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New Synthetic Routes to B-Halogenated Derivatives of Cobalt Dicarbollide

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The synthesis and characterization of the B(10),B(10′)-dihalogenated metallocarboranes $[\mathrm{Co(10\text{-}X\text{-}7,8\text{-}C_2B_9H_{10})_2}]^-$, where X = Cl or Br, are reported. The C_{2h} symmetry of these diamagnetic Co(III) compounds allows straightforward identification using ^{11}B and ^{11}B{^{1}H} NMR. The compound $[\mathrm{(CH_3)_4N}][\mathrm{Co(7,8\text{-}C_2B_9H_{11})_2}]$ reacts in acidic NaOCl/HCl(aq) to form the dichlorinated derivative $[\mathrm{(CH_3)_4N}][\mathrm{Co(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})_2}]$. Reaction of $[\mathrm{(CH_3)_3NH}][\mathrm{Co(7,8\text{-}C_2B_9H_{11})_2}]$ with *N*-chlorosuccinimide or *N*-bromosuccinimide in THF affords the dihalogenated derivatives $[\mathrm{(CH_3)_3NH}][\mathrm{Co(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})_2}]$ and $[\mathrm{(CH_3)_3NH}][\mathrm{Co(10\text{-}Br\text{-}7,8\text{-}C_2B_9H_{10})_2}]$, respectively. Reaction of $[\mathrm{(CH_3)_3NH}][\mathrm{Co(7,8\text{-}C_2B_9H_{11})_2}]$ with $\mathrm{Cl_2}$/Fe or $\mathrm{Br_2}$ in THF also gives the dihalogenated derivatives $[\mathrm{(CH_3)_3NH}][\mathrm{Co(10\text{-}Cl,7,8\text{-}C_2B_9H_{10})_2}]$ and $[\mathrm{(CH_3)_3NH}][\mathrm{Co(10\text{-}Br,7,8\text{-}C_2B_9H_{10})_2}]$, respectively. $[\mathrm{PPN}][\mathrm{Co(10\text{-}Cl,7,8\text{-}C_2B_9H_{10})_2}]$ (PPN = bis(triphenylphosphine)nitrogen(1+)) crystallizes in the monoclinic space group *C*2/c, with $a = 31.267(5)$ Å, $b = 9.0190(10)$ Å, $c = 18.706(3)$ Å, $\beta = 116.970(0)°$, $V = 4701.8(15)$ Å^3, $Z = 4$, and $R = 0.054$. The structure was determined by X-ray crystallography using 6830 independent reflections.

Introduction

Hawthorne reported the first metallocarborane in 1965.[2] Since that time, metallocarboranes from all areas of the periodic table have been prepared using the $[\mathrm{7,8\text{-}C_2B_9H_{11}}]^{2-}$ (dicarbollide) ligand[3] (see Figure 1 for dicarbollide and cobalt dicarbollide numbering schemes). Of these organometallic complexes, $[\mathrm{Co(7,8\text{-}C_2B_9H_{11})_2}]^-$ (cobalt dicarbollide) has attracted by far the most attention. This 18-electron low-spin d^6 complex is exceedingly robust, withstanding strong acid, moderate base, high temperatures, and intense radiation.[4] The stability of this anion makes it useful in such fields as neutron-capture therapy, tumor imaging, olefin polymerization catalysis, and nuclear waste remediation. The same stability makes it difficult to modify cobalt dicarbollide in attempting to adapt the anion for use in these areas. Most attempts at the modification of cobalt dicarbollide have resulted in poor yields or intractable mixtures.

The cobalt dicarbollide anion is under investigation for use in boron neutron capture therapy,[5] where $[\mathrm{Co(7,8\text{-}C_2B_9H_{11})_2}]^-$ is used as a carrier of ^{10}B. The ^{10}B nuclei absorb neutrons from an outside source and release α particles (^{10}B(n,α)^{7}Li). When a large number of ^{10}B atoms are concentrated near a tumor, the tumor can be destroyed by neutron irradiation.

Cobalt dicarbollide is also being investigated as a radioactive cobalt tumor imaging reagent.[6] The kinetic stability and resistance to radiolytic degradation of this compound ensure that radioactive cobalt is not released *in vivo*, possibly replacing natural cobalt. The radioactive cobalt is concentrated in the vicinity of interest, and the emitted radiation is used to image the tumor or other area of interest.

Cobalt dicarbollide is being investigated as a weakly coordinating counterion for polymerization catalysts such as $[\mathrm{Cp_2ZrCH_3}]^+$ (Cp = cyclopentadiene anion) and $[\mathrm{Cp_2ThCH_3}]^+$,[7] where turnover rates are dependent upon vacant sites on the metal center or the degree of dissociation of the anion. In these cases, the large size to charge ratio of cobalt dicarbollide aids in the coordinative unsaturation of the Zr or Th center.

