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Condensation Polymerization of Cobalt Dicarbollide Dicarboxylic Acid

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Introduction

Transition metal complexes have important utility as monomer units in polymer chains, because they ultimately determine the unique electronic, optical, and catalytic properties of the polymer.[1,2] Our interest in synthesizing organometallic polymers containing the cobalt bis(dicarbollide) anion is motivated by their possible application as cation exchange materials for the removal of cesium-137 and strontium-90 from nuclear wastes.[3] We are now directing work at the synthesis and characterization of polymeric materials which incorporate cobalt dicarbollide in the main polymer chain. Our initial efforts have focused on attaching organic functional groups at the carbon sites of cobalt dicarbollide to produce derivatives with reactivity toward addition and condensation polymerization. A few polymers containing grafted metallocarboranes[4] and a polyester containing a dicarbollide−cyclopentadienyl mixed sandwich complex in the main chain[5] have been reported. Recently, the condensation polymerization of metal (bis)dicarbollide compounds containing boron- and carbon-substituted terminal amino groups to produce main chain oligomeric and polymeric products has also appeared in the literature.[6] To our knowledge, the condensation polymerization of cobalt dicarbollide with attached carboxylic acid, acid chloride, and other functional groups has not yet been investigated. Herein, we report the application of a selective deprotonation reaction of cobalt dicarbollide,[7] leading to monomeric dicarboxylic acid and diacid chloride compounds. Reaction of the monomeric compounds with hexamethylenediamine leads to the formation of the first oligomeric amide compounds with cobalt dicarbollide in the main chain.

Experimental Section

General Procedures. *o*-Carborane (98%) was purchased from Consumer Health Products, Los Angeles, CA, and used as received. $Cs[Co(C_2B_9H_{11})_2]$ was prepared via literature methods,[8] and dried at 100 °C in a vacuum oven prior to use. THF for air-sensitive manipulations was freshly distilled from sodium/benzophenone ketyl. All other reagents were used as received. Air sensitive manipulations were carried out under nitrogen or helium atmospheres, using standard glovebox and Schlenk techniques.

NMR spectra were obtained on a Varian Unity Plus 200 MHz spectrometer. ^1H and ^{13}C spectra were referenced to TMS. FTIR spectra were obtained on a Nicolet 510P spectrometer. Thermal analysis was performed on a TA Instruments SDT 2960 simultaneous TGA−DTA. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer.

Preparation of $[Li(THF)_x][Co(C_2B_9H_{11})(C_2B_9H_{10})(COOH)]$ (3). To a vigorously stirred solution of orange $Cs[Co(C_2B_9H_{11})_2]$ (2.0 g, 4.3 mmol) in THF (200 mL) was slowly added nBuLi (2.7 mL, 4.3 mmol) under N_2 to give a purple solution of the monolithio complex. The purple solution was stirred for 10 min at 30 °C. Dry carbon dioxide was bubbled through the resulting purple solution for 5 min, resulting in a red-colored reaction mixture. The reaction mixture was exposed to air, and a large excess of HCl (8 mL, 37%) was slowly added with stirring. Precipitated CsCl was removed by suction filtration. Removal of THF from the red filtrate followed by gentle heating under vacuum gave the red solid **(3)**. FTIR (KBr pellet): 3104−3701 (b), 3048 (w), 2950 (m), 2878 (m), 2567 (s), 1697 (s), 1419 (w), 1270 (m), 1090 (w), 1029 (m), 989 (m), 842 (w), 725 (w).

Preparation of $[Li(THF)_x][Co(C_2B_9H_{10})_2(COOH)_2]$ (4). A similar procedure to that used for **3** except using 2 equiv of nBuLi gave the blue, dilithio complex as an intermediate and the red solid dicarboxylic acid **4** as the final product. FTIR (KBr pellet): 3099−3706 (b), 3058 (w), 2952 (m), 2881 (m), 2567 (s), 1704 (s), 1434 (m), 1272 (m), 1090 (w), 1039 (m), 994 (m), 867 (m), 715 (m). ^1H NMR (THF-d_8, 30 °C): δ 1.76, 3.61 (m, $Li(C_4H_8O)_x^+$); 3.82, 4.04 (s, cage-C*H*); 11.57 (b, COO*H*). Anal. Calcd for $[Li(THF)_2][Co(C_2B_9H_{10})_2(COOH)_2]$: C, 29.87; H, 6.80. Found: C, 29.19; H, 6.58.

