

Methylation of Boron Vertices of the Cobalt Dicarbollide Anion

Mark D. Mortimer, Carolyn B. Knobler, and M. Frederick Hawthorne*

Department of Chemistry and Biochemistry,
405 Hilgard Avenue, University of California,
Los Angeles, California 90095

Received April 1, 1996

Introduction

The cobalt bis(dicarbollide) anion (**1**) is probably the best studied of the family of carborane “sandwich” compounds which were first described in the mid-1960s.¹ This anion exhibits high chemical stability, being resistant to both acidic and basic conditions and high temperatures. Significantly, it is also resistant to γ -ray irradiation² and to degradation *in vivo*,³ features which are amenable to its use in applications for the removal of dangerous ¹³⁷Cs and ⁹⁰Sr isotopes from spent nuclear fuel^{2,4} and as a component of model radioimaging agents.³ The cobalt bis(dicarbollide) anion is also unusually “organophilic”; the hydridic nature of the BH vertices and the extensive delocalization of the negative charge over the surface of the deltahedral structure result in the remarkable feature of allowing the extraction of salts of this anion from water into lipophilic organic phases.⁵ A final desirable feature of **1** is that it shows little tendency to coordinate to cations. This characteristic has aroused the interest of workers studying Ziegler–Natta polymerization catalysts and related systems, where the activity of the catalytic cation is inversely related to the tightness of ion-pairing.⁶

Given the unique properties of the cobalt bis(dicarbollide) anion, it is not surprising that investigations of its derivatization have been carried out. The major disadvantage associated with the use of **1** as an extractant for radionuclide isolation is its radiochemical degradation and slow decomposition in the presence of nitric acid, whose use is essential in the overall process. Blocking the 8, 9, and 12 boron vertices of the dicarbollide ligands (respectively the boron vertex coordinated to the cobalt atom and β to the carbon vertices, and the two equivalent boron vertices furthest removed from the carbon vertices) with halogens, especially chlorine, markedly improves the stability of the anion without adverse effects on its ability to extract the desired isotopes from nitric acid solution.⁷ These vertices have been identified as the sites of maximum electron density in the dicarbollide ligand, and thus those most likely to

react with electrophiles.⁸ A study of the use of **1** as a non-coordinating anion in conjunction with an actinide-based polymerization catalyst^{6a} found that these three BH vertices interacted with the metal atom in the cation, effectively inhibiting all catalytic activity. Essentially all the modifications carried out on **1** to date have been halogenations,⁹ and it is clear that the ability to tune the properties of the anion in other ways might lead to desirable properties in the resulting derivatives. It is possible to introduce a variety of organic substituents to the carbon vertices of the ligands prior to metal ion coordination, but this usually has an adverse effect on the yield and ease of preparation of the resulting metal complex.^{1b} With this in mind, we here report a new synthesis of *commo*-3,3′-Co(8,9,12-I₃-3,1,2-CoC₂B₉H₈)₂ and its further modification to yield *commo*-3,3′-Co(8,9,12-(CH₃)₃-3,1,2-CoC₂B₉H₈)₂.

Experimental Section

General Considerations. All reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were reagent grade and were distilled under nitrogen before use from suitable drying agents. The cesium salt of cobalt bis(dicarbollide) (**1**) was prepared by literature methods.^{1a} Iodine monochloride, methyl magnesium bromide (3.0 M in diethyl ether), copper iodide and bis-(triphenylphosphine)palladium dichloride were purchased from Aldrich Chemical Co. and used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories. ¹H NMR spectra were recorded using a Bruker AM-200 spectrometer at 200 MHz, ¹³C NMR spectra were recorded on a Bruker ARX-400 spectrometer at 100.6 MHz, and ¹¹B NMR spectra were obtained on a Bruker ARX-500 spectrometer at 160.5 MHz. Proton chemical shifts were referenced to residual solvent protons, carbon chemical shifts were referenced to the solvent, and boron chemical shifts were referenced to external BF₃·OEt₂. Mass spectra were obtained at the UC Riverside Mass Spectroscopy Facility using a VG ZAB spectrometer with an NBA matrix.