Cobalt dicarbollide is also capable of removing cesium ions (and strontium ions under slightly different conditions) with high selectivity from complex mixtures of radioactive waste.[4,8] The large size to charge ratio and the hydrophobic nature of $[\mathrm{Co(7,8\text{-}C_2B_9H_{11})_2}]^-$ allow extraction of cesium ions from an aqueous phase to an organic phase, leaving other group 1 and higher-valent metals behind. Efforts to remove the relatively short-lived nuclei ^{137}Cs ($t_{1/2} = 30.17$ y) and ^{90}Sr ($t_{1/2} = 29$ y) from fission product waste are driven by the desire to make safe and efficient use of the proposed geologic repositories. ^{137}Cs and ^{90}Sr are used for the sterilization of medical equipment, for the treatment of sewage, and in thermoelectric generators, among other things, making the possibility of recycling these commercially important nuclei very attractive.

Resistance to degradation by radiolysis is necessary in the harsh environment of high-level nuclear waste. Although cobalt dicarbollide itself is quite stable, the chlorinated and brominated derivatives have shown even greater stability toward degradation by acidic media or intense radiation.[9] More importantly, the halogenated derivatives provide the same separation efficiency as the unsubstituted cobalt dicarbollide.[10] Multiply halogenated derivatives of the cobalt dicarbollide anion have been tested in

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(1) Howard University, Washington, DC.

(2) Hawthorne, M. F.; Young, D. C.; Wegner, P. A. *J. Am. Chem. Soc.* **1965,** *87,* 1818.

(3) Some lead references: (a) Saxena, A. K.; Hosmane, N. S. *Chem. Rev.* **1993,** *93,* 1081. (b) Rees, W. S., Jr.; Schubert, D. M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1986,** *108,* 5367. (c) Jeffery, J. C.; Jelliss, P. A.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1993,** 1073. (d) Bazan, G. C.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1993,** *12,* 2126.

(4) Rais, J.; Selucky, P. *Nucleon* **1992,** *1,* 17.

(5) (a) Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1993,** *32,* 950. (b) Barth, R. F.; Adams, D. A.; Soloway, A. H.; Alam, F.; Darby, M. V. *Bioconjugate Chem.* **1994,** *5,* 58.

(6) Hawthorne, F. M.; Varadarajan, A.; Knobler, C. B.; Chakrabarti, S. *J. Am. Chem. Soc.* **1990,** *112,* 5365.

(7) (a) Hlatky, G. G.; Eckman, R. R.; Turner, H. W. *Organometallics* **1992,** *11,* 1413. (b) Uhrhammer, R.; Crowther, D. J.; Olson, J. D.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1992,** *11,* 3098. (c) Yang, X.; King, W. A.; Sabat, M.; Marks, T. J. *Organometallics* **1993,** *12,* 4254.

(8) Reilly, S. D.; Mason, C. F. V.; Smith, P. H. Cobalt(III) Dicarbollide: A Potential ^{137}Cs and ^{90}Sr Waste Extraction Agent. Report LA-11695; Los Alamos National Laboratory: Los Alamos, NM, 1990.

(9) (a) Matel, L.; Macasek, H.; Kamenista, H. *Radiochem. Radioanal. Lett.* **1981,** *46,* 1. (b) Matel, L.; Macasek, F.; Rajec, P.; Hermanek, S.; Plesek, J. *Polyhedron* **1982,** *1,* 511.

0020-1669/95/1334-5215$09.00/0

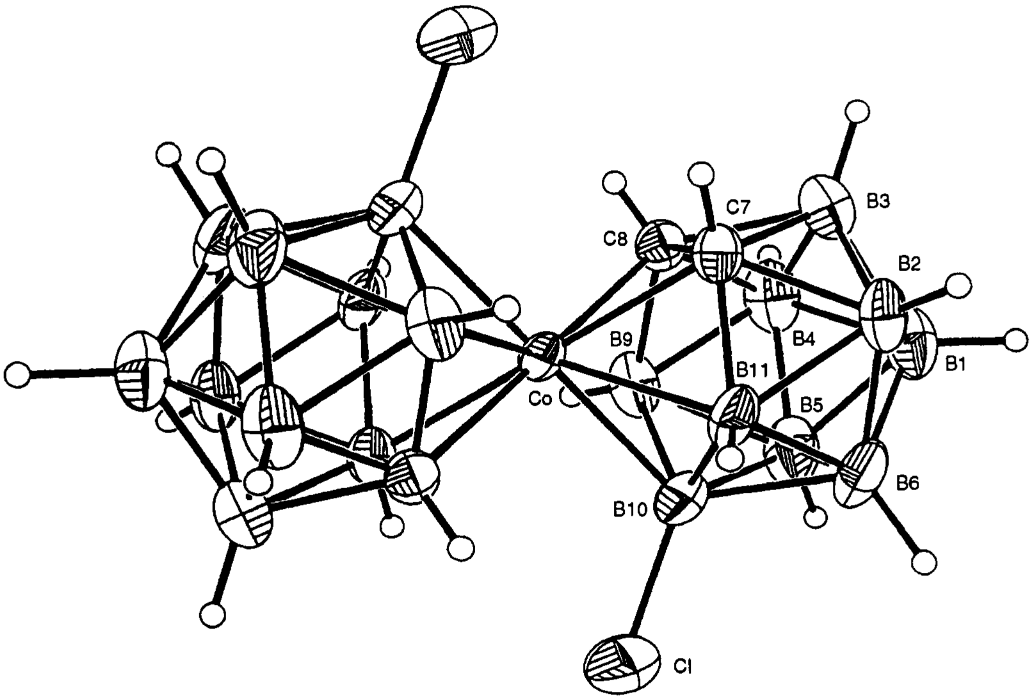

Figure 1. The anion of [PPN][$Co(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})_2$] showing the atom-labeling scheme.

solutions of 3 M nitric acid, with less than 5% decomposition even after 36 days, compared to 80% decomposition of the parent cobalt dicarbollide anion under the same conditions. Among the derivatives tested was one that was substituted at only the B(10), B(10)′ positions, [$Co(10\text{-}C_6H_5\text{-}7,8\text{-}C_2B_9H_{10})(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})]^-$. This latter compound resisted attack by acid as well as the multiply halogenated derivatives but was not as effective in extracting Cs. Although the *B*(10),*B*(10)′-diiodo cobalt dicarbollide was effective for removal of Cs, it decomposed more rapidly than chloro or bromo derivatives.

