). Anal. Calcd for $CsC_8B_9H_{24}O{\cdot}H_2O$: C, 25.00; H, 6.76. Found: C, 25.38; H, 6.33.

Preparation of Cs[7-$(CH_2)_3O(CH_2)_2OCH_3$-8-CH_3-7,8-$C_2B_9H_{10}$], Cs[3]. The procedure is as for Cs[**2**] by using monomethylethyleneglycol to produce 1.89 g (4.77 mmol) of Cs[**3**] (yield 75%). IR (KBr): ν (cm^{-1}) = 2927, 2870, 2832 (C−H), 2519, 2476 (B−H), 1451 (C−H), 1124, 1089 (C−O). ^{11}B NMR: δ = −37.26 (d, ^{1}J(B,H) = 110.06 Hz, 1B), −34.82 (d, ^{1}J(B,H) = 82.54 Hz, 1B), −18.37 (d, ^{1}J(B,H) = 82.54 Hz, 4B), −10.82 (d, ^{1}J(B,H) = 137.57 Hz, 2B), −9.29 (d, ^{1}J(B,H) = 137.57 Hz, 1B). ^{1}H{^{11}B} NMR: δ = 1.39 (s, 3H, Cc−CH_3), 1.74 (m, 4H, Cc−CH_2−, Cc−CH_2−CH_2−), 3.25 (s, 3H, −O−CH_3), 3.30 (t, ^{3}J(H,H) = 5.55 Hz, 2H, −CH_2−O−CH_3), 3.45 (m, 4H, −O−CH_2−CH_2−O−CH_3, Cc−CH_2−CH_2−CH_2−). ^{13}C{^{1}H} NMR: δ = 22.18 (Cc−CH_3), 31.76 (Cc−CH_2), 32.91 (Cc−CH_2−CH_2−), 58.66 (−O−CH_3), 70.44 (−CH_2−O−CH_3), 72.11 (Cc−CH_2−CH_2−CH_2−), 72.48 (−O−CH_2−CH_2−O−CH_3). Anal. Calcd for $CsC_9B_9H_{26}O_2$: C, 27.26; H, 6.61. Found: C, 27.25; H, 6.48.

Preparation of [N$(CH_3)_4$][7-$(CH_2)_3O(CH_2)_3CH_3$-8-CH_3-7,8-$C_2B_9H_{10}$], [N$(CH_3)_4$][4]. The procedure is as for Cs[**2**] and Cs[**3**] by utilizing *n*-butyl alcohol. The resulting aqueous solution is treated with tetramethylammonium chloride in 10 mL of water, and the precipitate is filtered off and washed with diethyl ether to produce 1.80 g (5.36 mmol) of [N$(CH_3)_4$][**4**] (yield 84%). IR (KBr): ν (cm^{-1}) = 2955, 2929, 2866 (C−H), 2513, 2507 (B−H), 1483, 947 (C−N), 1112, 1025 (C−O). ^{11}B NMR: δ = −36.73 (d, ^{1}J(B,H) = 144.45 Hz, 1B), −34.33 (d, ^{1}J(B,H) = 137.57 Hz, 1B), −17.84 (d, ^{1}J(B,H) = 137.57 Hz, 4B), −10.39 (d, ^{1}J(B,H) = 151.33 Hz, 2B), −8.83 (d, ^{1}J(B,H) = 151.33 Hz, 1B). ^{1}H{^{11}B} NMR: δ = 0.87 (t, ^{3}J(H,H) = 7.89 Hz, 3H, −CH_2−CH_3), 1.33 (m, 2H, −CH_2−CH_3), 1.38 (s, 3H, Cc−CH_3), 1.47 (m, 2H, Cc−CH_2−), 1.58 (m, 2H, −CH_2−CH_2−CH_3), 1.72 (m, 2H, Cc−CH_2−CH_2−), 3.29 (m, 2H, CH_2−CH_2−CH_2−CH_3), 3.33 (m, 2H, Cc−CH_2−CH_2−CH_2−), 3.39 (s, 12H, N(CH_3)$_4$). ^{13}C{^{1}H} NMR: δ = 13.21 (−CH_2−CH_3), 19.13 (−CH_2−CH_3), 21.30 (Cc−CH_3), 31.12 (Cc−CH_2−), 31.76 (−CH_2−CH_2−CH_3), 32.25 (Cc−CH_2−CH_2−), 55.22 (N$(CH_3)_4$), 69.92 (−CH_2−CH_2−CH_2−CH_3), 70.99 (Cc−CH_2−CH_2−CH_2−). Anal. Calcd for $C_{14}B_9H_{40}ON$: C, 50.08; H, 12.01; N, 4.17. Found: C, 49.78; H, 11.89; N, 3.80.