Synthesis of Cs[*commo*-3,3′-Co(8,9,12-I₃-3,1,2-CoC₂B₉H₈)₂] (2**).** A mixture of the cesium salt of the cobalt bis(dicarbollide) (**1**) (0.80 g, 1.75 mmol) and iodine monochloride (1.71 g, 10.51 mmol) in CH₂-Cl₂ (50 mL) was stirred for 16 h under reflux. Solvent was removed *in vacuo* and the residue washed several times in pentane. Recrystallization from hot water afforded compound **2** as an orange solid (1.95 g, 92%). Characterization data for this compound was in agreement with the original synthesis.^{9a}

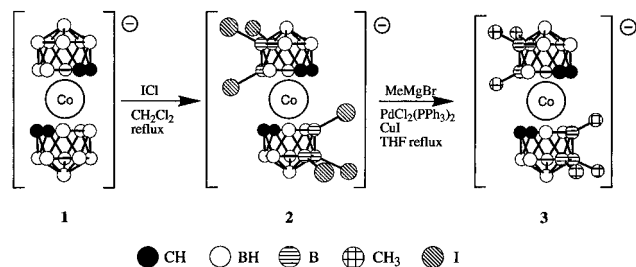
Synthesis of (MePPh₃)[3,3′-Co(8,9,12-(CH₃)₃-3,1,2-CoC₂B₉H₈)₂] (3**).** A solution of **2** (0.41 g, 0.34 mmol) in THF (40 mL) was treated with methyl magnesium bromide (3.0 M solution in diethyl ether, 1.57 mL, 4.72 mmol) at –78 °C, forming a heavy brown precipitate. The solution was allowed to warm to room temperature, and then bis-(triphenylphosphine)palladium dichloride (0.03 g, 0.04 mmol) and copper(I) iodide (0.01 g, 0.05 mmol) were added. The solution was refluxed for 16 h. Ten drops of water were added to quench excess Grignard reagent, and the solvent was removed *in vacuo*. The residue was extracted with methylene chloride (3 × 30 mL) and the remaining white insoluble material discarded. Solvent was removed and the residue redissolved in a minimum of THF/methanol (4:1). The solution was chromatographed on silica gel and eluted with the same solvent mixture. A small leading band was discarded. The main band adhered to the column and was eluted with neat methanol along with a small trailing band which was discarded. The combined fractions were dried under reduced pressure, and the residue was extracted with diethyl ether (3 × 30 mL), leaving some dark material, which was discarded. The solvent was removed, the product dissolved in hot water (50 mL), and triphenylmethylphosphonium bromide (240 mg, 0.68 mmol) was added to precipitate the product. The precipitate was isolated by filtration and then dissolved in methylene chloride and dried over anhydrous

- (1) (a) Hawthorne, M. F.; Young, D. C.; Wegner, P. A. *J. Am. Chem. Soc.* **1965**, *87*, 1818. (b) Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, L. F., Jr.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879. (c) Hawthorne, M. F.; Dunks, G. B. *Science* **1972**, *78*, 462.
- (2) Rais, J.; Selucky, P. *Nuclleon* **1992**, *1*, 17.
- (3) Paxton, R. J.; Beatty, B. G.; Hawthorne, M. F.; Varadarajan, A.; Williams, L. E.; Curtis, F. L.; Knobler, C. B.; Beatty, J. D.; Shively, J. E. *Proc. Natl. Acad. Sci. U.S.A.* **1991**, *88*, 3387.
- (4) (a) Rais, J.; Selucky, P.; Kryš, M. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1376. (b) Rukuola, E.; Vilkkamo, S. *Nucl. Eng. Int.* **1991**, *1*, 18.
- (5) (a) Janoušek, Z.; Heřmánek, S.; Plešek, J.; Štíbr, B. *Collect. Czech. Chem. Commun.* **1974**, *39*, 2371. (b) Plešek, J.; Heřmánek, S.; Štíbr, B. *Inorg. Synth.* **1983**, *22*, 231. (c) Plešek, J.; Baše, K.; Mareš, F.; Hanousek, F.; Štíbr, B.; Heřmánek, S. *Collect. Czech. Chem. Commun.* **1984**, *49*, 2776.
- (6) (a) Yang, X.; King, W.; Sabat, M.; Marks, T. J. *Organometallics* **1993**, *12*, 4254. (b) Hlatky, G. G.; Eckman, R. R.; Turner, H. W. *Organometallics* **1992**, *11*, 1413.
- (7) (a) Selucky, P.; Baše, K.; Plešek, J.; Heřmánek, S.; Rais, J. Czech Patent 215 282, 1986; *Chem. Abstr.* **1986**, *104*; 186637g. (b) Mátel, L.; Macáček, F.; Kamenista, H. *Radiochem. Radioanal. Lett.* **1981**, *46*, 1.