Protection at the B(10) and B(10)′ positions is necessary for increased stability of cobalt dicarbollide in 3 M HNO_3. When these positions are protected with halogens, the separation efficiency of the parent compound is retained. An important advance in the use of halogenated cobalt dicarbollide in nuclear waste remediation would be the synthesis of pure dichlorinated or dibrominated derivatives of cobalt dicarbollide. These compounds should exhibit both high separation efficiency and high resistance to attack by acid. They would produce less halogenated waste than the more highly substituted compounds if destruction or vitrification were necessary after use. Finally, dihalogenated cobalt dicarbollide could be produced at a reduced cost since less halogenating reagent would be needed.

Previous preparations of chlorinated cobalt dicarbollide have used Cl_2 with γ or ultraviolet radiation[9b] or $KClO_3$ in HCl(aq).[11] These preparations yield up to six different products, with up to seven chlorine atoms per anion, which are then separated chromatographically, while using harsh conditions or expensive reagents. Similarly, reported preparations of the brominated derivatives of the cobalt dicarbollide anion have yielded either the hexabromo derivative[12] or a mixture of products.

In this contribution, we report synthetic routes for obtaining pure dichlorinated and dibrominated derivatives of the cobalt dicarbollide anion in high yield. Both $[Co(10\text{-}Cl,7,8\text{-}C_2B_9H_{10})_2]^-$ and $[Co(10\text{-}Br,7,8\text{-}C_2B_9H_{10})_2]^-$ can be obtained by more than one route. We also discuss a possible mechanism for these substitutions.

Results and Discussion

Our work has focused on the possible use of cobalt dicarbollide derivatives for cesium and strontium removal in nuclear waste processing. In keeping with this goal, we sought reactions that would provide high yields of pure compounds and that could be scaled to large production levels.

Halogenation by Hypochlorous Acid. Hypochlorous acid is an inexpensive reagent that has been used for chlorination of many compounds, leading us to try this reagent with cobalt dicarbollide. The unstable hypochlorous acid can be prepared by several methods, but only the addition of aqueous NaOCl to 6 M HCl was used in this investigation.

The reaction of [$(CH_3)_4N$][$Co(7,8\text{-}C_2B_9H_{11})_2$] with acidified sodium hypochlorite (HCl/NaOCl) was studied as a method for preparing chlorinated cobalt dicarbollide. This reaction gives the pure product [$(CH_3)_4N$][$Co(10\text{-}Cl,7,8\text{-}C_2B_9H_{10})_2$] in 85% yield, using inexpensive reagents at ambient temperature. This reaction was successful for preparing the insoluble tetramethylammonium salt only. Other products are obtained when either the trimethylammonium or cesium salt is used, as evidenced by the ^{11}B NMR spectrum of the products. This spectrum consists of a large broad resonance at 20 ppm, probably due to borate or boric acid, and a series of broad resonances between 0 and −40 ppm, which are probably due to substituted or partially decomposed cobalt dicarbollide derivatives. While the tetramethylammonium salt is entirely insoluble under these conditions, the other salts investigated were slightly soluble under these same conditions, indicated by the light yellow color of the reaction solutions. Chlorination of tetramethylammonium cobalt dicarbollide by hypochlorous acid is unique in that the reaction gives exclusively B(10),B(10)′-disubstitution and does not proceed to further substitution at room temperature.

A report concerning the reaction of hypochlorous acid with amine−boranes suggests two competing four-centered inter-

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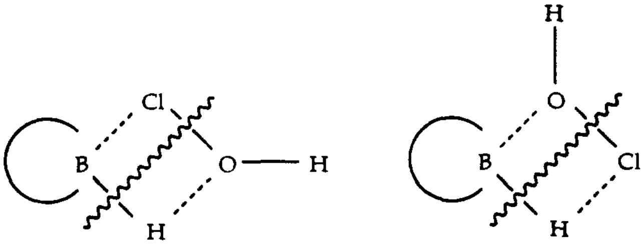
(10) Rais, J.; Plesek, J.; Selucky, P.; Kyrs, M.; Kadlecova, L. *J. Radioanal. Nucl. Chem.* **1991**, *148*, 349.

(11) Selucky, P.; Base, K.; Plesek, J.; Hermanek, S.; Rais, J. *Czech. Pat.* 215282, 1985.

(12) 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.

mediates (see below), one resulting in a B−O(H) bond and the



other in a B−Cl bond.[13] In the case where a B−O(H) bond is formed, the reaction quickly proceeds to $B(OH)_3$. In our system, when the tetramethylammonium salt is used, B-chlorination is observed. However, when either the trimethylammonium or cesium salts are used, the cobalt dicarbollide is degraded.

