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Syntheses of Charge-Compensated Dicarbollide Ligand Precursors
and Their Use in the Preparation of Novel Metallacarboranes

by

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A series of charge-compensated, boron-substituted carborane cage derivatives, [nido-9-L-7,8-C₂B₉H₁₁] or [nido-10-L-7,8-C₂B₉H₁₁] (L = nitrogen-containing ligand), were prepared by the ferric chloride-promoted oxidative coupling reaction of K[nido-7,8-C₂B₉H₁₂] with the Lewis base, L. Another series of neutral boron-substituted carborane cage derivatives, [nido-10-L-7,9-C₂B₉H₁₁], were synthesized directly from the reaction of [closo-1,8-C₂B₉H₁₁] with the nitrogen-containing ligand, L. When Na[nido-10-N-(C₂H₅)₂-7,8-C₂B₉H₁₀] (Na-2), Na[nido-9-(4-(C₂H₅N)CO₂CH₃)-7,8-C₂B₉H₁₀] (Na-3), or Na[nido-10-C₂H₅N-7,9-C₂B₉H₁₀] (Na-4) were reacted with anhydrous ferrous chloride in THF at 298 K, the three corresponding ferrocene-like neutral <i>commo</i>-ferracarboranes were obtained. The complex [commo-3,3'-Fe[8-N(C₂H₅)₂-3,1,2-FeC₂B₉H₁₀]₂ (5) was characterized both by spectroscopic methods and by a single-crystal X-ray diffraction study. The well-known unsubstituted iron sandwich [commo-3,3'-Fe[3,1,2-FeC₂B₉H₁₁]₂[(N(CH₃)₄)₂] (6) was also characterized crystallographically for the first time. Complexes 5 and 6 each crystallized in the monoclinic space group P2₁/c, with <i>a</i> = 9.017 (3) Å, <i>b</i> = 11.341 (3) Å, <i>c</i> = 32.941 (11) Å, β = 91.84 (1)°, <i>V</i> = 3409 Å³, and <i>Z</i> = 4 for 5 and <i>a</i> = 7.278 (2) Å, <i>b</i> = 15.830 (4) Å, <i>c</i> = 11.994 (3) Å, β = 91.80 (2)°, <i>V</i> = 1381 Å³, and <i>Z</i> = 2 for 6. The sandwich species [commo-3,3'-Fe[4-(4-(C₂H₅N)CO₂CH₃)-3,1,2-FeC₂B₉H₁₀]₂ (7) and [commo-2,2'-Fe[11-C₂H₅N-2,1,7-FeC₂B₉H₁₀]₂ (8) were characterized by spectroscopic means. A novel cationic cobaltacarborane sandwich analogous to the cobalticenium ion, [commo-3,3'-Co[4-(4-(C₂H₅N)CO₂CH₃)-3,1,2-CoC₂B₉H₁₀]₂Cl (9-Cl) was isolated and characterized. This is the first example of a cationic metallocarborane that incorporates the dicarborollide ligand.					
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