

The $[3,3'\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ anion as a platform for new materials: synthesis of its functionalized monosubstituted derivatives incorporating synthons for conducting organic polymers

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$[3,3'\text{-Co}(8\text{-C}_5\text{H}_{10}\text{O}-1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**2**) was synthesized by reaction of the caesium salt of $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ with dimethyl sulfate in the presence of sulfuric acid as catalyst and tetrahydropyran as solvent; the zwitterionic compound (**2**) yielded $[3,3'\text{-Co}(8\text{-C}_4\text{H}_4\text{N}(\text{CH}_2)_5\text{-O}-1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**6**), $[3,3'\text{-Co}(8\text{-C}_8\text{H}_6\text{N}(\text{CH}_2)_5\text{-O}-1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**7**), and $[3,3'\text{-Co}(8\text{-C}_{12}\text{H}_8\text{N}(\text{CH}_2)_5\text{-O}-1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**8**) through the nucleophilic addition of potassium pyrrolyl, indolyl and carbazolyl, respectively. The nucleophilic addition of the same salts on $[3,3'\text{-Co}(8\text{-C}_4\text{H}_8\text{O}_2-1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**1**) yielded, respectively, $[3,3'\text{-Co}(8\text{-C}_4\text{H}_4\text{N}(\text{CH}_2)_2\text{-O}(\text{CH}_2)_2\text{-O}-1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**3**), $[3,3'\text{-Co}(8\text{-C}_8\text{H}_6\text{N}(\text{CH}_2)_2\text{-O}(\text{CH}_2)_2\text{-O}-1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**4**), and $[3,3'\text{-Co}(8\text{-C}_{12}\text{H}_8\text{N}(\text{CH}_2)_2\text{-O}(\text{CH}_2)_2\text{-O}-1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**5**). All these products were isolated, purified and characterized by means of ^1H , $^1\text{H}\{^{11}\text{B}\}$, ^{11}B , $^{11}\text{B}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ -NMR and IR spectroscopies, MS MALDI-TOF spectrometry and elemental analysis. The behavior of the *exo*-cluster chain has been proven to be, in solution, very similar irrespective of the nucleophilic agent introduced into the molecule. The X-ray diffraction study of the potassium salt of **3** has proven the evidence of $\text{B-H} \cdots \text{K}^+$ interactions in solid state. The $^1\text{H}\{^{11}\text{B}\}$ -NMR spectra recorded in the range between 37 °C and -58 °C have proven the presence of the three intramolecular $\text{B-H} \cdots \text{K}^+$ interactions in solution. The possible role of $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ as a doping agent in conducting organic polymers is also discussed.

Introduction

Since the cobaltabisdicarbollide anion, $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$, was described for the first time by Hawthorne *et al.*,¹ its stability with respect to acid, moderate base, high temperature and intense radiation² has made it an interesting compound in the nuclear waste remediation area,^{2,3} especially concerning the extraction of ^{137}Cs and ^{90}Sr ions from an aqueous to an organic phase.^{2,3} In recent years, new extracting agents have been produced that combine the extraction capability of $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ and that of an organic oxygen containing fragment in the same molecule⁴ have been produced. However, most of the polyether derivatives of $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ described to date incorporate the substituting groups on the carbon atoms of the carborane clusters (C_c atoms).⁴

The synthesis of the zwitterionic $[3,3'\text{-Co}(8\text{-C}_4\text{H}_8\text{O}_2-1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**1**) in 1996⁵ by electrophilically induced nucleophilic substitution (EINS) opened up a wide interesting field for the synthesis of new monosubstituted cobaltacarborane complexes. Compound **1** has been shown to be susceptible to nucleophilic attack on the positively charged oxygen atom, *e.g.* by alkoxy salts,⁶ imide, cyanide or amines,⁷ phenolate, dialkyl or diarylphosphite⁸ and *N*-alkylcarbonyldiphenylphosphine oxides⁹ resulting in one anionic species formed by the opening of the dioxane ring.

Conceptually, this or related systems provide the possibility to organize the coordinating units around the metal atom to be sequestered by changing the nucleophile meant to open the formally positive ring in the zwitterions, *e.g.* the dioxanate in **1**, the heteroatoms of the aliphatic chain or the length of the *exo*-cluster chain. The efficiency of the resulting compounds towards hard ions could be, thus, modulated. The aim of this work is to synthesize and characterize new derivatives of

$[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ incorporating hard elements that may be useful to complex hard ions in future work.

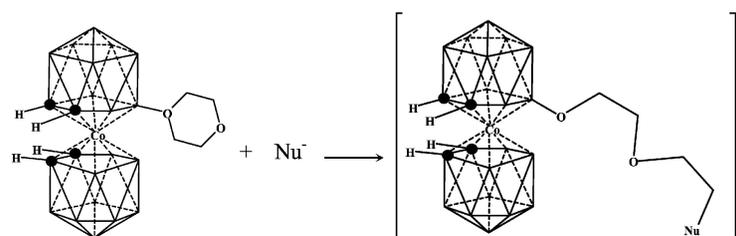
For this purpose, the reaction of $\text{Cs}[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]$ with tetrahydropyran in the presence of dimethyl sulfate and sulfuric acid was conducted to yield a new zwitterionic species ($[3,3'\text{-Co}(8\text{-C}_5\text{H}_{10}\text{O}-1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$) (**2**) which would be added to the already reported **1**.

Reaction of potassium salts of pyrrolyl, indolyl and carbazolyl anions on **1** yields $[3,3'\text{-Co}(8\text{-C}_4\text{H}_4\text{N}(\text{CH}_2)_2\text{-O}(\text{CH}_2)_2\text{-O}-1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**3**), $[3,3'\text{-Co}(8\text{-C}_8\text{H}_6\text{N}(\text{CH}_2)_2\text{-O}(\text{CH}_2)_2\text{-O}-1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**4**), and $[3,3'\text{-Co}(8\text{-C}_{12}\text{H}_8\text{N}(\text{CH}_2)_2\text{-O}(\text{CH}_2)_2\text{-O}-1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**5**), respectively (Scheme 1). Similarly the same reagents react with **2** to yield $[3,3'\text{-Co}(8\text{-C}_4\text{H}_4\text{N}(\text{CH}_2)_5\text{-O}-1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**6**), $[3,3'\text{-Co}(8\text{-C}_8\text{H}_6\text{N}(\text{CH}_2)_5\text{-O}-1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**7**), and $[3,3'\text{-Co}(8\text{-C}_{12}\text{H}_8\text{N}(\text{CH}_2)_5\text{-O}-1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**8**), respectively (Scheme 2). All described compounds have been characterized by means of ^1H , $^1\text{H}\{^{11}\text{B}\}$, ^{11}B , $^{11}\text{B}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectroscopies, IR spectroscopy, MALDI-TOF MS spectrometry, elemental analysis, and the crystal structure of $\text{K}[3,3'\text{-Co}(8\text{-C}_4\text{H}_4\text{N}(\text{CH}_2)_2\text{-O}(\text{CH}_2)_2\text{-O}-1,2\text{-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ is reported as an example of the coordinating motif.