The cobalt dicarbollide anion and, to a lesser extent, the halogenated derivatives are unstable in prolonged contact with strong base, and degradation is observed. In the system investigated in this work, a 10% solution of NaOCl was added dropwise to a 6 M HCl slurry of cobalt dicarbollide to generate the HOCl used. The solubility of the cesium and trimethylammoniun salts of cobalt dicarbollide may allow intimate contact with the localized areas of high pH caused by the drops of NaOCl solution being added to the 6 M HCl solution, causing degradation by base as observed previously. In the case of the insoluble tetramethylammonium salt of cobalt dicarbollide, the reaction with the solution was heterogeneous and possibly slow enough to allow generation of HOCl from NaOCl and HCl.

While it is unlikely that Cl^+ is responsible for chlorination,[14] the mechanism of chlorination by hypochlorous acid is generally considered to be electrophilic substitution. In a study of the mechanism of chlorination by HOCl,[15] a second-order dependence was observed at high [HOCl], suggesting chlorination by Cl_2O. Chlorine monoxide (Cl_2O) has been used directly for electrophilic chlorination,[16] and in aqueous solution, Cl_2O and HOCl are in equilibrium (eq 1).

$$2HOCl \rightleftharpoons 2Cl_2O + H_2O \qquad (1)$$

Reactions using HOF, HOBr, or HOI were not investigated.

Halogenation by Elemental Halogen. Since the mechanism of chlorination of cobalt dicarbollide by hypochlorous acid at least looked like an electrophilic substitution, it seemed to conflict with the preparation of the highly chlorinated derivatives using elemental chlorine with ultraviolet or γ radiation. We decided to try to chlorinate cobalt dicarbollide using elemental chlorine in the presence of iron powder. The addition of iron powder should favor an electrophilic substitution mechanism by first making $FeCl_3$ followed by $^{\delta-}Cl_3FeCl\cdots Cl^{\delta+}$, which provides an electrophilic chlorine.

The reaction of chlorine gas with a THF/2-propanol solution of cobalt dicarbollide in the presence of iron powder produces $[Co(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})_2]^-$. This reaction stops at dichlorination, while the same reaction without iron powder present continues to hexa- and heptachlorination.[9] The apparent dependence of the extent of chlorination on the presence of iron powder suggests either two possible mechanisms for the same substitution or a different mechanism of reaction for the first two chlorine substitutions (at B(10) and B(10)′) versus further chlorine substitutions.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[PPN][Co(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})_2]$

Cl−B(10)	1.823(7)	B(1)−B(2)	1.751(12)	B(4)−B(5)	1.741(12)
Co−C(7)	2.020(5)	B(1)−B(3)	1.747(10)	B(4)−B(9)	1.770(11)
Co−C(8)	2.016(6)	B(1)−B(4)	1.758(10)	B(5)−B(6)	1.780(13)
Co−B(9)	2.099(8)	B(1)−B(5)	1.788(11)	B(5)−B(9)	1.781(8)
Co−B(10)	2.134(6)	B(1)−B(6)	1.777(13)	B(5)−B(10)	1.785(12)
Co−B(11)	2.093(5)	B(2)−B(3)	1.751(11)	B(6)−B(10)	1.797(9)
C(7)−C(8)	1.620(8)	B(2)−B(6)	1.768(11)	B(6)−B(11)	1.782(10)
C(7)−B(11)	1.706(8)	B(2)−B(11)	1.798(10)	B(9)−B(10)	1.760(11)
C(8)−B(9)	1.689(9)	B(3)−B(4)	1.763(12)	B(10)−B(11)	1.780(10)

Co−B(10)−Cl	117.3(3)	P−N−P	147.2(4)
B(9)−B(10)−B(11)	107.7(5)		

The reaction of elemental bromine with a THF solution of cobalt dicarbollide anion produces only the B(10),B(10)′-disubstituted compound after 20 min at reflux. The elemental bromine is sufficiently less reactive than elemental chlorine that this reaction stops at dibromination without the need to inhibit further substitution. The reactivity of elemental iodine is insufficient to afford disubstitution of cobalt dicarbollide in a THF solution even after 24 h at reflux.

Fluorination of $[Cs][Co(7,8\text{-}C_2B_9H_{11})_2]$ in anhydrous HF was attempted using elemental fluorine diluted 1:1 with nitrogen. This produced no apparent reaction after 1 h at room temperature, as evidenced by a ^{11}B NMR spectrum of the yellow powder.

As with chlorination by HOCl, the reactions using elemental chlorine or bromine may be suitable for large-scale production of $[Co(10\text{-}X\text{-}7,8\text{-}C_2B_9H_{10})_2]^-$ (X = Cl or Br).

