

Clusters as Substituents. Synthesis and Thermal Decomposition of Metal Carboranecarboxylates

Otomar Kříž,[†] Arnold L. Rheingold,^{*‡} Maoyu Shang,[§] and Thomas P. Fehlner^{*§}

Institute of Inorganic Chemistry, Czech Academy of Sciences, 250 68 Rez, Czech Republic, Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, and Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

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The synthesis of the metal carboxylates $M^{II}(1,2-C_2B_{10}H_{11}CO_2)_2$, $M = Zn, Cu, Ni$, and Mo , and $M^{II}\{1,2-C_2B_{10}H_{10}(CO_2)_2\}_2$, $M = Cu$ and Ni , are reported. All have been characterized spectroscopically and by elemental analysis. $M^{II}(1,2-C_2B_{10}H_{11}CO_2)_2$, $M = Cu$ and Ni , have been structurally characterized in the solid state by single-crystal X-ray diffraction as $Cu_2(C_2B_{10}H_{11}CO_2)_4(THF)_2$ ($P2_1/n$, $a = 10.327(2)$ Å, $b = 13.428(2)$ Å, $c = 19.605(6)$ Å, $\beta = 90.58(2)^\circ$, $V = 2718.5(12)$ Å³, $d(\text{calcd}) = 1.246$ g/cm³, $Z = 2$) and $Ni_2(C_2B_{10}H_{11}CO_2)_4(THF)_4 \cdot EtOH \cdot H_2O$ ($Pca2_1$, $a = 22.403(4)$ Å, $b = 13.996(3)$ Å, $c = 23.104(5)$ Å, $V = 7244(3)$ Å³, $d(\text{calcd}) = 1.134$ g/cm³, $Z = 4$). The thermolyses of $Cu_2(C_2B_{10}H_{11}CO_2)_4(THF)_2$, $Cu\{1,2-C_2B_{10}H_{10}(CO_2)_2\}$, $Ni_2(C_2B_{10}H_{11}CO_2)_4(THF)_4 \cdot H_2O \cdot 2THF$, and $Ni\{1,2-C_2B_{10}H_{10}(CO_2)_2\}$ have been investigated by weight loss, infrared spectroscopy, and isolation of the volatile products. The solid-state products have been characterized by elemental analysis, powder X-ray diffraction of crystallized materials, and X-ray photoelectron spectroscopy. This work reveals some further aspects of cluster substituent effects and emphasizes the importance of cluster–central metal link stability relative to cluster stability in making useful solids from linked cluster precursors.

Introduction

The idea of a metal cluster as a substituent with unusual steric and electronic properties^{1,2} has led to the synthesis of large cluster systems exhibiting both expected and unexpected structure and bonding. When used to replace a methyl group in the acetate ligand, the metal cluster substituent $[(CO)_9Co_3C]$ allows the synthesis of tractable, high molecular weight metal carboxylates.^{3,4} Steric effects resulting from cluster size are evidenced in carboxylate exchange rates whereas electronic effects dramatically change optical and redox properties.⁵ The relatively fragile nature of the $[(CO)_9Co_3C]$ cluster fragment results in a number of complications. The cluster acid itself spontaneously forms $Co_4O[(CO)_9Co_3CCO_2]_6$ ^{4,6} and unexpected reaction products containing $Co(CO)_x$ fragments have been observed.⁷

These cluster carboxylates give rise to new materials with considerably different properties from those derived from $RCCO_3(CO)_9$.⁸ For example, $M_4O[(CO)_9Co_3CCO_2]_6$, $M = Zn$ and Co , as well as other closely related compounds, serve as precursors for highly metallic materials with a regular porous structure.⁹ These materials show catalytic activities and selectivities which depend on the composition of the precursor cluster and which are different from those of conventional supported catalysts prepared from the same metals at similar loadings.¹⁰

However, our knowledge of the material microstructure and

its relationship to the precursor structures is imprecise. Although extended networks utilizing multifunctional clusters would improve the situation, we desired to better understand the decomposition process of the present molecular solids. One complication is that, in the conversion of these cluster carboxylates into the catalytic materials, degradation of the metal cluster is competitive with loss of the carboxylate cluster–metal connectors. Thus, it is of interest to examine related systems in which either the cluster substituent is more stable or the central metal–cluster link is a different one. This study concerns the first variation. Herein we report some simple coordination chemistry of the well known¹¹ C-substituted cage carboxylate ligands $[1,2-C_2B_{10}H_{11}(CO_2)]^-$, I, and $[1,2-C_2B_{10}H_{10}(CO_2)_2]^{2-}$, II (Chart 1), and a study of the thermal decomposition of selected derivatives.

Besides the comparison of main group vs transition metal cluster substituent effects on carboxylate formation as well as thermal decomposition, there was a possibility that the carborane cluster carboxylates would generate new materials. Hence, a secondary, but still important, objective of this work was to investigate the possible utilization of these compounds for the synthesis of new M–B–C phases at relatively low temperatures. There are many boron-rich refractory borides with structures that are based on various packing arrangements of B_{12} icosahedra. Although important materials, the synthesis and characterization of these materials is fraught with difficulties not the least of which is establishment of the role of adventitious carbon.¹² Depending on the course of the pyrolysis, the proposed metal complexes of cages may constitute precursors to new, but related, materials utilizing C_2B_{10} . Note that the “borocarbides” of some metals are well characterized¹³ and related compounds have been shown to serve as precursors to borides.^{14,15}

Results and Discussion

Synthesis of Complexes of I. The compounds $M(C_2B_{10}H_{11}CO_2)_2$, $M = Zn, Cu, Ni$, and Mo , have been synthesized in a

[†] Czech Academy of Sciences.