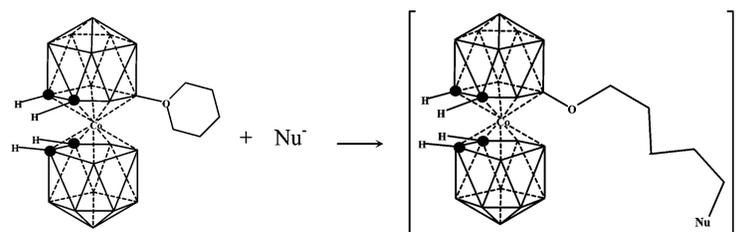
Results and discussion

I Synthesis and characterization of functionalized monosubstituted cobaltacarborane $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ derivatives

The high nucleophilic character of pyrrolyl and dimethylpyrrolyl anions has been used in our research group to get partially degraded, one boron atom removal from the cluster, forms of *o*-carborane.¹⁰ Thus, it was expected that they could have



Scheme 1 Reaction of formation of complexes **3–5** by nucleophilic attack and opening of the *exo*-cluster ring. Atoms with riding hydrogen atoms are C. The rest of the vertices in the clusters are BH.



Scheme 2 Reaction of formation of complexes **6–8** by nucleophilic attack and opening of the *exo*-cluster ring. Atoms with riding hydrogen atoms are C. The rest of the vertices in the clusters are BH.

sufficient nucleophilic power to open the *exo*-cluster aliphatic ring of the zwitterionic derivatives of $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$, e.g. **1** and **2**, and yield the corresponding potassium salts.

In the present work potassium salts of the pyrrolyl and its derivatives indolyl and carbazolyl have been used as nucleophilic agents. The larger derivatives would provide information about the nucleophilic dependence on the size and on the possibilities to modulate solubility in the resulting ligands. All salts were prepared by refluxing the corresponding protonated species with potassium in THF. Once the potassium salts had been formed, the addition of solid **1** or **2** to the previously cooled suspension of the nucleophilic agent yielded, in less than 30 minutes, the addition compound. The nucleophilic attack was carried out at room temperature to avoid secondary reactions.

The nucleophilic attack of pyrrolyl, indolyl and carbazolyl salts was almost quantitative but it was necessary to remove any excess nucleophile. The reaction course was monitored using thin layer chromatography (TLC), and it was stopped when the spot of the starting zwitterionic species disappeared on TLC. The pure compounds $[\text{3,3}'\text{-Co}(8\text{-C}_4\text{H}_4\text{N}(\text{CH}_2)_2\text{-O}(\text{CH}_2)_2\text{-O-1,2-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**3**), $[\text{3,3}'\text{-Co}(8\text{-C}_8\text{H}_6\text{N}(\text{CH}_2)_2\text{-O}(\text{CH}_2)_2\text{-O-1,2-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**4**), and $[\text{3,3}'\text{-Co}(8\text{-C}_{12}\text{H}_8\text{N}(\text{CH}_2)_2\text{-O}(\text{CH}_2)_2\text{-O-1,2-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**5**) were obtained following purification. The ^1H spectra of these compounds are very similar, excluding the aromatic region, displaying six resonances between 4.60 and 3.47 ppm: two broad singlets corresponding to the hydrogen atoms bonded to the cluster carbon atoms and four triplet signals that correspond to the methylene units of the *exo*-cluster chain. The $^1\text{H}\{^{11}\text{B}\}$ -NMR spectra displayed 10 additional signals, in the range from +3.26 to +1.46 ppm, assigned to the B–H *exo*-cluster hydrogen atoms. The $^{11}\text{B}\{^1\text{H}\}$ -NMR spectra corresponding to compounds **3–5** displayed an identical 1 : 1 : 1 : 1 : 2 : 2 : 4 : 2 : 2 : 1 : 1 pattern in the range +23.7 to –28.2 ppm. The resonance at the lowest field remained as a singlet in the ^{11}B spectrum, and was assigned to the B(8) substituted boron atom. The MALDI-TOF mass spectrum of **3** displays a signal group centered at m/z 477.0 corresponding to the anionic fragment **3**. The observed ^{11}B -NMR pattern reflects the C_s symmetry of the molecules (12 different signals). The signal corresponding to

four boron atoms is due to coincidental overlap of two different resonances with 2 : 2 pattern.

In similarity to the synthesis of **1**, a new zwitterionic compound was obtained using tetrahydropyran instead of dioxane, giving the compound $[\text{3,3}'\text{-Co}(8\text{-C}_5\text{H}_{10}\text{O-1,2-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**2**). Purification by chromatography with methylene chloride as the mobile phase yielded **2** in a 68% yield as an orange solid.

Compounds $[\text{3,3}'\text{-Co}(8\text{-C}_4\text{H}_4\text{N}(\text{CH}_2)_5\text{-O-1,2-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**6**), $[\text{3,3}'\text{-Co}(8\text{-C}_8\text{H}_6\text{N}(\text{CH}_2)_5\text{-O-1,2-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**7**), and $[\text{3,3}'\text{-Co}(8\text{-C}_{12}\text{H}_8\text{N}(\text{CH}_2)_5\text{-O-1,2-C}_2\text{B}_9\text{H}_{10})(1',2'\text{-C}_2\text{B}_9\text{H}_{11})]^-$ (**8**) were obtained in a similar manner as **3–5**. Again, the ^1H -NMR spectra of **6–8** show very similar patterns, with four sets of resonances in the region 4.42 to 3.41 ppm: the results of two non-equivalent methylene units linked to the heteroatoms (N and O), and to the two non-equivalent sets of C–H; additionally three multiplet signals are found at higher field, between 1.88 and 1.31 ppm, corresponding to the three remaining methylene units. For compounds **7–8**, no unambiguous determination of all proton resonances associated with the B–H groups was possible, due to overlap with the methylene resonances. The $^{11}\text{B}\{^1\text{H}\}$ spectra display an identical 1 : 1 : 1 : 1 : 2 : 2 : 4 : 2 : 2 : 1 : 1 pattern for all three compounds with the signal at the lowest field corresponding, once again, to the substituted boron atom.

II Coordination motif to hard metal ions

The set of ligands **3–5** and **6–8** mostly differ in the additional chelating capacity in **3–5** provided by the $-\text{OCH}_2\text{CH}_2\text{O}-$ units. To determine its effect on coordination, solid and solution studies were conducted on the potassium salt of **3**.