Halogenation by *N*-Halosuccinimide. THF solutions of *N*-chlorosuccinimide and *N*-bromosuccinimide are used to prepare $[Me_3NH][Co(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})_2]$ and $[Me_3NH][Co(10\text{-}Br\text{-}7,8\text{-}C_2B_9H_{10})_2]$, respectively, from $[Me_3NH][Co(7,8\text{-}C_2B_9H_{11})_2]$. These reactions are similar to the bromination of $CsCB_{11}H_{12}$ by *N*-bromosuccinimide.[17] These preparations give only the B(10),B(10)′-disubstituted cobalt dicarbollide products in high yields. When a THF solution of $[Cs][Co(7,8\text{-}C_2B_9H_{11})_2]$ and 1-fluoro-2,4,6-trimethylpyridinium triflate was refluxed for 15 min, no reaction was observed. The reaction of cobalt dicarbollide with *N*-iodosuccinimide was not attempted.

The reaction of *N*-chlorosuccinimide or *N*-bromosuccinimide with cobalt dicarbollide is well behaved and is not dependent upon the cation used. Both reactions stop at disubstitution after 20 min at reflux, even when an excess of the *N*-halosuccinimide is used. These reactions are useful for laboratory-scale syntheses and allow a choice of cation. While these reactions are more expensive, they are also conducted under milder conditions, which may allow chlorination or bromination of a polymer-supported cobalt dicarbollide, another area of interest in this laboratory.

Halogenation by Other Methods. While, in general, the reagents above worked well here, several attempts at halogenation failed. The chlorinating agent phenyl dichloroiodate in THF gave no reaction with the cobalt dicarbollide anion.

^{11}B NMR. There is little difference between the ^{11}B NMR spectra of the dichloro and dibromo cobalt dicarbollides. Both anions retain approximate C_{2h} symmetry in solution (although in the crystal structure, the dichloro anion has C_i symmetry see Figure 1 and Table 1). With equivalence of the boron atoms related by a mirror plane or an inversion center, the ^{11}B NMR spectrum is greatly simplified to only six unique environments

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[13] Bell, K. E.; Kelly, C. R.; Minter, D. E.; Kelly, H. C. *Inorg. Chim. Acta* **1993**, *211*, 187.

[14] Swain, C. G.; Crist, D. K. *J. Am. Chem. Soc.* **1972**, *94*, 3195.

[15] de la Mare, P. B. D. *Electrophilic Halogenation*; Cambridge University Press: Cambridge, U.K., 1976.

[16] Marsh, F. D.; Farnham, W. B.; Sam, D. J.; Smart, B. E. *J. Am. Chem. Soc.* **1982**, *104*, 4680.

[17] Jelinek, T.; Baldwin, P.; Scheidt, W. R.; Reed, C. A. *Inorg. Chem.* **1993**, *32*, 1982.

Table 2. Comparison of B−X and C−X Bond Lengths

compd	*r*(B−X)/Å	compd	*r*(B−X)/Å	calcd *r*(B−X)/Å
BCl_3	1.75	$[Co(C_2B_9H_{10}Cl)_2]^-$	1.82	1.77
BBr_3	1.87	$[Co(C_2B_9H_8Br_3)_2]^-$	1.94−1.97	1.94
BI_3	2.10	$[Co(C_2B_9H_{10}I)_2]^-$	2.22	2.13

compd	*r*(C−X)/Å	compd	*r*(C−X)/Å
CCl_4	1.77	C_6H_5Cl	1.70
CBr_4	1.94	C_6H_5Br	1.85
CI_4	2.14	C_6H_5I	2.05

for the 18 boron atoms in the metallocarborane cluster. This produces a 2:2:8:4:2 pattern, with the peak of ratio 8 being a superposition of two sets of four unique boron atoms. The first peak of ratio 2 is due to the B(10) and B(10)′ atoms.[18] This peak shifts from 6.5 ppm for the parent compound to 13.0 ppm for the dichlorinated compound and back to 7.2 ppm for the dibrominated compound. The remaining peaks are within 1 ppm for all three compounds. The assignments of the substituted boron atoms are confirmed by the X-ray crystal structure of $[PPN][Co(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})_2]$, since the carbon and boron atoms of the carborane cage are unambiguously assigned.

X-ray Structure of $[PPN][Co(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})_2]$. The X-ray structure of $[PPN][Co(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})_2]$ (anion shown in Figure 1) reveals a centrosymmetric anion. All atoms, including the hydrogen atoms, were placed unambiguously by difference maps. Excepting the B−X bonds, the bond lengths and angles in the compound $[Cs][Co(10\text{-}I\text{-}7,8\text{-}C_2B_9H_{10})_2]$[19] do not differ in any substantive way from those in $[PPN][Co(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})_2]$ or $[K][Co(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})_2]$.[20] The dibrominated analog $[Co(10\text{-}Br\text{-}7,8\text{-}C_2B_9H_{10})_2]^-$ is reported here, but an X-ray structural characterization was not attempted, and no fluorinated derivatives of the cobalt dicarbollide anion have been reported.

Reactivity. Substitution reactions involving *o*-carborane have been described as "nucleophilic substitutions under electrophilic conditions" [21] with the explanation that a hydridic hydrogen is first abstracted by the electrophile, with subsequent nucleophilic attack at the boron. It is evident that the reactivity of $[Co(C_2B_9H_{11})_2]^-$ (cobalt dicarbollide anion) also shows some similarity to that of aromatic hydrocarbons. The dicarbollide ligand has been compared to the aromatic cyclopentadiene anion due to its η^5 6-electron bonding through π-orbitals to metals.[2] The syntheses presented in this work use halogenation schemes normally employed in organic syntheses to afford electrophilic aromatic substitution. While analogies to organic chemistry can be used to explain some of the reactivity in dicarbollide chemistry, these analogies are not necessarily useful in making predictions.

