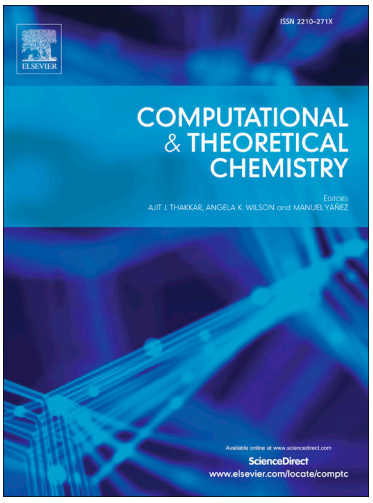

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Exohedral Complexation of B_{39}^- with ECp^{*+} Half-sandwich Complexes (E= Si, Ge, Sn, Pb) : A DFT Study

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Abstract

The hexagonal and heptagonal holes of B_{39}^- allow its complexation with a half sandwich complex ECp^{*+} (E= Si, Ge, Sn, Pb). Structure and the nature of bonding of $(\eta^{6/7}\text{-}B_{39})E(\eta^5\text{-}Cp^*)$ are explored through the density functional theory based computation. $(\eta^6\text{-}B_{39})E(\eta^5\text{-}Cp^*)$ isomers are more stable than $(\eta^7\text{-}B_{39})E(\eta^5\text{-}Cp^*)$ and the energy difference between these two isomers decreases down the group from Si to Pb. The dissociation path, $(\eta^{6/7}\text{-}B_{39})E(\eta^5\text{-}Cp^*) \rightarrow B_{39}^- + ECp^{*+}$ is studied. For all E, $(\eta^{6/7}\text{-}B_{39})E(\eta^5\text{-}Cp^*)$ is formed exergonically at 298 K temperature as given by the ΔG values of dissociation path [60.1(Si) to 68.3(Pb) kcal/mol for $(\eta^6\text{-}B_{39})E(\eta^5\text{-}Cp^*)$ and 58.3(Si) to 67.8(Pb) kcal/mol for $(\eta^7\text{-}B_{39})E(\eta^5\text{-}Cp^*)$]. The adduct becomes bent around the central E atom when B_{39}^- gets attached to ECp^{*+} and the amount of bending increases gradually down the group from Si to Pb. Bonding analysis of the stable isomer, $(\eta^6\text{-}B_{39})E(\eta^5\text{-}Cp^*)$ has been done by natural bonding orbital (NBO) and energy decomposition analyses (EDA). The electron density from B_{39}^- is transferred to the ECp^{*+} moiety as revealed by the NBO analysis. All the complexes are mainly stabilized by the electrostatic and orbital interactions between B_{39}^- and ECp^{*+} fragments as highlighted by the EDA results.

KEYWORDS

Sandwich compound; Borospherene; Thermochemical stability; Electron density analysis

Introduction