A Coordination in the solid state. Crystallization by slow diffusion of hexane into a saturated dichloromethane solution of **3** at controlled temperature (4 °C) afforded air and moisture insensitive orange plate shaped monocrystals suitable for X-ray analysis. An X-ray diffraction study of the potassium salt of **3** confirmed the proposed structure. A drawing of the compound is shown in Fig. 1 and selected interatomic distances are listed in Table 1.

Table 1 Selected interatomic distances (Å) for the potassium salt of **3**, $K[3,3'-Co(8-C_4H_4N-(CH_2)_2-O-(CH_2)_2-O-1,2-C_2B_9H_{10})(1',2'-C_2B_9H_{11})]$. $H(5'_i)$ refers to $H(5)$ at equivalent position $x, 0.5 - y, 0.5 + z$, and $H(6'_j)$ and $H(11'_j)$ refer to $H(6')$ and $H(11')$ at $1 - x, 0.5 + y, 1.5 - z$

Co(3)–C(1)	2.032(5)
Co(3)–C(2)	2.035(5)
Co(3)–B(4)	2.093(5)
Co(3)–B(7)	2.095(6)
Co(3)–B(8)	2.147(6)
Co(3)–C(1')	2.076(5)
Co(3)–C(2')	2.053(5)
Co(3)–B(4')	2.097(6)
Co(3)–B(7')	2.070(6)
Co(3)–B(8')	2.117(6)
K–O(1)	2.656(4)
K–O(2)	2.937(5)
K–H(7)	2.897
K–H(12)	3.213
K–H(4')	2.949
K–H(5 _i)	2.961
K–H(11' _j)	2.988
K–H(6' _j)	3.229

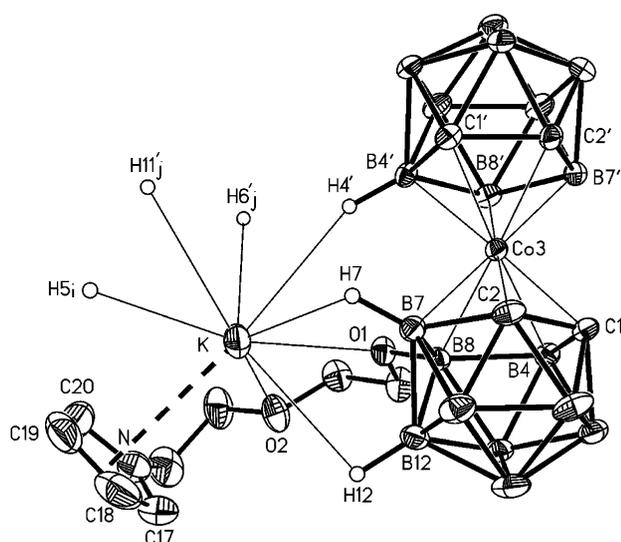


Fig. 1 Perspective drawing of the potassium salt of **3** showing the environment of K^+ . $H5_i$ refers to $H(5)$ at equivalent position $x, 0.5 - y, 0.5 + z$, and $H6'_j$ and $H11'_j$ refer to $H(6')$ and $H(11')$ at $1 - x, 0.5 + y, 1.5 - z$.

In the solid state the potassium atom is σ -bonded with the two oxygen atoms of the *exo*-cluster chain and π -bonded to the pyrrole unit with a K^+ –pyrrole centroid distance of 3.080 Å, which is smaller than the calculated¹¹ van der Waals radii. The π -bonding of pyrrole moiety is unsymmetrical as the distances from K^+ to N, C(17), C(18), C(19) and C(20) are 3.360(6), 3.249(8), 3.167(8), 3.281(9) and 3.396(9) Å, respectively. Six extra coordinating positions of the potassium cation are satisfied by B–H $\cdots K^+$ interactions from the carborane cages in the following way: i) three are intramolecular with the hydrogen atoms placed on B(7) and B(12) (cluster which contains the *exo*-cluster chain) and with the B(4')–H (from the non-substituted carborane cluster); and ii) three intermolecular interactions with the hydrogen atoms on B(5) and B(6') and B(11') of two neighboring molecules. The B–H $\cdots M^+$ interactions (M^+ , alkali metal cation) have been described in the literature, mainly with Li,¹² Na,¹³ and occasionally potassium,¹⁴ but no examples of such alkali interactions had been found with icosahedral carborane or metallocarborane clusters.

B Coordination in solution. Although definitive evidence for B–H $\cdots K^+$ interactions in the solid state is given by the X-ray analysis of potassium salt of **3**, no proof of its existence in solution has been found by measuring the $^1H\{^{11}B\}$ -NMR spectrum at room temperature. We have run low temperature

experiments with the aim of freezing out the more stable rotamers and fix specific B–H $\cdots K^+$ interactions.

Variable temperature $^1H\{^{11}B\}$ -NMR spectra recorded in the range between 37 °C and –58 °C (Fig. 2) show i) that the two