- (8) Goursot, A.; Penigault, E.; Chermette, H.; Fripiat, J. G. *Can. J. Chem.* **1986**, *64*, 1752.

- (9) (a) Mátel, L.; Macáček, F.; Rajec, P.; Heřmánek, S.; Plešek, J. *Polyhedron* **1982**, *1*, 511. (b) Hurlburt, P. K.; Miller, R. L.; Abney, K. D.; Foreman, T. M.; Butcher, R. J.; Kinkead, S. A. *Inorg. Chem.* **1995**, *34*, 5215.

Scheme 1



magnesium sulfate. A second filtration and removal of the solvent *in vacuo* afforded **3** as an orange solid (0.14 g, 60%): ^1H NMR (acetone- d_6) 7.83–7.94 (m, 15H, C_6H_5), 4.26 (br s, 4H, CH), 3.23 (d, 3H, PCH_3 , $J_{\text{PH}} = 28$ Hz), 0.7–3.1 (vbr, 12H, BH), 0.75 (br s, 6H, BCH_3), –0.11 (br s, 12H, BCH_3) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (acetone- d_6) 135.2 (C^4 , PC_6H_4 , $J_{\text{PC}} = 3$ Hz), 133.4 (C^2 , PC_6H_4 , $J_{\text{PC}} = 11$ Hz), 130.4 (C^3 , PC_6H_4 , $J_{\text{PC}} = 13$ Hz), 119.8 (C^1 , PC_6H_4 , $J_{\text{PC}} = 89$ Hz), 46.8 (br, CH), 8.3 (PCH_3 , $J_{\text{PC}} = 58$ Hz), 3.5, 1.9 (vbr, BCH_3) ppm; $^{11}\text{B}\{^1\text{H}\}$ NMR (acetone) 13.9 (2B, BCH_3), 2.9 (4B, BCH_3), –3.4 (4B), –17.4 (4B), –24.0 (2B) ppm; HRMS (negative ion FAB with DMK/NBA matrix) (m/z) obsd 408.3773, calcd 408.3776 (M^-).

Results and Discussion

A number of methods aimed at elaborating the BH vertices of the icosahedral carboranes have been reported. It is possible to introduce halogens, main group elements and organic groups to either the most electron-rich vertices *via* electrophilic reagents, or to the most electron-deficient vertices by removal of such a boron vertex with base followed by the introduction of a BX group (X = halogen, alkyl, aryl, or others) to reconstitute the icosahedron.¹⁰ Of these methods, probably the widest in scope is the introduction of an iodine substituent to the target vertex followed by its replacement with an organic group by reaction with a Grignard reagent in the presence of a palladium catalyst.¹¹ This approach was used to introduce organic substituents to boron vertices of the cobalt bis(dicarbollide) (**1**) anion as described here (Scheme 1).

Reaction of the cesium salt of **1** with six equivalents of iodine monochloride in refluxing methylene chloride affords the previously described cesium salt of **2** in 92% yield.^{9a} This compound was formerly synthesized by the reaction of **2** with iodine in the presence of aluminum trichloride catalyst in a benzene slurry. We have previously commented on the superiority of iodine monochloride over iodine as an iodinating agent for carboranes,^{11c,d} and in this case the greater reactivity of iodine monochloride renders the use of a catalyst unnecessary. Treatment of **2** with 14 molar equivalents of methyl magnesium bromide in the presence of bis(triphenylphosphine)palladium dichloride and copper(I) iodide in refluxing THF solution served to exchange all the B-iodo vertices for B-methyls. Precipitation from water with triphenylmethylphosphonium bromide allowed isolation of triphenylmethylphosphonium salt of **3** in 60% yield after purification. The anion **3** is easily identified by its characteristic NMR spectra. In particular, the ^{11}B NMR spectrum displays two markedly downfield signals for the B-methyl groups at 13.9 and 2.9 ppm, which remain singlets in a fully proton-coupled spectrum. These groups appear in the ^1H NMR spectrum at 0.75 and –0.11 ppm; the broadness and upfield shift of the signals are characteristic of methyl groups bonded directly to boron vertices. In the ^{13}C NMR spectrum of **3**, the