Preparation of $[Li(THF)_x][Co(C_2B_9H_{11})(C_2B_9H_{10})(COCl)]$ (5). Compound **3** (0.44 g, 0.76 mmol) was dissolved in $SOCl_2$ (15 mL) and 1 drop of DMF added. The solution was refluxed for 4 h, and the $SOCl_2$ was removed under vacuum. Gentle heating of the product under vacuum gave the water sensitive acid chloride **5** as a brown solid. Due to the air sensitive nature of **5**, the FTIR was taken as a thin film from dry THF between salt plates: 3046 (m), 2969 (m), 2873 (m), 2583 (s), 1757 (s), 1439 (m), 1333 (m), 1282 (m), 1201 (m), 1110 (s), 1049 (s), 983 (m), 908 (m), 842 (m), 756 (m).

Preparation of $[Li(THF)_x][Co(C_2B_9H_{10})_2(COCl)_2]$ (6). A similar procedure to that used for **5**, except refluxing **4** in $SOCl_2$, gave the water sensitive diacid chloride **6** as a brown solid. FTIR (thin film from dry THF between salt plates): 3046 (w), 2969 (m), 2873 (m),

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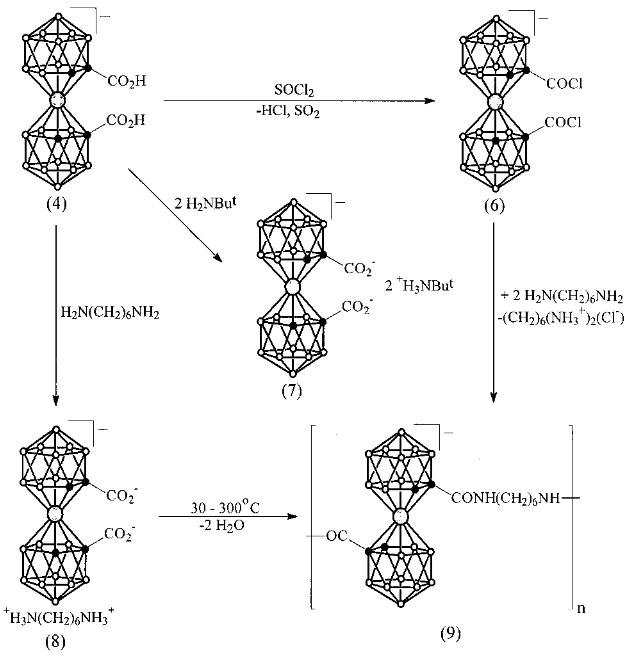
Scheme 1



2850 (s), 1761 (s), 1424 (m), 1338 (s), 1203 (m), 1107 (m), 1049 (s), 986 (m), 900 (m), 765 (w).

Preparation of $[Li(THF)_x][Co(C_2B_9H_{10})_2(COO^-)_2\ (Bu^tNH_3^+)_2]$ (7). To a vigorously stirred solution of *tert*-butylamine (0.20 mL, 1.9 mmol) in THF (10 mL) was added the red dicarboxylic acid **4** (0.40 g, 0.64 mmol) in THF (10 mL). The reaction mixture was stirred for 2 h at 30 °C. Removal of THF gave the amine salt **7** as a red, air-stable solid. FTIR (KBr pellet): 2676−3706 (b), 2560 (s), 1583 (s), 1347 (s), 1747 (w), 1535 (m), 1473 (w), 1208 (m), 1044 (m), 996 (m), 890 (w), 770 (w). ^{1}H NMR (THF-d_8, 30 °C): δ 7.70 (broad s, NH_3^+); 3.57, 1.76 (m, $Li(C_4H_8O)_x$); 1.36 (s, $^+H_3NC(CH_3)_3$). ^{13}C NMR (THF-d_8, 30 °C): δ 172.6 (COO^-); 57.2 (cage-CH); 52.5 ($(CH_3)_3CNH_3^+$); 28.4 ($(CH_3)_3CNH_3^+$); 26.4, 68.3 ($(Li(C_4H_8O)_x^+)$).