For example, aryl halides typically have shorter carbon−halogen bond lengths than do the corresponding alkyl halides (Table 2). This difference is attributed to a partial carbon−halogen double bond in the aryl halide, with only single carbon−halogen bonds possible in the alkyl halide. In the boron trihalide series (Table 2), partial multiple bonding is used to explain the boron−halogen distances being shorter than the distance calculated for a boron−halogen single bond.[22] In the halogenated cobalt dicarbollide series, the boron−halogen bonds are all longer than the corresponding lengths in the boron trihalides and even longer than the distances calculated for a boron−halogen single bond. It is unlikely that the six-coordinate boron atoms in cobalt dicarbollide compounds could participate in multiple bonding with halogens, and the bond lengths indicate that they certainly do not. The limited number of orbitals on the boron atom can explain the boron−halogen bond in halogenated cobalt dicarbollide being limited to a bond order of 1 or less. Steric congestion may explain the fact that these boron−halogen bonds are actually longer than the value accepted for a full single bond. These longer B−X bonds in the halogenated cobalt dicarbollide series would be expected to be more reactive than the shorter B−X bonds of the boron trihalide series, but they are actually much less reactive. This stability is not predicted by analogy to organic chemistry or by inspection of the change in B−X bond lengths.

The $[Co(10\text{-}X\text{-}7,8\text{-}C_2B_9H_{10})_2]^-$ complexes where X = Cl, Br, and I are unchanged when refluxed in a THF solution of $NaNH_2$ or when treated with a toluene solution of butyllithium at room temperature. Again, this is probably explained by steric congestion, imparting a kinetic stability to the halogenated cobalt dicarbollides. The kinetic stability of this boron−halogen bond allows these compounds to withstand 3 M HNO_3 for periods in excess of 1 month. The attack and destruction of halogenated cobalt dicarbollide is slow as long as the B(10) atom is protected.

Experimental Methods

Reagents and Solvents. The following were used as received: THF (Baker), 1-propanol (Baker), CH_3CN (Baker), CD_3CN (Aldrich), $(CD_3)_2CO$ (Aldrich), *o*-carborane (Aster Limited), $CoCl_2$ (Janssen), NaOH (Janssen), NaOCl(aq) (Janssen), HCl(aq) (Baker), F_2 (Matheson), Cl_2 (Matheson), Br_2 (Janssen), I_2 (Baker), 1-fluoro-2,4,6-trimethylpyridinium triflate (Aldrich), *N*-chlorosuccinimide (Aldrich), *N*-bromosuccinimide (Janssen), HF (Matheson), CsF (Janssen), Me_4NCl (Aldrich), Me_3NHCl (Janssen), [PPN]Cl (Aldrich).

The compounds $[Cs][Co(7,8\text{-}C_2B_9H_{11})_2]$, $[Me_4N][Co(7,8\text{-}C_2B_9H_{11})_2]$, and $[Me_3NH][Co(7,8\text{-}C_2B_9H_{11})_2]$ were prepared by following literature procedures,[12] except that 1-propanol was substituted for ethanol as a solvent in the preparation of the intermediate $[Me_3NH][C_2B_9H_{12}]$, due to the low reflux temperature of ethanol at this altitude.

NMR Spectroscopy. Samples for ^{11}B NMR and $^{11}B\{^1H\}$ NMR were solutions in $(CD_3)_2CO$ or CD_3CN using $BF_3{\cdot}OEt_2$ ($\delta = 0$) in CD_3CN as an external standard. Samples for ^1H NMR were solutions in $(CD_3)_2CO$ or CD_3CN using TMS ($\delta = 0.0$) or residual $(CD_3)(CD_2H)CO$ ($\delta = 2.05$) or CHD_2CN ($\delta = 1.94$) as an internal standard. All samples were run on an IBM AF250 NMR spectrometer at 250.13 MHz (^1H) or 80.21 MHz (^{11}B).

X-ray Crystallography of $[PPN][Co(C_2B_9H_{10}Cl)_2]$. A yellow crystal, grown from THF, was centered on a Siemens R3m diffractometer. Unit cell dimensions were determined from a least squares fit of 25 centered reflections. These dimensions and other parameters, including conditions of data collection, are summarized in Table 3, with the final atomic coordinates given in Table 4. Data were collected at 298 K in the ω-scan mode. Three reflections were monitored every 97 reflections to check stability, with no significant trends observed. Of the 6830 independent reflections collected, 2746 reflections were considered observed ($F > 4.0\sigma(F)$). An absorption correction was applied to the data. The PPN^+ cation is unexceptional, with a P−N−P angle of 147.2(4)°. Details of the PPN^+ ion are available in the supplementary material.

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(18) Siedle, A. R.; Bodner, G. M.; Todd, L. J. *J. Organomet. Chem.* **1971**, *33*, 137.

(19) Sivy, P.; Preisinger, A.; Baumgartner, O.; Valach, F.; Koren, B.; Matel, L. *Acta Crystallogr.* **1986**, *C42*, 28.