Preparation of Cs[3,3′-Co(1-$(CH_2)_3OCH_2CH_3$-2-CH_3-1,2-$C_2B_9H_9$)$_2$], Cs[5]. In a two-necked flask, 1.00 g (2.73 mmol) of Cs[**2**], 0.97 g (8.65 mmol) of potassium *tert*-butylate, and 1.75 g (13.48 mmol) of anhydrous cobalt chloride are dissolved in dried dimethoxyethane under stirring. The reaction mixture is maintained under reflux for 30 h. The solvent is then evaporated in vacuo, and 20 mL of hot water is added. After extraction with diethyl ether and evaporation of the organic layer, the residue is dissolved in a minimum volume of ethanol. Then, 20 mL of water and a solution of CsCl in water are added to the mixture. The red product is filtered off, washed with hexane, and purified by

---

(13) (a) Hill, C.; Dozol, J. F.; Rouquette, H.; Eymard, S.; Tournois, B. *J. Membrane Sci.* **1996**, *114*, 73. (b) Arnaud-Neu, F.; Böhmer, V.; Dozol, J. F.; Grüttner, C.; Jakobi, R. A.; Kraft, D.; Mauprivez, O.; Rouquette, H.; Schwing-Weill, M. J.; Simon, N.; Vogt, W. *J. Chem. Soc., Perkin Trans.* **1996**, *2*, 1175. (c) Cristau, H. J.; Mouchet, P.; Dozol, J. F.; Rouquette, H. *Heteroatom Chem.* **1995**, *6*, 533.

TLC (ethyl acetate/acetonitrile:10:2, $R_f = 0.475$) to produce 0.80 g (1.21 mmol) of Cs[**5**] (yield 90%). IR (KBr): ν (cm^{-1}) = 2931, 2853 (C−H), 2551 (B−H), 1454 (C−H), 1089, 1011 (C−O). ^{11}B NMR: δ = {−14.05 (d, ^1J(B,H) = 159.86 Hz), −10.70 (m), −8.60 (d, ^1J(B,H) = 112.35 Hz), −4.95 (d, ^1J(B,H) = 128.40 Hz), −3.62 (d, ^1J(B,H) = 192.60 Hz), −1.28 (d, ^1J(B,H) = 128.40 Hz), 16B}, 7.20 (d, ^1J(B,H) = 96.30 Hz, 2B). ^{1}H{^{11}B} NMR: δ = 1.13 (m, 6H, $-\mathrm{CH_2}-\mathrm{C}H_3$), 2.43 (s, 6H, $\mathrm{Cc}-\mathrm{C}H_3$), 2.51 (m, 4H, $\mathrm{Cc}-\mathrm{C}H_2-$), 2.64 (m, 4H, $\mathrm{Cc}-\mathrm{CH_2}-\mathrm{C}H_2-$), 3.46 (m, 8H, $-\mathrm{C}H_2-\mathrm{O}-\mathrm{CH_2}-\mathrm{CH_3}$, $-\mathrm{O}-\mathrm{C}H_2-\mathrm{CH_3}$). ^{13}C{^{1}H} NMR: δ = 14.79 ($-\mathrm{CH_2}-C\mathrm{H_3}$), 30.66 ($\mathrm{Cc}-C\mathrm{H_3}$), 32.04 ($\mathrm{Cc}-C\mathrm{H_2}-$), 34.42 ($\mathrm{Cc}-\mathrm{CH_2}-C\mathrm{H_2}-$), 65.58 ($-\mathrm{O}-C\mathrm{H_2}-\mathrm{CH_3}$), 70.25 ($-C\mathrm{H_2}-\mathrm{O}-\mathrm{CH_2}-\mathrm{CH_3}$). Anal. Calcd for $\mathrm{CsC_{16}B_{18}H_{46}O_2Co{\cdot}CH_3CN}$: C, 30.97; H, 7.02. Found: C, 30.75; H, 6.61.