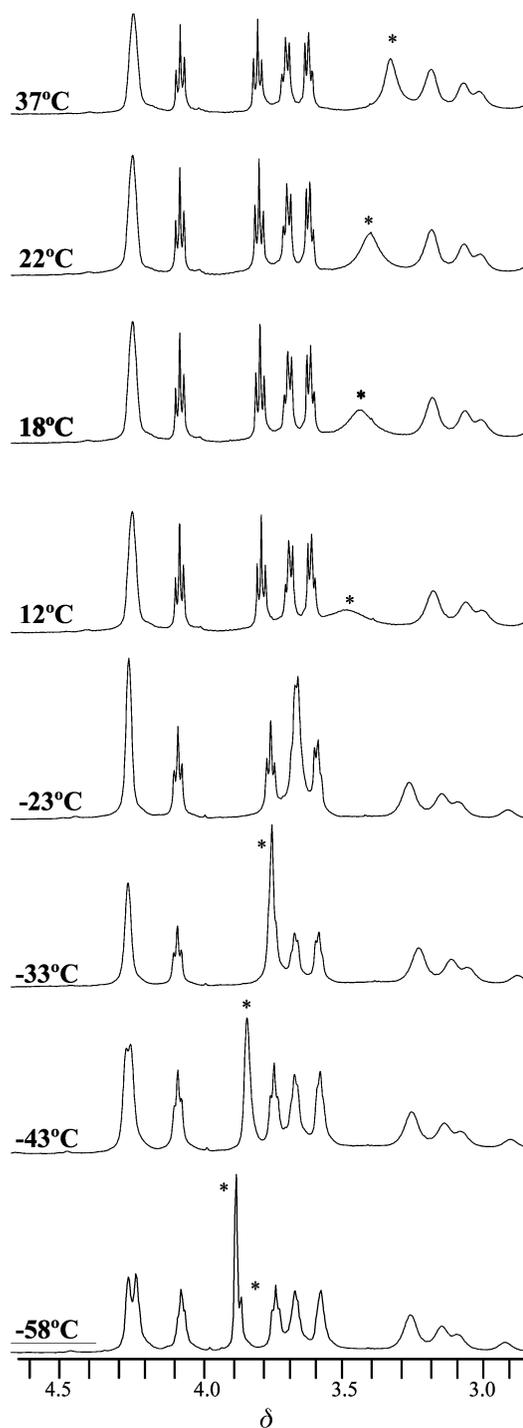


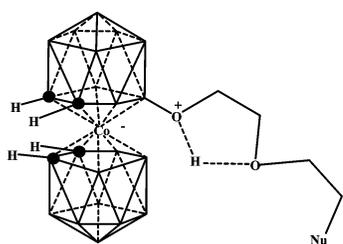
Fig. 2 $^1H\{^{11}B\}$ -NMR spectra for **3** as a function of temperature. * Signals corresponding to H atoms from intramolecular B–H $\cdots K^+$ interactions.

resonances from the pyrrolyl unit at the aromatic region exhibit a very minor shift from $\delta = 6.72$ and 5.98 to 6.79 and 5.96 ppm respectively, and ii) a high dependence of the chemical shift of the less shielded B–H signal with temperature. This B–H resonance becomes broader and shifts to lower fields as temperature decreases. At $T \geq$ room temperature the signal is a well defined singlet. When T decreases, the signal becomes a very broad singlet overlapped with the resonances corresponding to the

exo-cluster methylene units. Below $-43\text{ }^{\circ}\text{C}$, the broad signal splits into two sharp peaks at 3.87 and 3.85 ppm (3H, 2 : 1 pattern). These spectroscopic data are in agreement with the three intramolecular B–H \cdots K⁺ interactions, most probably corresponding to those observed in the solid state (Fig. 1). The NMR data above $-43\text{ }^{\circ}\text{C}$ could be explained either by the rapid exchange between the available geometric rotamers providing different B–H \cdots K⁺ interactions, or by a progressive increase in the number of molecules whose B–H \cdots K⁺ interactions have been replaced by coordinating solvent molecules.

III The role of the electron rich atom (O) directly bonded to a cluster boron atom

It has been proven that anionic clusters containing electron-rich *exo*-cluster substituents (S or P) dissipate electron density into the electron rich element. This element becomes a strong Lewis base and a very good coordinating ligand.¹⁵ Most probably the oxygen atom in the B(8)–O bond in **3–5** can play the same role as S and P atoms dissipating the negative charge and becoming a strong Lewis base. Thus, the protonated form shown in Scheme 3 could easily be formed in an almost irreversible



Scheme 3 Zwitterionic compound probably formed by protonation of the oxygen atom in addition compounds.

reaction in contact with proton atoms from an acidic media. A high pK_a acid is generated due to the strong basicity of the B–O group and the existence of a second oxygen atom that can also interact with the proton forming an O \cdots H \cdots O interaction.

IV The possible role of [3,3'-Co(1,2-C₂B₉H₁₁)₂]⁻ as a doping agent in conducting organic polymers

In a recent publication by our research group¹⁶ [3,3'-Co(1,2-C₂B₉H₁₁)₂]⁻ was used as a doping agent for conducting organic polymers providing outstanding properties to polypyrrole (PPy), the most striking one being high over-oxidation resistance. The large volume of [3,3'-Co(1,2-C₂B₉H₁₁)₂]⁻ imposes low mobility inside the polymeric matrix without any significant loss of dopant when a reducing potential is applied to the material.¹⁷ Under these conditions cation capture prevails during the reversible “doping–undoping” electrochemical redox process instead of the competing anion doping loss. Compound **3** incorporates a pyrrole unit covalently bonded to the cobaltabisdicarbollide unit by a diether aliphatic chain [3,3'-Co(8-C₄H₄N-(CH₂)₂-O-(CH₂)₂-O-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)₂]⁻. As the pyrrolyl derivatization is performed on the nitrogen atom, the α carbon atoms remain unsubstituted and are ready for subsequent polymerization of the monomer. The direct polymerization of monomer **3** as well as copolymerization with pyrrole units led to the formation of a new group of conducting polymers with the outstanding properties described for PPy-[Co(C₂B₉H₁₁)₂]¹⁶ and improved doping anion retention, self doping,¹⁸ due to covalent linkage to the pyrrolyl unit.¹⁹ In this case, the charge balancing is achieved by cation capture in the reduction process¹⁷ in contrast with common doped conducting polymers in which charge compensation in the same process is due to anion liberation.

Conclusions

The synthesis of **3–8** opens the possibility to get many derivatives of [3,3'-Co(1,2-C₂B₉H₁₁)₂]⁻ with a large variety of poor nucleophiles, such as indolyl and carbazolyl, that can lead to new conducting organic polymers. Thus, the B–O oxygen atom in **1** and **2** seems to allow the formation of addition compounds with hard (pyrrolyl) and soft (indolyl, carbazolyl) nucleophiles.

Experimental

Elemental analyses were performed using a Carlo Erba EA 1108 micro analyzer. IR spectra were recorded with KBr pellets on a FTIR-8300 Shimadzu spectrophotometer. ¹H and ¹H{¹¹B} NMR (300.13 MHz), ¹³C{¹H} NMR (75.47 MHz) and ¹¹B and ¹¹B{¹H} NMR (96.29 MHz) spectra were recorded in (CD₃)₂CO with a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories at room temperature. Chemical shift values for ¹H, ¹H{¹¹B} and ¹³C{¹H} NMR spectra were referenced to Si(CH₃)₄, and those for ¹¹B and ¹¹B{¹H} NMR spectra were referenced to (C₂H₅)₂O→BF₃. Chemical shifts are reported in units of part per million downfield from Si(CH₃)₄ and coupling constants in Hertz. MS spectra were recorded using a Bruker Biflex MALDI-TOF-MS (negative-ion mode).

