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Controlled Direct Synthesis of C-Mono- and C-Disubstituted Derivatives of $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ with Organosilane Groups: Theoretical Calculations Compared with Experimental Results

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Abstract: Mono- and dilithium salts of $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$, ($\mathbf{1}^-$), react with different chlorosilanes (Me_2SiHCl, Me_2SiCl_2, Me_3SiCl and $MeSiHCl_2$) with an accurate control of the temperature to give a set of novel C_c-mono- ($C_c = C_{cluster}$) and C_c-disubstituted cobaltabis(dicarbollide) derivatives with silyl functions: $[1\text{-}SiMe_2H\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$ ($\mathbf{3}^-$); $[1,1'\text{-}\mu\text{-}SiMe_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ ($\mathbf{4}^-$); $[1,1'\text{-}\mu\text{-}SiMeH\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ ($\mathbf{5}^-$); $[1\text{-}SiMe_3\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$ ($\mathbf{6}^-$) and $[1,1'\text{-}(SiMe_3)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ ($\mathbf{7}^-$). In a similar way, the $[8,8'\text{-}\mu\text{-}(1'',2''\text{-}C_6H_4)\text{-}1,1'\text{-}\mu\text{-}SiMe_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_9)_2]^-$ ($\mathbf{8}^-$); $[8,8'\text{-}\mu\text{-}(1'',2''\text{-}C_6H_4)\text{-}1,1'\text{-}\mu\text{-}SiMeH\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_9)_2]^-$ ($\mathbf{9}^-$) and $[8,8'\text{-}\mu\text{-}(1'',2''\text{-}C_6H_4)\text{-}1\text{-}SiMe_3\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_9)(1',2'\text{-}C_2B_9H_{10})]^-$ ($\mathbf{10}^-$) ions have been prepared from $[8,8'\text{-}\mu\text{-}(1'',2''\text{-}C_6H_4)\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ ($\mathbf{2}^-$). Thus, depending on the chlorosilane, the temperature and the stoichiometry of *n*BuLi used, it has been possible to control the number of substituents on the C_c atoms and the nature of the attached silyl function. All compounds were characterised by NMR and UV/Vis spectroscopy and MALDI-TOF mass spectrometry; $[NMe_4]$-**3**, $[NMe_4]$-**4** and $[NMe_4]$-**7** were successfully isolated in crystalline forms suitable for X-ray diffraction analyses. The $\mathbf{4}^-$ and $\mathbf{8}^-$ ions, which contain one bridging -μ-$SiMe_2$ group between each of the dicarbollide clusters, were unexpectedly obtained from the reaction of the monolithium salts of $\mathbf{1}^-$ and $\mathbf{2}^-$, respectively, with Me_2SiHCl at −78 °C in 1,2-dimethoxyethane. This suggests that an intramolecular reaction has taken place, in which the acidic C_c–H proton reacts with the hydridic Si–H, with subsequent loss of H_2. Some aspects of this reaction have been studied by using DFT calculations and have been compared with experimental results. In addition, DFT theoretical studies at the B3LYP/6-311G(d,p) level of theory were applied to optimise the geometries of ions $\mathbf{1}^-$–$\mathbf{10}^-$ and calculate their relative energies. Results indicate that the racemic mixtures, *rac* form, are more stable than the *meso* isomers. A good concordance between theoretical studies and experimental results has been achieved.

Keywords: carboranes · cluster compounds · density functional calculations · sandwich complexes · silanes

Introduction

In the last four decades, interest in the functionalisation and application of the cobaltabis(dicarbollide) ion $\mathbf{1}^-$ and its derivatives has grown due to their extraordinary chemical, thermal and radiation stability, and their similar properties to the inorganic superacids.[1] In addition, these compounds are hydrophobic[2,3] and weakly coordinating anions,[4] which have made them appropriate to be used as solid electrolytes,[3] strong non-oxidizing acids,[3] doping agents in conducting polymers[5] and extractants of radionuclides.[6] Cobaltabis(dicarbollide) derivative have also been used in diverse applications such as medical imaging and radiothera-

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