Preparation of $[Li(THF)_x][Co(C_2B_9H_{10})_2(COO^-)_2(^+H_3N(CH_2)_6NH_3^+)]$ (8). To a vigorously stirred solution of the dicarboxylic acid **4** (0.08 g, 0.13 mmol) in THF (5 mL) was added hexamethylenediamine (0.03 g, 0.26 mmol) in THF (10 mL). A red solid precipitated from the reaction mixture immediately upon addition of the hexamethylenediamine. Removal of THF gave the amine salt **8** as a red, air-stable solid. FTIR (KBr pellet): 2685−3687 (b), 2560 (s), 1583 (s), 1352 (s), 1463 (w), 1049 (m), 996 (m), 890 (w), 770 (w). Anal. Calcd for $[Li(THF)][Co(C_2B_9H_{10})_2(COO^-)_2(^+H_3N(CH_2)_6NH_3^+)]$: C, 31.66; H, 7.64; N, 4.62. Found: C, 31.73; H, 8.20; N, 5.14.

Preparation of $[Li]_n[-OC(C_2B_9H_{10})Co(C_2B_9H_{10})CONH(CH_2)_6NH-]_n$ (9). The procedure for the preparation of the diacid chloride **6** was carried out only using 2.0 g (3.5 mmol) of the dicarboxylic acid **4**. Diacid chloride **6** so produced was dissolved in THF (40 mL) under nitrogen and was slowly added to a vigorously stirred solution of hexamethylenediamine (0.75 g, 6.5 mmol) in THF (50 mL). A solid precipitated from THF solution immediately upon addition of **6** to the hexamethylenediamine/THF solution. The reaction mixture was stirred for 1 h at 30 °C, then exposed to the air, and filtered to obtain a dark brown crude product. The crude product was dried under vacuum and then washed with water to extract hexamethylenediamine dihydrochloride. A second filtration followed by drying at 80 °C in a vacuum oven gave the amide condensation product **9** as a brown solid. FTIR (KBr pellet): 3417 (b), 3268 (b), 3046 (b), 2926 (s), 2859 (m), 2565 (s), 1636 (s), 1526 (s), 1458 (m), 1343 (s), 1088 (b), 837 (w), 755 (w). ^{1}H NMR (DMSO-d_6, 30 °C): δ 5.17 (b, $HN(CH_2)_6NH$); 3.34, 2.98 (b, cage-CH); 2.48, 1.28 (b, $HN(CH_2)_6NH$).

Thermal Analysis of $[Li(THF)_x][Co(C_2B_9H_{10})_2(COO^-)_2(^+H_3N(CH_2)_6NH_3^+)]$ (8). An 8.3545 mg sample of red **8** was placed in the TGA−DTA instrument and heated under N_2 from 30 to 300 °C at 10 °C/min. The sample was held at 300 °C for 60 min and then allowed to air cool. The experimental percentage weight changes due to loss of THF (10%, 14 min) and water (7%, 30 min) were obtained by integrating the separate areas under the first-derivative plot of the TGA curve. The total weight loss (30%) was obtained by integrating the total area under the first derivative plot. Calculation of the expected weight changes from THF loss (12%) and water loss (6%) during thermolysis of **8** was carried out assuming loss of 1 THF molecule and loss of 2 water molecules per formula unit of the amine salt. An FTIR spectrum (KBr pellet) was taken on the brown product remaining in the pan after thermolysis: 3417 (b), 3046 (w), 2931 (s), 2864 (s), 2556 (s), 1646 (s), 1530 (m), 1362 (b), 1092 (b), 986 (b), 731 (m).