Materials

Experiments were carried out, except when noted otherwise, under a dry, oxygen free dinitrogen atmosphere using standard Schlenk techniques, with some subsequent manipulation in the open laboratory. 1,4-Dioxane was freshly distilled from sodium benzophenone. The rest of the solvents were of reagent grade purity and were used without further purification. Dimethyl sulfate, indole and carbazole (Aldrich) and sulfuric acid (Merck) were used as received. The caesium salt of cobaltabisdicarbollide, Cs[Co(C₂B₁₀H₁₂)₂], was obtained from Katchem and was used without further purification. Pyrrole (Aldrich) was freshly distilled prior to use. Potassium was refluxed in anhydrous THF prior to use. Compound **1** was prepared according to literature methods.⁵

Preparation of the complexes

Synthesis and isolation of [3,3'-Co(8-C₅H₁₀O-1,2-C₂B₉H₁₀)-(1',2'-C₂B₉H₁₁)₂]⁻ (2**).** A mixture of tetrahydropyran (15 ml), the caesium salt of [Co(C₂B₉H₁₁)₂]⁻ (2.3 g, 5.0 mmol), dimethyl sulfate (1.0 ml, 10.0 mmol) and sulfuric acid (0.25 ml, 4.5 mmol) was heated at 80 °C for 10 hours with continuous stirring. The reaction mixture was filtered and the filtrate was evaporated under vacuum at room temperature to a volume of 5 ml. Purification by thin layer chromatography (silica G/dichloromethane, $R_f = 0.7$) yielded a pure orange solid (**2**) (1.40 g, 68%), (Found: C, 26.52; H 7.51. C₉B₁₈OC₅H₃₁ requires C, 26.44; H 7.64%); $\nu_{\max}/\text{cm}^{-1}$ (C–H) 3035, (C–H) 2962, 2927, (B–H) 2580, 2561 (KBr pellet); $\delta_{\text{H}} = 4.66$ [2H, s, C_c-H], 4.36 [2H, s, C_c-H], 3.98 [4H, br s, CH₂-O], 1.77 [4H, m, CH₂], 1.50 [2H, m, CH₂]; $\delta_{\text{H(B)}} = 4.66$ [2H, s, C_c-H], 4.36 [2H, s, C_c-H], 3.98 [4H, br s, CH₂-O], 3.49 [1H, br s, B–H], 3.18 [3H, br s, B–H], 2.88 [2H, br s, B–H], 2.72 [1H, br s, B–H], 2.29 [2H, br s, B–H], 2.14 [2H, br s, B–H], 1.77 [4H, m, CH₂], 1.70–1.60 [3H, B–H], 1.66 [3H, br s, B–H], 1.50 [2H, m, CH₂]; $\delta_{\text{C(HB)}} = 86.72$ [s, CH₂-O], 53.99 [s, C_c], 47.78 [s, C_c], 25.48 [s, CH₂], 19.56 [s, CH₂]; $\delta_{\text{B}} = 25.1$ [1B, s], 8.9 [1B, d, ¹J(B,H) 142], 5.1 [1B, d, ¹J(B,H) 135], -2.3 [1B], -3.7 [d, 4B, ¹J(B,H) 141], -7.3 [2B, d, ¹J(B,H) 136], -8.7 [2B, d, ¹J(B,H) 130], -14.6 [2B, d, ¹J(B,H) 156], -18.1 [2B, d, ¹J(B,H) 162], -20.5 (1B), -26.0 [1B, d, ¹J(B,H) 165].

Synthesis and isolation of [3,3'-Co(8-C₄H₄N-(CH₂)₂-O-(CH₂)₂-O-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)₂]⁻ (3**).** [3,3'-Co(8-C₄H₄N-(CH₂)₂-O-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)₂]⁻ (1.0 g, 2.4 mmol) was added to

a suspension of $K[NC_4H_4]$ (0.25 g, 2.4 mmol) in 50 ml of THF at room temperature. After 1 hour of stirring, the solvent was removed under vacuum. The resultant solid was extracted with 100 ml of diethyl ether/water (1/1), and the organic phase washed twice with water and dried under vacuum overnight (1.05 g, 84%), (Found: C, 28.21; H, 6.52; N, 2.70). $KC_{12}H_{33}B_{18}CoNO_2$ requires C, 27.93; H, 6.45; N, 2.71%; ν_{max}/cm^{-1} ($C-C-H$) 3043, ($C-H$) 2931, 2873, ($B-H$) 2565, 2546 (KBr pellet); $\delta_H = 6.73$ [2H, s, $N-C_{pyr}-H$], 5.98 [2H, s, $C_{pyr}-C_{pyr}-H$], 4.26 [4H, br s, $C-C-H$], 4.06 [2H, t, $^1J(H,H)$ 5.6, CH_2], 3.70 [2H, t, $^1J(H,H)$ 5.6, CH_2], 3.56 [2H, t, $^1J(H,H)$ 4.7, CH_2], 3.47 [2H, t, $^1J(H,H)$ 4.7, CH_2]; $\delta_{H(B)}$ = 6.73 [2H, s, $N-C_{pyr}-H$], 5.98 [2H, s, $C_{pyr}-C_{pyr}-H$], 4.26 [4H, br s, $C-C-H$], 4.06 [2H, t, $^1J(H,H)$ 5.6, CH_2], 3.70 [2H, t, $^1J(H,H)$ 5.6, CH_2], 3.56 [2H, br s, CH_2], 3.47 [2H, t, $^1J(H,H)$ 4.7, CH_2], 3.26 [3H, br s, $B-H$], 2.91 [2H, br s, $B-H$], 2.75 [1H, br s, $B-H$], 2.69 [1H, br s, $B-H$], 2.45 [1H, br s, $B-H$], 1.98 [2H, br s, $B-H$], 1.79 [2H, br s, $B-H$], 1.66 [2H, br s, $B-H$], 1.55 [2H, br s, $B-H$], 1.46 [1H, br s, $B-H$]; $\delta_{C(H)}$ = 120.73 [s; $N-C_{pyr}$], 107.48 [s, $C_{pyr}-C_{pyr}$], 71.78, 70.99, 68.31, 54.34, 49.08, 46.40 [s, C_c and CH_2]; $\delta_B = 23.7$ [s, 1B], 4.7 [1B, d, $^1J(B,H)$ 133], 1.2 [1B, d, $^1J(B,H)$ 141], -1.7 [1B, d, $^1J(B,H)$ 148], -3.5 [2B, d, $^1J(B,H)$ 162], -6.6 [2B], -7.4 [4B], -16.5 [2B, d, $^1J(B,H)$ 162], -19.6 [2B, d, $^1J(B,H)$ 151], -21.2 [1B], -27.7 [1B, d, $^1J(B,H)$ 151].

