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Preliminary communication

A new approach to the coordination of anions, novel polycobalticinium macrocyclic receptor molecules

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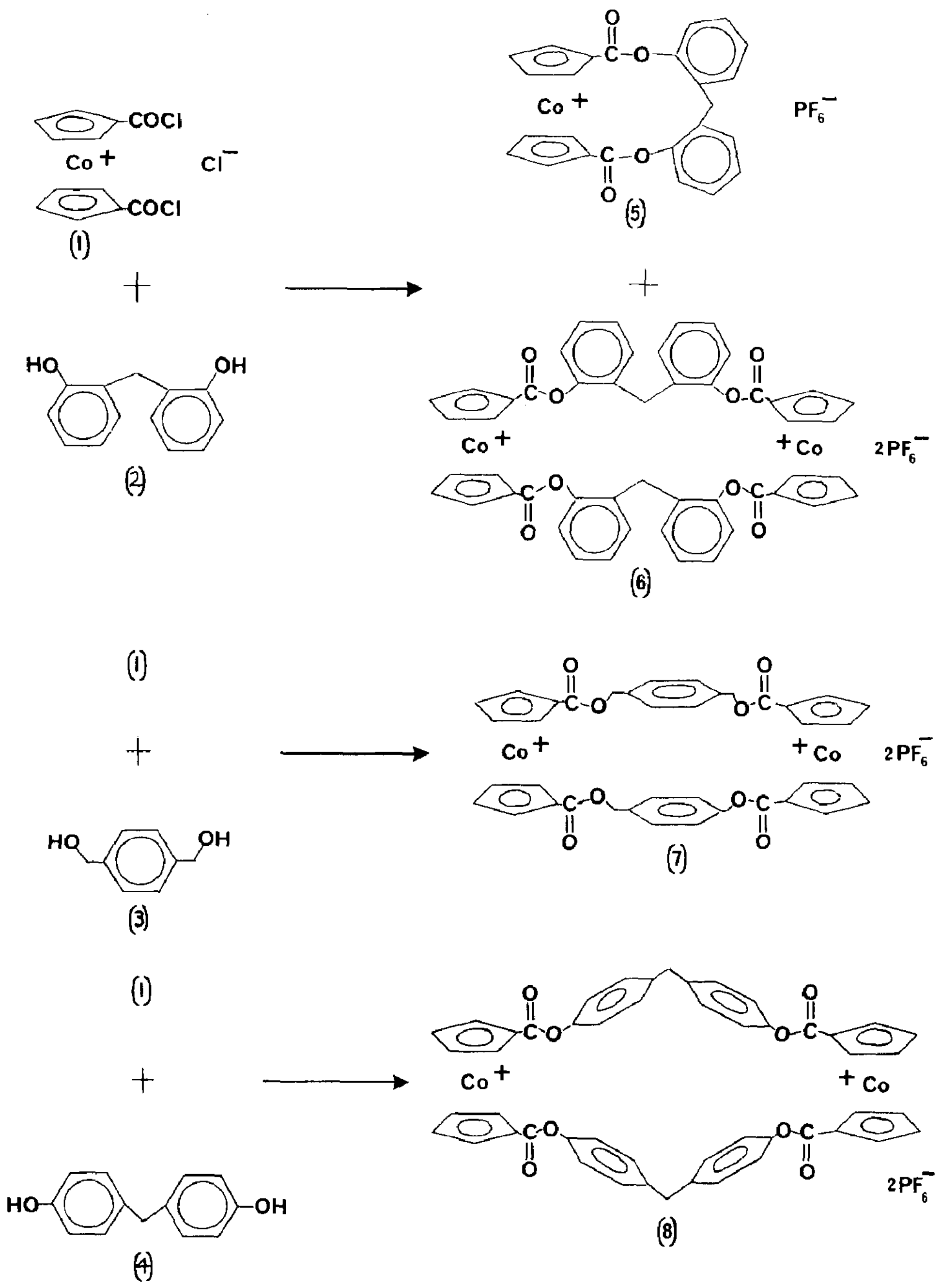
Abstract

The syntheses and electrochemistry of four novel polycobalticinium macrocyclic receptor molecules are reported. Preliminary anion coordination studies in one case reveal the receptor to be redox responsive to the binding of a Br^- guest anion, shifting the respective cobalticinium reduction wave to more negative potentials.