Results and Discussion

Selective deprotonation of the cage C−H sites of $Cs[Co(C_2B_9H_{11})_2]$ in THF (30 °C) with 1 and 2 equiv of nBuLi gives purple and blue solutions of $[Co(LiC_2B_9H_{10})(C_2B_9H_{11})]\cdot(THF)_x$ **(1)** and $[Co(LiC_2B_9H_{10})_2]\cdot(THF)_x$ **(2)**, respectively.[7] Synthesis of the carboxylic acid compounds $[Li(THF)_x][Co(C_2B_9H_{11})(C_2B_9H_{10})(COOH)]$ **(3)** and $[Li(THF)_x][Co(C_2B_9H_{10})_2(COOH)_2]$ **(4)** is carried out as a one-pot procedure by bubbling CO_2 through THF solutions of **1** or **2** under nitrogen, followed by protonation with HCl and filtration of precipitated CsCl (eqs 1 and 2). Removal of THF from the red supernatant gives compounds **3** and **4** as air-stable, hygroscopic, red solids. In the FTIR spectrum of **4**, cage-stretching bands are observed at 3058 (ν_{CH}) and 2567 cm^{-1} (ν_{BH}) in addition to the carboxylic acid stretching bands at 3099−3706 (ν_{OH}) and 1704 cm^{-1} (ν_{CO}). A broad singlet at δ 11.57 in the ^{1}H NMR (THF-d_8, 30 °C) spectrum of **4** is assigned to the hydrogen-bonded carboxylic acid protons. The singlet, cage-CH resonances (δ 3.82, 4.04) in addition to resonances for coordinated THF (δ 3.61, 1.76) are also observed in the ^{1}H NMR of **4**. Elemental analysis data for **4** indicates that the counterion is most likely $Li(THF)_2^+$.

$$Cs[Co(C_2B_9H_{11})_2] \xrightarrow[-C_4H_{10}]{nBuLi/THF}$$

$$\underset{\mathbf{1}}{[Co(LiC_2B_9H_{10})(C_2B_9H_{11})]\cdot(THF)_x^-} + Cs^+ \xrightarrow[-CsCl]{CO_2/HCl/THF}$$

$$\underset{\mathbf{3}}{Li(THF)_x[Co(C_2B_9H_{11})(C_2B_9H_{10})(COOH)]} \quad (1)$$

$$Cs[Co(C_2B_9H_{11})_2] \xrightarrow[-C_4H_{10}]{2nBuLi/THF}$$

$$\underset{\mathbf{2}}{[Co(LiC_2B_9H_{10})_2]\cdot(THF)_x^-} + Cs^+ \xrightarrow[-CsCl]{2CO_2/HCl/THF}$$

$$\underset{\mathbf{4}}{Li(THF)_x[Co(C_2B_9H_{10})_2(COOH)_2]} \quad (2)$$

Compounds **3** and **4** show reactivity typical of carboxylic acids. Comparison of the FTIR spectra obtained before and after refluxing dicarboxylic acid **4** in neat $SOCl_2$ shows disappearance of the ν_{OH} stretching band (3099−3706 cm^{-1}) and a shift of the carbonyl, ν_{CO}, stretching band (1704 cm^{-1}) to higher frequency (1761 cm^{-1}), consistent with the formation of the diacid chloride, $[Li(THF)_x][Co(C_2B_9H_{10})_2(COCl)_2]$ **(6)** (Scheme 1). Similar IR spectral features are observed for the acid chloride product obtained by refluxing **3** in neat $SOCl_2$. Conversion of dicarboxylic acid **4** to amine salts was also carried out (Scheme 1). When **4** is stirred with a slight excess of Bu^tNH_2 in THF, a red amine salt, $[Li(THF)_x][Co(C_2B_9H_{10})_2(COO^-)_2(Bu^tNH_3^+)_2]$ **(7)**, is obtained after removal of THF and unreacted Bu^tNH_2. A similar reaction between **4** and hexamethylenediamine in THF forms an amine salt which precipitates as a red solid, $[Li(THF)]\ [Co(C_2B_9H_{10})_2(COO^-)_2\ (^+H_3N(CH_2)_6NH_3^+)]$ **(8)**. Amine salt COO^- and NH_3^+ functional groups give rise to prominent features in the FTIR spectra of compounds **7** and **8.** The FTIR spectrum of **7** displays intense, overlapping bending and stretching bands, $\delta_{NH_3^+}$ asym-ν_{COO}−, at 1583 cm^{-1}, and an additional stretching band, sym-ν_{COO}−, at 1347 cm^{-1}. In the FTIR spectrum of **8** similar bands are observed at 1583 and 1352 cm^{-1}, respectively. Proton and ^{13}C NMR for **7** show resonances for THF and the COO^- and NH_3^+ functional groups. The formulation of the counterion of **8** as $Li(THF)^+$ is based upon elemental analysis data.