Synthesis and isolation of [3,3'-Co(8-C₈H₆N-(CH₂)₂-O-(CH₂)₂-O-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)]⁻ (4). [3,3'-Co(8-C₄H₈-O₂-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)] (1) (0.50 g, 1.2 mmol) was dissolved in a suspension of $K[NC_4H_4]$ (0.22g, 1.4 mmol) in 50 ml of THF at room temperature. After 30 minutes of stirring, the solvent was removed under vacuum. The resultant dark oil was extracted with 100 ml of diethyl ether/water (1/1). The organic phase was dried with magnesium sulfate and evaporated. The resultant orange solid was submitted to soxhlet extraction with hexane for 10 hours. The amount of indole present was followed by TLC. The resultant orange solid was dried under vacuum and characterized (0.60 g, 87%), (Found: C, 33.80; H, 6.40; N, 2.51). $KC_{16}B_{18}NO_2CoH_{35}$ requires C, 33.95; H, 6.23; N, 2.47%; ν_{max}/cm^{-1} ($C-C-H$) 3031, ($C-H$) 2923, 2869, ($B-H$) 2563, 2540 (KBr pellet); $\delta_H = 7.53$ [1H, d, $^1J(H,H)$ 8.2, $C_{aryl}-H$], 7.43 [1H, d, $^1J(H,H)$ 8.2, $C_{aryl}-H$], 7.35 [1H, d, $^1J(H,H)$ 2.8, $C_{aryl}-H$], 7.14 [1H, t, $^1J(H,H)$ 8.2, $C_{aryl}-H$], 7.01 [1H, t, $^1J(H,H)$ 8.2, $C_{aryl}-H$], 6.43 [1H, d, $^1J(H,H)$ 2.8, $C_{aryl}-H$], 4.37 [2H, t, $^1J(H,H)$ 5.6, CH_2], 4.32 [2H, br s, $C-C-H$], 4.29 [2H, br s, $C-C-H$], 3.82 [2H, t, $^1J(H,H)$ 5.6, CH_2], 3.57 [2H, t, $^1J(H,H)$ 4.1, CH_2], 3.49 [2H, t, $^1J(H,H)$ 4.1, $N-CH_2$]; $\delta_{H(B)}$ = 7.53 [1H, d, $^1J(H,H)$ 8.2, $C_{aryl}-H$], 7.43 [1H, d, $^1J(H,H)$ 8.2, $C_{aryl}-H$], 7.35 [1H, d, $^1J(H,H)$ 2.8, $C_{aryl}-H$], 7.14 [1H, t, $^1J(H,H)$ 8.2, $C_{aryl}-H$], 7.01 [1H, t, $^1J(H,H)$ 8.2, $C_{aryl}-H$], 6.43 [1H, d, $^1J(H,H)$ 2.8, $C_{aryl}-H$], 4.37 [2H, t, $^1J(H,H)$ 5.6, CH_2], 4.32 [2H, br s, $C-C-H$], 4.29 [2H, br s, $C-C-H$], 3.82 [2H, t, $^1J(H,H)$ 5.6, CH_2], 3.57 [2H, t, $^1J(H,H)$ 4.1, CH_2], 3.49 [2H, t, $^1J(H,H)$ 4.1, $N-CH_2$], 2.95 [3H, br s, $B-H$], 2.81 [2H, br s, $B-H$], 2.71 [1H, br s, $B-H$], 2.49 [1H, br s, $B-H$], 2.00 [2H, br s, $B-H$], 1.82 [2H, br s, $B-H$], 1.76 [1H, br s, $B-H$], 1.71 [2H, br s, $B-H$], 1.58 [2H, br s, $B-H$], 1.49 [1H, br s, $B-H$]; $\delta_{C(H)}$ = 140.21, 131.94, 128.71, 120.95, 120.38, 118.85, 109.57, 100.62 [s, C_{aryl}], 71.89, 69.89, 68.34, 54.34, 50.18, 45.90 [s, C_c ; s, CH_2]; $\delta_B = 23.2$ [1B, s], 4.3 [1B, d, $^1J(B,H)$ 135], 0.7 [1B, d, $^1J(B,H)$ 141], -2.2 [1B, d, $^1J(B,H)$ 155], -4.0 [2B, d, $^1J(B,H)$ 162], -7.1 [2B], -8.0 [4B], -17.0 [2B, d, $^1J(B,H)$ 153], -20.1 [2B, d, $^1J(B,H)$ 153], -21.6 [1B], -28.2 [1B, d, $^1J(B,H)$ 164]; MALDI-TOF MS: m/z 529.7 ($M^+ - K$).

Synthesis and isolation of [3,3'-Co(8-C₁₂H₈N-(CH₂)₂-O-(CH₂)₂-O-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)]⁻ (5). The procedure was the same as that used for 4 but a suspension of potassium carbazolyl (0.29 g, 1.4 mmol) in 50 ml of THF was used as a nucleophilic agent at room temperature. Soxhlet extraction time: 24 hours (0.62 g, 83%), (Found: C, 39.02; H, 6.02; N, 2.10). $KC_{20}B_{18}NO_2CoH_{37}$ requires C, 38.99; H, 6.05; N, 2.27%; ν_{max}/cm^{-1} ($C-C-H$) 3028, ($C-H$) 2931, 2862, ($B-H$) 2558, 2542 (KBr

pellet); $\delta_H = 8.13$ [2H, d, $^1J(H,H)$ 8.1, $C_{aryl}-H$], 7.64 [2H, d, $^1J(H,H)$ 8.2, $C_{aryl}-H$], 7.47 [2H, dd, $^1J(H,H)$ 8.1, $^1J(H,H)$ 7.7, $C_{aryl}-H$], 7.20 [2H, dd, $^1J(H,H)$ 8.2, $^1J(H,H)$ 7.7, $C_{aryl}-H$], 4.60 [2H, t, $^1J(H,H)$ 5.4, CH_2], 4.38 [2H, s, $C-C-H$], 4.31 [2H, s, $C-C-H$], 3.89 [2H, t, $^1J(H,H)$ 5.4, CH_2], 3.54 [2H, t, $^1J(H,H)$ 4.1, CH_2], 3.48 [2H, t, $^1J(H,H)$ 4.1, CH_2]; $\delta_{H(B)}$ = 8.13 [2H, d, $^1J(H,H)$ 8.1, $C_{aryl}-H$], 7.64 [2H, d, $^1J(H,H)$ 8.2, $C_{aryl}-H$], 7.47 [2H, dd, $^1J(H,H)$ 8.1, $^1J(H,H)$ 7.7, $C_{aryl}-H$], 7.20 [2H, dd, $^1J(H,H)$ 8.2, $^1J(H,H)$ 7.7, $C_{aryl}-H$], 4.60 [2H, t, $^1J(H,H)$ 5.4, CH_2], 4.38 [2H, s, $C-C-H$], 4.31 [2H, s, $C-C-H$], 3.89 [2H, t, $^1J(H,H)$ 5.4, CH_2], 3.54 [2H, t, $^1J(H,H)$ 4.1, CH_2], 3.48 [2H, t, $^1J(H,H)$ 4.1, CH_2], 2.97 [3H, br s, $B-H$], 2.85 [2H, br s, $B-H$], 2.73 [1H, br s, $B-H$], 2.48 [1H, br s, $B-H$], 2.01 [2H, br s, $B-H$], 1.84 [3H, br s, $B-H$], 1.75 [2H, br s, $B-H$], 1.60 [2H, br s, $B-H$], 1.51 [1H, br s, $B-H$]; $\delta_{C(H)}$ = 140.76, 125.56, 122.71, 119.86, 109.41 [s, C_{aryl}], 72.15, 69.17, 68.34, 54.56, 46.43, 43.07 [s, C_c ; s, CH_2]; $\delta_B = 23.1$ [1B, s], 4.1 [1B, d, $^1J(B,H)$ 136], 0.7 [1B, d, $^1J(B,H)$ 138], -2.2 [1B, d, $^1J(B,H)$ 153], -3.9 [2B, d, $^1J(B,H)$ 156], -7.2 [2B], -8.0 [4B], -17.0 [2B, d, $^1J(B,H)$ 151], -20.2 [2B, d, $^1J(B,H)$ 152], -21.6 [1B], -28.2 [1B, d, $^1J(B,H)$ 159]; MALDI-TOF MS: m/z 579.7 ($M^+ - K$).

