

Synthesis and Reactivity of Boron-Functionalized C_2B_5 -*closo*-Carboranes

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Treatment of the *nido*-2,3-Et₂C₂B₄H₄²⁻ dianion (**1**) with monoboron reagents led to *closo*-C₂B₅ carborane derivatives with functional substituents at the inserted apical boron atom. The reactions of **1** with BX₃ (X = Br, I) afforded the corresponding *closo*-1-X-2,3-Et₂C₂B₅H₄ (**2a,b**), and with PhC≡CBcat (cat = O₂C₆H₄) produced the alkynyl-substituted *closo*-1-C≡CPh-2,3-Et₂C₂B₅H₄ (**2c**). Pd-catalyzed Negishi-type cross-coupling reactions of **2b** with RC≡CZnCl at room temperature gave the corresponding *closo*-1-C≡CR-2,3-Et₂C₂B₅H₄ derivatives **2d-f**, R = SiMe₃, Me, and *t*Bu, respectively. Compound **3** with two C₂B₅ moieties linked *via* a C=C unit was obtained by a similar boron incorporation reaction with *cis*-Cl₂B(Et)C=C(Et)BCl₂. The reactions of **2c,d** with Co₂(CO)₈ afforded the dicobaltatetrahedrane-substituted carboranes **4c** and **d**, in which the clusters C₂B₅ and Co₂C₂ are connected by a B-C bond. Compounds **4c,d** lost the apical boron on wet silica gel or sand to give the *nido*-C₂B₄-C₂Co₂ compounds **5c,d**. Formation of the carboranyl-substituted (η^5 -C₅H₅)Co(cyclobutadiene) complex **6c** was observed in the reaction of **2c** with (η^5 -C₅H₅)Co(C₂H₄)₂. The composition of the products follows from NMR and MS data.

Key words: Boron, Carborane, Cross Coupling, Cobalt, Cluster Linkage