ABSTRACT

Compounds with carboxylic and amidic functions belong to basic structural blocks, which are used for construction of functional molecules in organic, organometallic and also in carborane chemistry. However, considering cobalt bis(dicarbollide)(1-) ion, the synthetic ways to these derivatives have been virtually unknown. A published procedure on lithiation in THF and reaction with CO_2 leading to mono- and dicarboxylic acids had failed in our hands. Nevertheless, a detailed revision of the experimental conditions provided finally good yields of mixture of both acids, which could be separated by chromatography and crystallization, and compound of general formulation $[(1\text{-}HOOC\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{10})\text{-}3,3'\text{-}Co(III)]^-$ and stereoisomeric mixture of $[(HOOC)_2\text{-}(1,2\text{-}C_2B_9H_{10})_2\text{-}3,3'\text{-}Co(III)]^-$ were characterized for the first time by combination of NMR, MS and HPLC. Also, the carboxylic acid derivatives with methylene and ethylene connectors of the general formula $[(1\text{-}HOOC\text{-}(CH_2)_n\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{10})\text{-}3,3'\text{-}Co(III)]^-$ were prepared by lithiation of Cs**1** in DME at low temperatures followed by reaction with $BrCH_2COOEt$ and subsequent hydrolysis of the resulting ester or by oxidation of the respective propylhydroxy derivative. The acids were converted to reactive *p*-nitrophenyl esters $[1\text{-}(1,4\text{-}NO_2C_6H_4OOC\text{-}(CH_2)_n\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{10})\text{-}3,3'\text{-}Co(III)]^-$, which readily reacts with various amines under mild conditions with formation of amidic bonds. The synthetic ways to these compounds open new possibilities in design of biologically active metallacarboranes addressing various therapeutic targets. Indeed, syntheses of new covalently bonded compounds were performed and research on biologically active derivatives is still in the progress.