Synthesis and isolation of [3,3'-Co(8-C₄H₄N-(CH₂)₅-O-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)]⁻ (6). The procedure was the same as that used for 4 but [3,3'-Co(8-C₅H₁₀O-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)] (2) (0.57 g, 1.4 mmol) was used as starting material and a suspension of $K[NC_4H_4]$ (0.13 g, 1.2 mmol) in THF at room temperature was used as nucleophilic agent. Soxhlet extraction time: 2 hours (0.50 g, 80%), (Found: C, 30.28; H, 6.72; N, 2.71). $KC_{13}B_{18}NOCoH_{35}$ requires C, 30.37; H, 6.86; N, 2.72%; ν_{max}/cm^{-1} ($C-C-H$) 3035, ($C-H$) 2928, 2858, ($B-H$) 2572, 2541 (KBr pellet); $\delta_H = 6.68$ [2H, s, $N-C_{pyr}-H$], 5.97 [2H, s, $C_{pyr}-C_{pyr}-H$], 4.26 [2H, br s, $C-C-H$], 4.22 [2H, br s, $C-C-H$], 3.88 [2H, t, $^1J(H,H)$ 7.4, $O-CH_2$], 3.42 [2H, t, $^1J(H,H)$ 6.1, $N-CH_2$], 1.73 [2H, m, CH_2], 1.47 [2H, m, CH_2], 1.31 [2H, m, CH_2]; $\delta_{H(B)}$ = 6.68 [2H, s, $N-C_{pyr}-H$], 5.97 [2H, s, $C_{pyr}-C_{pyr}-H$], 4.26 [2H, br s, $C-C-H$], 4.22 [2H, br s, $C-C-H$], 3.88 [2H, t, $^1J(H,H)$ 7.4, $O-CH_2$], 3.42 [2H, t, $^1J(H,H)$ 6.1, $N-CH_2$], 3.02 [3H, br s, $B-H$], 2.74 [2H, br s, $B-H$], 2.69 [2H, br s, $B-H$], 2.43 [1H, br s, $B-H$], 1.98 [3H, br s, $B-H$], 1.73 [2H, m, CH_2], 1.65 [3H, br s, $B-H$], 1.54 [3H, br s, $B-H$], 1.47 [2H, m, CH_2], 1.31 [2H, m, CH_2]; $\delta_{C(H)}$ = 120.18 [s, $N-C_{pyr}$], 107.33 [s, $C_{pyr}-C_{pyr}$], 68.43, 54.28, 49.10, 46.34 [s, C_c ; s, $O-CH_2$; s, $N-CH_2$], 31.45, 31.30, 23.18 [s, CH_2]; $\delta_B = 23.8$ [1B, s], 4.6 [1B, d, $^1J(B,H)$ 138], 1.0 [1B, d, $^1J(B,H)$ 142], -1.7 [1B, d, $^1J(B,H)$ 165], -3.6 [2B, d, $^1J(B,H)$ 65], -6.7 [2B], -7.4 [4B], -16.6 [2B, d, $^1J(B,H)$ 153], -19.6 [2B, d, $^1J(B,H)$ 157], -21.3 [1B], -27.8 [1B, d, $^1J(B,H)$ 157]; MALDI-TOF MS: m/z 477.7 ($M^+ - K$).

Synthesis and isolation of [3,3'-Co(8-C₈H₆N-(CH₂)₅-O-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)]⁻ (7). The procedure was the same as that used for 4 but [3,3'-Co(8-C₅H₁₀O-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)] (0.57 g, 1.4 mmol) was used as starting material (0.60 g, 89%), (Found: C, 36.31; H, 6.80; N, 2.33). $KC_{17}B_{18}NOCoH_{37}$ requires C, 36.19; H, 6.61; N, 2.48%; ν_{max}/cm^{-1} ($C-C-H$) 3038, ($C-H$) 2932, 2860, ($B-H$) 2558, 2529 (KBr pellet); $\delta_H = 7.53$ [1H, d, $^1J(H,H)$ 7.7, $C_{aryl}-H$], 7.45 [1H, d, $^1J(H,H)$ 8.2, $C_{aryl}-H$], 7.28 [1H, d, $^1J(H,H)$ 2.8, $C_{aryl}-H$], 7.13 [1H, dd, $^1J(H,H)$ 8.2, $^1J(H,H)$ 7.4, $C_{aryl}-H$], 6.99 [1H, dd, $^1J(H,H)$ 7.7, $^1J(H,H)$ 7.4, $C_{aryl}-H$], 6.43 [1H, d, $^1J(H,H)$ 2.8, $C_{aryl}-H$], 4.27 [2H, br s, $C-C-H$], 4.22 [2H, br s, $C-C-H$], 4.19 [2H, t, $^1J(H,H)$ 7.4, $O-CH_2$], 3.41 [2H, t, $^1J(H,H)$ 6.0, $N-CH_2$], 1.83 [2H, m, CH_2], 1.51 [2H, m, CH_2], 1.37 [2H, m, CH_2]; $\delta_{H(B)}$ = 7.53 [1H, d, $^1J(H,H)$ 7.7, $C_{aryl}-H$], 7.45 [1H, d, $^1J(H,H)$ 8.2, $C_{aryl}-H$], 7.28 [1H, d, $^1J(H,H)$ 2.8, $C_{aryl}-H$], 7.13 [1H, dd, $^1J(H,H)$ 8.2, $^1J(H,H)$ 7.4, $C_{aryl}-H$], 6.99 [1H, dd, $^1J(H,H)$ 7.7, $^1J(H,H)$ 7.4, $C_{aryl}-H$], 6.43 [1H, d, $^1J(H,H)$ 2.8, $C_{aryl}-H$], 4.27 [2H, br s, $C-C-H$], 4.22 [2H, br s, $C-C-H$], 4.19 [2H, t, $^1J(H,H)$ 7.4, $O-CH_2$], 3.41 [2H, t, $^1J(H,H)$ 6.0, $N-CH_2$], 2.90 [3H, br s, $B-H$], 2.79 [2H, br s, $B-H$], 2.71 [1H, br s, $B-H$], 2.48 [1H, br s, $B-H$], 2.00 [2H, br s, $B-H$], 1.90-1.80