(20) (a) The X-ray crystal structure of $[K][Co(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})_2]$ has been published.[20b] We include the X-ray crystal structure of $[PPN][Co(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})_2]$ in this report since it aids in the characterization of a compound in this work, it provides a visual aid and numbering scheme for discussion of both $[Co(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})_2]^-$ and $[Co(10\text{-}Br\text{-}7,8\text{-}C_2B_9H_{10})_2]^-$, and it provides a complete set of data for the anion. (b) Kirillova, N. I.; Zhdanov, A. S.; Gusev, A. I.; Kirin, V. N.; Knyazev, S. P.; Sokolova, T. V. *Metalloorg. Khim.* **1989**, *2*, 859.

(21) Plesek, J.; Plzak, Z.; Stuchlik, J.; Hermanek, S. *Collect. Czech. Chem. Commun.* **1981**, *46*, 1748.

(22) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960.

Table 3. Crystal Data Collection Parameters

compd	$[PPN][Co(C_2B_9H_{10}Cl)_2]$
formula	$C_{40}H_{50}B_{18}Cl_2CoNP_2$
fw	465.6
crystal size/mm	0.55 × 0.45 × 0.15
space group	*C*2/*c*
temp/K	296
a/Å	31.267(5)
b/Å	9.0190(10)
c/Å	18.706(3)
β/deg	116.970(0)
V/Å^3	4701.8(15)
Z	4
ϱ_{calcd}/(g/cm^3)	1.315
no. of unique reflns	6830
no. of obsd reflns	2746 ($F > 4.0\sigma(F)$)
radiation (*λ*/Å)	Mo Kα (0.710 73)
scan technique	*ω*
2*θ* range/deg	7.0−45.0
R, R_w	5.38, 7.2
GOF	0.58

Table 4. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	*y*	*z*	*U*(eq)[a]
Co	2500	2500	5000	32(1)
Cl	3095(1)	5632(2)	5904(1)	97(1)
P	−58(1)	−873(1)	1652(1)	27(1)
N 0	−1366(5)	2500	33(2)	
C(7)	2354(2)	1349(6)	5788(3)	43(2)
C(8)	2821(2)	744(6)	5713(3)	42(2)
C(11P)	−44(2)	1101(5)	1527(2)	31(2)
C(12P)	333(2)	1801(5)	1463(3)	36(2)
C(13P)	345(2)	3327(6)	1428(3)	51(2)
C(14P)	−23(2)	4145(6)	1442(3)	57(3)
C(15P)	−403(2)	3469(5)	1493(3)	49(2)
C(16P)	−418(2)	1946(5)	1531(3)	38(2)
C(21P)	−623(1)	−1504(5)	857(3)	30(2)
C(22P)	−817(2)	−809(6)	111(3)	45(2)
C(23P)	−1232(2)	−1349(7)	−501(3)	56(2)
C(24P)	−1451(2)	−2597(7)	−385(3)	61(2)
C(25P)	−1259(2)	−3293(7)	350(3)	54(2)
C(26P)	−843(2)	−2745(5)	977(3)	39(2)
C(31P)	419(1)	−1701(5)	1497(3)	30(2)
C(32P)	884(2)	−1637(6)	2124(3)	43(2)
C(33P)	1260(2)	−2266(6)	2029(4)	57(2)
C(34P)	1170(2)	−2971(6)	1319(4)	59(3)
C(35P)	716(2)	−3033(7)	712(3)	56(3)
C(36P)	339(2)	−2397(6)	790(3)	43(2)
B(1)	3118(3)	1547(9)	7282(4)	66(3)
B(2)	2758(3)	277(8)	6551(4)	58(3)
B(3)	3313(2)	805(9)	6614(4)	56(3)
B(4)	3403(2)	2711(9)	6859(4)	65(3)
B(5)	2889(3)	3365(9)	6938(4)	66(3)
B(6)	2498(3)	1872(9)	6738(4)	61(3)
B(9)	3214(2)	2152(7)	5846(4)	48(2)
B(10)	2947(2)	3736(8)	6048(4)	54(3)
B(11)	2387(2)	3190(8)	5973(4)	51(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Synthesis. $[(CH_3)_4N][Co(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})_2]$. The orange solid $[(CH_3)_4N][Co(7,8\text{-}C_2B_9H_{11})_2]$ (0.62 g, 1.36 mmol) was added to a mixture of 50 mL of 10% NaOCl (by weight in H_2O) and 20 mL of 6 M HCl in H_2O, and the resulting mixture was stirred at 25 °C for 24 h. To the yellow slurry was added 50 mL of CH_3CN. After brief shaking, the clear yellow top layer was separated from the clear colorless bottom layer, and the yellow CH_3CN solution was evaporated to dryness, yielding 0.62 g (85% yield) of $[(CH_3)_4N][Co(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})_2]$. NMR (acetone-$d_6$) (assignment; integral; multiplicity): ^{11}B 13.6 (B10; 1; s), 0.5 (B1; 1; d), −4.9 (B2,4,5,6; 4; d), −18.1 (B9,11; 2; d), −24.6 (B3; 1; d); ^{1}H 3.8 ((B)-C-**H**; 1; s), 3.4 (N(CH_3)$_4$; 3; s).