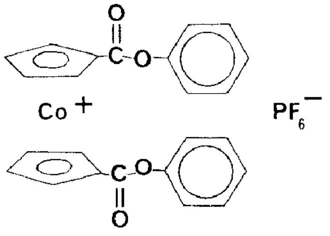
Anion coordination chemistry, the complexation of anionic species by organic receptor molecules has only recently been recognised and developed as a new field of coordination chemistry [1,2]. This is somewhat surprising in view of the fundamental role played by anions in chemical as well as in biological processes [3]. Several classes of anion ligands have been reported, including Lewis acidic bicyclic tin cryptands [4], organomercury [5] and silicon [6] macrocycles, quaternary ammonium [7], polyguanidinium and polyammonium macrocyclic molecules [8–10]. The latter positively charged pH-dependent class of host form strong and sometimes selective complexes with a variety of anions, including the binding of linear dicarboxylates with chain length selectivity [11]. We report here the synthesis and electrochemistry of the first redox responsive class of anion-receptor polycobalticinium macrocycles which are designed to ultilise the pH-independent positively charged eighteen electron air stable organometallic and redox-active cobalticinium fragment to coordinate and respond electrochemically to the binding of anionic guest species.

The condensation of 1,1′-bis(chlorocarbonyl)cobalticinium chloride (**1**) [12] with respectively 2,2′-bis(hydroxyphenyl)methane (**2**), 1,4-benzene dimethanol (**3**) and 4,4′-bis(hydroxyphenyl)methane (**4**) in the presence of triethylamine followed by column chromatography (Sephadex LH20, acetonitrile) and excess ammonium hexafluorophosphate gave the new macrocycles **5**, **6**, **7** and **8** as yellow powders Scheme 1. Elemental analyses, fast atom bombardment mass spectrometry (FABMS), ^{1}H NMR and conductivity measurements confirmed the proposed structures.



Scheme 1

The first evidence indicating that these receptors could complex anionic guests came from FABMS studies. The FABMS spectrum of **8** revealed, in addition to the molecular ion peak at 882, smaller signals at 899, 917 and 1027 mass units tentatively assigned to hydroxide, chloride and hexafluorophosphate complexes respectively. Analogous results were found with **6** and **7**. Fourier transform infrared (FTIR) investigations of the chloride and hexafluorophosphate salts of **6**, **7** and **8** revealed up to 8 cm^{-1} differences in the respective carbonyl ester absorption



(9)

positions. For example, the hexafluorophosphate salt of **6** gave an ester carbonyl stretch at 1747 cm^{-1}, whereas the analogous chloride salt absorbed at 1739 cm^{-1}. Interestingly, this effect was not observed with the hexafluorophosphate and chloride salts of the acyclic model **9**, suggesting the presence of a macrocyclic effect [13] in these systems.

Cyclic voltammetric investigations were carried out in acetonitrile using $[n\text{-}Bu_4N]BF_4$ as the supporting electrolyte and standard calomel electrode (SCE) as reference. Reversible two electron reduction waves in the region −0.25 to −0.35 V were observed with **6**, **7** and **8**. The addition of stoichiometric amounts of tetrabutyl ammonium bromide to electrochemical solutions of **6** led to gradual cathodic shifts of the host's reduction wave. A maximum shift of 45 mV was observed after four equivalents of bromide salt had been added. No cathodic shifts were observed with **9**, suggesting bromide anion complexation within the macrocyclic cavity of **6** is essential for electrochemical detection. Analogous experiments with **7**, **8** and bromide and other halide salts were unfortunately hampered by spontaneous precipitation reactions of the corresponding anion-complexed species [14]. Complexation studies of these and related polycobalticinium receptors with other anions such as phosphate, sulphate and nitrate are currently under investigation.

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14 ^1H NMR complexation studies were also not possible because of solubility and precipitation problems.