Reaction of water sensitive diacid chloride **6** with 2 equiv of hexamethylenediamine in THF forms an insoluble brown product (Scheme 1). The FTIR and elemental analysis data for the brown product, taken after water extraction of hexamethylenediamine dihydrochloride, are consistent with an oligomeric derivative of cobalt dicarbollide $[Li]_n[-OC(C_2B_9H_{10})Co(C_2B_9H_{10})CONH(CH_2)_6NH-]_n$ **(9)**. Key features in the FTIR spectrum of **9** include the presence of ν_{NH} (3417, 3268, 3046 cm^{-1}) and the amide I, ν_{CO} (1636 cm^{-1}) and amide II, δ_{NH} (1526 cm^{-1}), bands. The hexamethylene backbone also gives rise to broad, aliphatic resonances in the ^{1}H NMR. The amide proton resonance gives a concentration dependent chemical shift indicating hydrogen bonding between oligomer chains. Simultaneous thermogravimetric−differential thermal analysis (TGA−DTA) of **9** (30−100 °C, 10 °C/min) shows minimal weight loss (3.5%) and no change in the FTIR spectrum after 20 min at 100 °C. Thermal analysis and ^{1}H NMR results indicate that the counterion is most likely Li^+.

An alternative approach for the synthesis of a polyamide derivative of cobalt dicarbollide is the thermal conversion of the amine salt compound **8**. The TGA−DTA results for the thermolysis (30−300 °C, 10 °C/min) of **8** in a N_2 atmosphere are shown in Figure 1. Comparison of calculated and observed weight losses from the two steepest regions of the TGA curve is consistent with weight loss due to THF (calcd, 12%; obsd, 10% at 14 min) and water (calcd, 6%; obsd, 7% at 30 min). Amide bond formation is shown by the exothermic event at 33 min in the DTA curve, coincident with water loss, and by the presence of the amide I, ν_{CO} (1646 cm^{-1}) and amide II, δ_{NH} (1530 cm^{-1}) bands in the FTIR spectrum of the brown product $[Li]_n[-OC(C_2B_9H_{10})Co(C_2B_9H_{10})CONH(CH_2)_6NH-]_n$ **(9)** formed after thermolysis of **8**.

We are currently investigating the chemical and physical properties of **9** and its model compounds.[9] Molecular weight determinations of **9** using size-exclusion chromatography and laser light scattering have so far been inconclusive. Nevertheless, carbon-site substitution of dilithio(cobalt dicarbollide) appears to be a general route to difunctionalized monomers which will provide entry into different types of condensation polymers. Due to the extreme pH and high radiation environments of nuclear waste, we plan to focus our future work on the development of cobalt dicarbollide polymers with robust backbones such as polybenzimidazole.

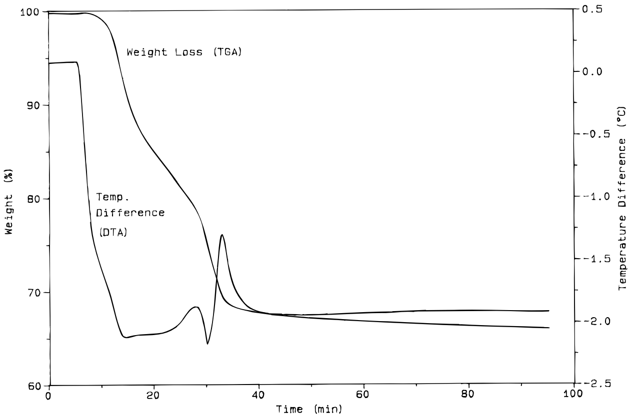


Figure 1. Simultaneous thermogravimetric (TGA)−differential thermal analysis (DTA) trace of **8** under N_2 atmosphere. Temperature profile is 30−300 °C at 10 °C/min.

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Supporting Information Available: FTIR spectra for compounds **3**−**9**, ^{1}H NMR spectra for compounds **4**, **7**, and **9**, a ^{13}C NMR spectrum for compound **7**, and a TGA−DTA trace and first-derivative plot for compound **8** (24 pages). Ordering information is given on any current masthead page.

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(9) The synthesis of a model compound of **9** was attempted by reacting acid chloride **5** with excess $H_2N(CH_2)_6NH_2$. The product obtained has FTIR spectral features similar to those of **9** but has not yet been purified.