Preparation of Cs[3,3′-Co(1-$\mathbf{(CH_2)_3O(CH_2)_2OCH_3}$-2-$\mathbf{CH_3}$-1,2-$\mathbf{C_2B_9H_9)_2}$], Cs[6]. The procedure is as for Cs[**5**] by using 1.00 g (2.52 mmol) of Cs[**3**], 2.09 g (18.62 mmol) of potassium *tert*-butylate, and 1.64 g (12.63 mmol) of anhydrous cobalt chloride to produce 0.69 g (0.96 mmol) of the red product Cs[**6**] ($R_f = 0.387$, yield 77%). IR (KBr): ν (cm^{-1}) = 2931, 2868 (C−H), 2551 (B−H), 1461 (C−H), 1082, 1011 (C−O). ^{11}B NMR: δ = {−13.97 (d, ^1J(B,H) = 192.60 Hz), −10.01 (m), −8.58 (d, ^1J(B,H) = 160.50 Hz), −4.78 (d, ^1J(B,H) = 128.40 Hz), −3.54 (d, ^1J(B,H) = 128.40 Hz), −1.22 (d, ^1J(B,H) = 128.40 Hz), 16B}, 7.31 (d, ^1J(B,H) = 96.30 Hz, 2B). ^{1}H{^{11}B} NMR: δ = 2.09 (s, 6H, $\mathrm{Cc}-\mathrm{C}H_3$), 2.43 (m, 4H, $\mathrm{Cc}-\mathrm{C}H_2-$), 2.86 (s, 6H, $-\mathrm{O}-\mathrm{C}H_3$), 3.30 (m, 8H, $\mathrm{Cc}-\mathrm{CH_2}-\mathrm{C}H_2-$, $\mathrm{Cc}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{C}H_2-$), 3.51 (m, 8H, $-\mathrm{O}-\mathrm{C}H_2-\mathrm{CH_2}-\mathrm{O}-\mathrm{CH_3}$, $\mathrm{C}H_2-\mathrm{O}-\mathrm{CH_3}$). ^{13}C{^{1}H} NMR: δ = 25.53 ($\mathrm{Cc}-C\mathrm{H_3}$), 31.59 ($\mathrm{Cc}-C\mathrm{H_2}-$), 32.57 ($\mathrm{Cc}-\mathrm{CH_2}-C\mathrm{H_2}-$), 57.93 ($-\mathrm{O}-C\mathrm{H_3}$), 69.68 ($-C\mathrm{H_2}-\mathrm{O}-\mathrm{CH_3}$), 70.84 ($\mathrm{Cc}-\mathrm{CH_2}-\mathrm{CH_2}-C\mathrm{H_2}-$), 71.79 ($-\mathrm{O}-C\mathrm{H_2}-\mathrm{CH_2}-\mathrm{O}-\mathrm{CH_3}$). Anal. Calcd for $\mathrm{CsC_{18}B_{18}H_{50}O_4Co{\cdot}CH_3CN}$: C, 31.66; H, 7.00. Found: C, 31.37; H, 7.38.