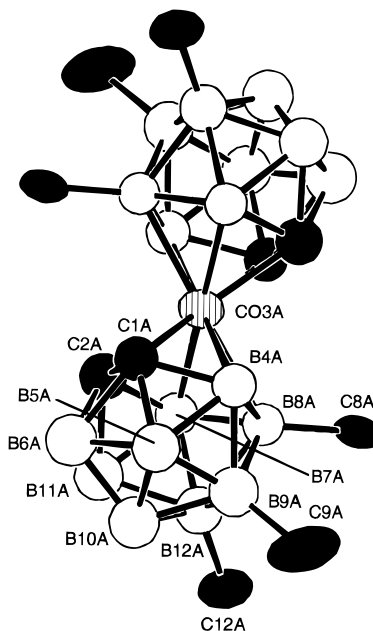


Figure 1. ORTEP representation of the anion of compound **3**, showing the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity. Significant distances (Å) are as follows: CO3A–C1A 2.001(14), CO3A–C2A 2.00(2), CO3A–B4A 2.11(2), CO3A–B7A 2.11(2), CO3A–B8A 2.210(12), B8A–C8A 1.679(12), B9A–C9A 1.66(2), B12A–C12A 1.63(2) Å.

position of the carborane CH resonance, at 46.8 ppm, is significantly upfield from the more usual position of 60–80 ppm observed in metallocarboranes, probably due to the electron density donated to the cage by the attached methyl groups.

The structure of **3** was determined by X-ray crystallography. There are four crystallographically distinct centrosymmetric anions in the unit cell, given the designations A, B, C, and D. Anion A is shown in Figure 1, and the others are labeled in an analogous manner. In anions B and C, anomalies in the temperature factors of some of the methyl groups and greater than expected B–C bond lengths suggest that a small percentage of species with B–I groups was present in the crystal in an ordered fashion. In anion B, C8B and C12B were refined as 5% partial iodine occupancy and C9C and C12C were refined with 10% partial iodine occupancy. In the solid state, the presence of the methyl groups appears to have no significant effect on the bonding of the dicarbollide ligands to the cobalt atom. The metal is centered over the bonding faces of the ligands with no evidence of “slippage”, and the five atoms of these faces are planar to within 0.02 Å averaged over the four independent anions. Since the anions are centrosymmetric, the bonding faces of the two ligands attached to a single cobalt atom are of necessity parallel.

The use of iodine substituents on boron vertices of icosahedral carboranes to provide precursor species for further modification has proved to be a powerful tool. Our observation that similar chemistry is possible with the cobalt bis(dicarbollide) anion suggests a number of elaborations of this ion beyond simple halogenation reactions. Given the unique properties of the metallocarborane sandwiches, we believe that this will prove to be useful in further studies of their commercial potential.

Acknowledgment. This work was funded by the National Science Foundation under Grant CHE-93-14037.

Supporting Information Available: Text giving experimental details of crystallographic data collection, solution, and refinement, a figure showing the atom numbering, and tables of bond distances and angles and positional and thermal parameters for compound **3** (17 pages). Ordering information is given on any current masthead page.

IC960353S

(10) This field has been reviewed: (a) Bregadze, V. I. *Chem. Rev.* **1992**, 92, 209. (b) Grushin, V. V.; Bregadze, V. I.; Kalinin, V. N. *J. Organomet. Chem. Libr.* **20** **1988**, 20, 1.

(11) (a) Zakharkin, L. I.; Kovredov, A. I.; Ol'shevskaya, V. A.; Shaugumbekova, Zh. S. *J. Organomet. Chem.* **1982**, 226, 217. (b) Li, J.; Logan, C. F.; Jones, M., Jr. *Inorg. Chem.* **1991**, 30, 4866. (c) Zheng, Z.; Jiang, W.; Zinn, A. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1995**, 34, 2095. (d) Jiang, W.; Knobler, C. B.; Curtis, C. E.; Mortimer, M. D.; Hawthorne, M. F. *Inorg. Chem.* **1995**, 34, 3491.