Table 2 Crystallographic data for potassium salt of **3**, K[3,3'-Co(8-C₄H₄N-(CH₂)₂-O-(CH₂)₂-O-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)]

Empirical formula	C ₁₂ H ₃₃ B ₁₈ CoKNO ₂
Formula weight	516.00
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	15.305(3)
b/Å	12.316(2)
c/Å	13.848(3)
β/°	99.31(3)
V/Å ³	2575.9(9)
Z	4
D _{calc} /g cm ⁻³	1.331
μ(Mo-Kα)/cm ⁻¹	8.42
Data/parameters	4547/316
R1(F _o) ^a [I > 2σ(I)]	0.0560
wR2(F _o ²) ^b [I > 2σ(I)]	0.1264

^a R1 = Σ||F_o| - |F_c||/Σ|F_o|. ^b wR2 = [Σw(|F_o² - |F_c²||²)/Σw|F_o²|²]^{1/2}.

[2H, B-H], 1.83 [2H, m, CH₂], 1.70 [3H, br s, B-H], 1.51 [2H, m, CH₂], 1.60–1.40 [3H, B-H], 1.37 [2H, m, CH₂]; δ_{C(HH)} = 137.26, 129.91, 129.19, 122.10, 121.62, 119.91, 110.69, 101.59 [s, C_{aryl}], 69.53, 55.45, 47.51, 47.12, [s, C_c; s, O-CH₂; s, N-CH₂], 32.53, 31.17, 24.55 [s, CH₂]; δ_B = 23.4 [1B, s], 4.2 [1B, d, ¹J(B,H) 138], 0.5 [1B, d, ¹J(B,H) 141], -2.2 [1B, d, ¹J(B,H) 164], -4.1 [2B, d, ¹J(B,H) 165], -7.2 [2B], -8.0 [4B], -17.1 [2B, d, ¹J(B,H) 153], -20.1 [2B, d, ¹J(B,H) 158], -21.8 [1B], -28.3 [1B, d, ¹J(B,H) 156]; MALDI-TOF MS: m/z 527.8 (M⁺ - K).

Synthesis and isolation of [3,3'-Co(8-C₁₂H₈N-(CH₂)₅-O-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)]⁻ (8**).** The procedure was the same as that used for **5** but [3,3'-Co(8-C₅H₁₀O-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)] (0.57 g, 1.4 mmol) was used as starting material (0.60 g, 80%), (Found: C, 41.17; H, 6.21; N, 2.31. KC₂₁B₁₈NOC₁₀H₃₉ requires C, 41.07; H, 6.40; N, 2.28%); ν_{max}/cm⁻¹ (C_c-H) 3036, (C-H) 2937, 2854, (B-O) 2560, 2535 (KBr pellet); δ_H = 8.12 [2H, d, ¹J(H,H) 7.7, C_{aryl}-H], 7.60 [2H, d, ¹J(H,H) 8.2, C_{aryl}-H], 7.47 [2H, dd, ¹J(H,H) 8.2, ¹J(H,H) 7.4, C_{aryl}-H], 7.20 [2H, dd, ¹J(H,H) 7.4, ¹J(H,H) 7.7, C_{aryl}-H], 4.42 [2H, t, ¹J(H,H) 7.1, O-CH₂], 4.29 [2H, s, C_c-H], 4.26 [2H, s, C_c-H], 3.46 [2H, t, ¹J(H,H) 6.0, N-CH₂], 1.88 [2H, m, CH₂], 1.54 [4H, m, CH₂]; δ_{H(B)} = 8.12 [2H, d, ¹J(H,H) 7.7, C_{aryl}-H], 7.60 [2H, d, ¹J(H,H) 8.2, C_{aryl}-H], 7.47 [2H, dd, ¹J(H,H) 8.2, ¹J(H,H) 7.4, C_{aryl}-H], 7.20 [2H, dd, ¹J(H,H) 7.1, O-CH₂], 4.29 [2H, s, C_c-H], 4.26 [2H, t, ¹J(H,H) 6.0, N-CH₂], 2.92 [3H, br s, B-H], 2.84 [2H, br s, B-H], 2.72 [1H, br s, B-H], 2.51 [1H, br s, B-H], 2.02 [2H, br s, B-H], 1.88 [2H, m, CH₂], 1.85–1.75 [2H, B-H], 1.73 [3H, br s, B-H], 1.54 [4H, m, CH₂], 1.60–1.35 [3H, B-H]; δ_{C(HH)} = 140.41, 125.60, 122.66, 120.00, 118.56, 109.04 [s, C_{aryl}], 68.25, 54.30, 46.38, 42.72 [s, C_c; s, O-CH₂; s, N-CH₂], 31.53, 30.16, 23.56 [s, CH₂]; δ_B = 23.3 [1B, s], 4.2 [1B, d, ¹J(B,H) 133], 0.5 [1B, d, ¹J(B,H) 148], -2.2 [1B, d, ¹J(B,H) 161], -4.1 [2B, d, ¹J(B,H) 162], -7.2 [2B], -8.0 [4B], -17.1 [2B, d, ¹J(B,H) 152], -20.1 [2B, d, ¹J(B,H) 158], -21.8 [1B], -28.3 [1B, d, ¹J(B,H) 153]; MALDI-TOF MS: m/z 577.8 (M⁺ - K).

X-Ray crystallographic study

Single-crystal data collection for potassium salt of **3**, K[3,3'-Co(8-C₄H₄N-(CH₂)₂-O-(CH₂)₂-O-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)], was performed at 294 K on a Rigaku AFC7S diffractometer using graphite monochromatized Mo-Kα radiation (2θ_{max} = 50°). The structure was solved by direct methods and refined on F² by the SHELX-97 program package.²⁰ Non-hydrogen atoms were refined with anisotropic displacement parameters, and the hydrogen atoms were treated as riding atoms using the SHELX-97 default parameters. Crystallographic data for the potassium salt of **3** are given in Table 2.

CCDC reference number 168258.

See <http://www.rsc.org/suppdata/dt/b2/b211860m/> for crystallographic data in CIF or other electronic format.

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