Preparation of Cs[3,3′-Co(1-$\mathbf{(CH_2)_3O(CH_2)_3CH_3}$-2-$\mathbf{CH_3}$-1,2-$\mathbf{C_2B_9H_9)_2}$], Cs[7]. Utilizing a similar procedure as for Cs[**5**] and Cs[**6**] but with 1.00 g (2.98 mmol) of $\mathrm{[N(CH_3)_4]}$[**4**], 2.66 g (23.71 mmol) of potassium *tert*-butylate, and 1.93 g (14.86 mmol) of anhydrous cobalt chloride, a red product (0.94 g (1.32 mmol), yield 89%) is obtained with a TLC (ethyl acetate/acetonitrile:10:2, $R_f = 0.62$). IR (KBr): ν (cm^{-1}) = 2959, 2928, 2862 (C−H), 2549, 2545 (B−H), 1464 (C−H), 1095, 1015 (C−O). ^{11}B NMR: δ = {−13.98 (m), −10.39 (m), −8.63 (d, ^1J(B,H) = 128.40 Hz), −4.82 (d, ^1J(B,H) = 117.70 Hz), −3.68 (d, ^1J(B,H) = 192.60 Hz), −1.28 (d, ^1J(B,H) = 139.10 Hz), 16B}, 7.25 (d, ^1J(B,H) = 117.70 Hz, 2B). ^{1}H{^{11}B} NMR: δ = 1.17 (s, 6H, $-\mathrm{CH_2}-\mathrm{C}H_3$), 1.28 (m, 12H, $-\mathrm{C}H_2-\mathrm{CH_3}$, $-\mathrm{C}H_2-\mathrm{CH_2}-\mathrm{CH_3}$, $\mathrm{Cc}-\mathrm{CH_2}-\mathrm{C}H_2-$), 2.43 (m, 4H, $\mathrm{Cc}-\mathrm{C}H_2-$), 2.61 (s, 6H, $\mathrm{Cc}-\mathrm{C}H_3$), 3.37 (m, 8H, $\mathrm{C}H_2-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_3}$, $\mathrm{Cc}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{C}H_2-$). ^{13}C{^{1}H} NMR: δ = 13.47 ($-\mathrm{CH_2}-C\mathrm{H_3}$), 19.30 ($-C\mathrm{H_2}-\mathrm{CH_3}$), 30.84 ($\mathrm{Cc}-C\mathrm{H_3}$), 31.72 ($\mathrm{Cc}-C\mathrm{H_2}-$), 34.57 ($-C\mathrm{H_2}-\mathrm{CH_2}-\mathrm{CH_3}$), 38.32 ($\mathrm{Cc}-\mathrm{CH_2}-C\mathrm{H_2}-$), 69.92 ($-C\mathrm{H_2}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_3}$), 70.38 ($\mathrm{Cc}-\mathrm{CH_2}-\mathrm{CH_2}-C\mathrm{H_2}-$). Anal. Calcd for $\mathrm{CsC_{20}B_{18}H_{54}O_2Co{\cdot}H_2O}$: C, 32.82; H, 7.66. Found: C, 32.99; H, 7.00.

Determination of Distribution Coefficients. The distribution coefficients D, defined as the equilibrium ratio of the radionuclide species between the organic and the aqueous phases, were determined at room temperature (25 °C) by mixing the same volume of each phase at 100 rpm in a polypropylene test tube and then measuring the radioactivity in each phase by γ spectrometry.

To perform the extraction experiments, the extractant was washed previously with an aqueous 1 M $\mathrm{HNO_3}$ solution, leading to the formation of the protonated species (H[**5**], H[**6**], and H[**7**]). Then, 5 mL of the organic phase, i.e., a 0.01 M solution of the studied extractant in nitrophenylhexyl ether, and 5 mL of aqueous feed solution ($\mathrm{HNO_3}$ containing traces of ^{137}Cs, ^{90}Sr, and ^{152}Eu) were mixed. To determine D in the stripping experiments, 4 mL of the last organic phase was mixed with 4 mL of aqueous stripping solution containing a lanthanide-complexing agent (oxalic acid (0.5 M) or sodium citrate (0.25 M)). Duplicate runs of each experiment were routinely performed.

Supported Liquid Membranes. A thin flat sheet SLM device described by Stolwijk was used.[14] The volume of both aqueous solutions was 50 mL. The membrane was a Celgard 2500 (of 25-μm thickness and 45% volume porosity) polypropylene microporous support soaked with a 0.01 M solution of the tested compound in nitrophenylhexyl ether. The surface area of the membrane was about 15−16 cm^2, depending on the device; the mass of the organic phase is about 25-μg. This mass is determined by measuring the activity of the membrane after soaking it in an organic phase containing nuclides.

Permeability Determination. The transport of ^{137}Cs from the synthetic aqueous solutions of $\mathrm{HNO_3}$ (pH 3) was followed by regular measurement of the decrease of radioactivity in the feed solution and of the increase in the strip solution (sodium citrate (0.25 M)) by γ spectrometry analysis. Plotting the logarithm of the ratio C/C^0 vs time allowed graphical determination of the constant permeabilities P (cm/h) of cesium permeation through the SLM for 24 h.

Acknowledgment. We thank the EU for financial support under project CIPA-CT93-0133. J.B. also thanks the Generalitat de Catalunya for a Predoctoral Grant (FIAP/96-98.469).

IC971467M

---

(14) Stolwijk, T. B.; Sudholter, E. J. R.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 7042.