$[(CH_3)_4N][Co(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})_2]$. The solid $[(CH_3)_4N][Co(7,8\text{-}C_2B_9H_{11})_2]$ (0.57 g, 1.43 mmol) was added to 120 mL of a 1:1 mixture of THF and 2-propanol. Iron filings (0.40 g, 0.72 mmol) were added to the solution. Chlorine gas (Cl_2) was sparged through the orange solution for 2 h. The resulting yellow solution was evaporated to dryness, and the residue was washed with two 50 mL portions of water. The resulting dark yellow solid was redissolved in THF, the solution filtered, and the filtrate evaporated to dryness, yielding 0.61 g (91% yield) of $[(CH_3)_4N^+][Co(10\text{-}Cl,7,8\text{-}C_2B_9H_{10})_2^-]$. NMR (acetone-$d_6$) (assignment; integral; multiplicity): ^{11}B 13.6 (B10; 1; s), 0.5 (B1; 1; d), −4.9 (B2,4,5,6; 4; d), −18.1 (B9,11; 2; d), −24.6 (B3; 1; d); ^{1}H: 3.8 ((B)-C-**H**; 1; s), 3.4 (N(CH_3)$_4$; 3; s).

$[(CH_3)_3NH][Co(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})_2]$. In 100 mL THF, *N*-chlorosuccinimide (0.20 g, 1.5 mmol) and $[(CH_3)_3NH][Co(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})_2]$ (0.25 g, 0.65 mmol) were refluxed for 20 min. The resulting solution was evaporated to dryness, and the residue was washed with water. A dark orange solid (0.24 g, 89% yield) was isolated. NMR (acetone-d_6) (assignment; integral; multiplicity): ^{11}B 13.6 (B10; 1; s), 0.5 (B1; 1; d), −4.9 (B2,4,5,6; 4; d), −18.1 (B9,11; 2; d), −24.6 (B3; 1; d); ^{1}H 3.8 ((B)-C-**H**; 1; s), 2.7 (HN(CH_3)$_3$; 3; d).

$[(CH_3)_3NH][Co(10\text{-}Br\text{-}7,8\text{-}C_2B_9H_{10})_2]$. In 100 mL of THF, Br_2 (1.60 g, 10.0 mmol) and $[Me_3NH][Co(7,8\text{-}C_2B_9H_{11})_2]$ (0.40 g, 1.03 mmol) were dissolved, and the dark brown clear solution was refluxed for 20 min. The resulting solution was evaporated to dryness, and the brown solid was dissolved in water. Addition of trimethylammonium chloride (2.0 g, 2.1 mmol) produced an orange precipitate. A dark orange solid (0.24 g, 89% yield) was isolated by filtration. NMR (acetone-d_6) (assignment; integral; multiplicity): ^{11}B 7.2 (B10; 1; s), 1.3 (B1; 1; d), −4.4 (B2,4,5,6; 4; d), −18.1 (B9,11; 2; d), -24.1 (B3; 1; d); ^{1}H 4.4 ((B)-C-**H**; 1; s), 2.7 (HN(CH_3)$_3$; 3; d).

$[(CH_3)_3NH][Co(10\text{-}Br\text{-}7,8\text{-}C_2B_9H_{10})_2]$. In 100 mL of THF, *N*-bromosuccinimide (0.60 g, 3.37 mmol) and $[Me_3NH][Co(7,8\text{-}C_2B_9H_{11})_2]$ (0.40 g, 1.03 mmol) were dissolved, and the dark brown clear solution was refluxed for 20 min. The resulting solution was evaporated to dryness, and the residue was washed with water. A dark orange solid (0.24 g, 89% yield) was isolated. NMR (acetone-d_6) (assignment; integral; multiplicity): ^{11}B 7.2 (B10; 1; s), 1.3 (B1; 1; d), −4.4 (B2,4,5,6; 4; d), −18.1 (B9,11; 2; d), -24.1 (B3; 1; d). ^{1}H 4.4 ((B)-C-**H**; 1; s), 2.7 (HN(CH_3)$_3$; 3; d).

Conclusions

Although the $[Co(7,8\text{-}C_2B_9H_{11})_2]^-$ anion is extremely stable, several relatively mild conditions afford halogenation. New synthetic routes leading exclusively to the anions $[Co(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})_2]^-$ and $[Co(10\text{-}Br\text{-}7,8\text{-}C_2B_9H_{10})_2]^-$ have been developed, for the first time providing high yields of the pure dihalogenated compounds.

The Cs^+ and Sr^{2+} extraction efficiencies of $[Co(10\text{-}Cl\text{-}7,8\text{-}C_2B_9H_{10})_2]^-$ were determined to be equal to that of the parent compound, to within experimental error.[23]

These compounds are designed to be robust, resisting reaction under acidic oxidizing conditions and intense radiation. Consequently, the use of these halogenated compounds as starting materials in further reactions is severely limited. The few reactions that are possible with these compounds will be the subject of a future publication.

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Supporting Information Available: Tables giving complete crystallographic details of the structure solution of $[PPN][Co(C_2B_9H_{10}Cl)_2]$, anisotropic thermal parameters, hydrogen coordinates, and complete bond distances and bond angles (8 pages). Ordering information is given on any current masthead page.

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(23) Hurlburt, P. K.; Pinkerton, A. B.; Abney, K. D.; Miller, R. L.; Kinkead, S. A. Submitted for publication in *Solvent Extr. Ion Exch.*