[‡] University of Delaware.

[§] University of Notre Dame.

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- Worth, G. H.; Robinson, B. H.; Simpson, J. *J. Organomet. Chem.* **1990**, *387*, 337.
- Meng, X.; Rath, N. P.; Fehlner, T. P.; Rheingold, A. L. *Organometallics* **1991**, *10*, 1986.
- Cen, W.; Haller, K. W.; Fehlner, T. P. *Inorg. Chem.* **1991**, *30*, 3120.
- Cen, W.; Haller, K. J.; Fehlner, T. P. *Inorg. Chem.* **1993**, *32*, 995.
- Cen, W.; Lindenfeld, P.; Fehlner, T. P. *J. Am. Chem. Soc.* **1992**, *114*, 5451.
- Sturgeon, R. L.; Olmstead, M. M.; Schore, N. E. *Organometallics* **1991**, *10*, 1649.
- Cen, W.; Haller, K. J.; Fehlner, T. P. *Organometallics* **1992**, *11*, 3499.
- Worth, G. H.; Robinson, B. H.; Simpson, J. *Appl. Organomet. Chem.* **1990**, *4*, 481.
- Cen, W.; Ladna, B.; Fehlner, T. P.; Miller, A. E.; Yue, D. *J. Organomet. Chem.* **1993**, *449*, 19.
- Kalenik, Z.; Ladna, B.; Wolf, E. E.; Fehlner, T. P. *Chem. Mater.* **1993**, *5*, 1247.

(11) Beal, H. In *Boron Hydride Chemistry*; Muettterties, E. L., Ed.; Academic Press: New York, 1975; p 327.

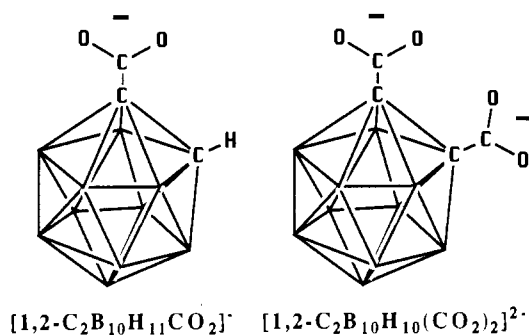
(12) Matkovich, V. I. *Pure Appl. Chem.* **1974**, *39*, 525.

(13) Halet, J.-F.; Saillard, J.-Y.; Bauer, J. *J. Less Common Met.* **1990**, *158*, 239.

(14) Volkov, V. V.; Yur'ev, G. S.; Solomatina, L. Y.; Voronina, G. S.; Myakishev, K. G. *Bull. Acad. Sci. USSR, Div. Chem.* **1990**, 435.

(15) White, J. P. I.; Shore, S. G. *Inorg. Chem.* **1992**, *31*, 2756.

Chart 1



straightforward manner. The analytical and selected infrared spectroscopic data on these compounds are given in Table 1. The compounds generally have THF ligands coordinated in the axial positions. The Mo compound, prepared via a carboxylate exchange reaction, appears to be a mixed ligand derivative.

An interesting point observed in the copper system is that the basic salt $Cu(OH)(C_2B_{10}H_{11}CO_2)THF$ is isolated when the reaction is carried out at room temperature with a Cu/carborane acid ratio of 1:1. It is characterized by a sharp band at 3638 cm^{-1} , which is assigned to a stretching vibration associated with a Cu-(OH)-Cu bridge, as well as changes in the carboxylate region. The compound is stable for several hours in strongly acidic media. However, it is not stable in the mother liquor or the solid state for long periods. The observed lifetime depends on preparative conditions, but gradually over a period of hours or days the solubility of all the samples in THF, and then acetone, decreases drastically. However, the solid-state IR still exhibits the band at 3638 cm^{-1} . The apparent polymerization (decrease in solubility with no change in the IR spectrum) is accompanied by a change in color from olive-green to green to dark green.

Spectroscopic Data on Complexes of I. For metal acetates, the difference between the frequencies of the symmetric and antisymmetric stretches associated with the carboxylate functionality constitutes a guide to the mode of bonding of the ligand.^{16,17} However, it may be seen from Table 1 that for the carboranecarboxylates the differences in symmetric and antisymmetric stretches unexpectedly lie between the ranges quoted for unidentate ($340\text{--}460\text{ cm}^{-1}$) and bidentate ($160\text{--}180\text{ cm}^{-1}$) bridging ligands. The solid-state structures of the copper and nickel compounds (see below) show that they are dimeric with the former having the expected bidentate bridging carboxylates. However, the nickel compound, which exhibits the highest difference between symmetric and antisymmetric frequencies, is found to have both unidentate and bidentate-bridging carboxylates in the solid state (see below).

In two cases a direct comparison of the main group and transition metal cluster substituted complexes is possible. The pertinent IR data are compared in Table 2. $Mo(C_2B_{10}H_{11}CO_2)_{1.5}(CH_3CO_2)_{0.5}THF$ has not been crystallographically characterized, but the others are known to have dimeric bridged structures. The frequencies of the symmetric, ν_s , and antisymmetric, ν_{as} , modes are very sensitive to the O-C-O angle. As this angle increases the symmetric frequency decreases and the antisymmetric frequency increases.¹⁶ Thus, the low values of $\Delta\nu = \nu_{as} - \nu_s$ for the molybdenum complexes reflect the short Mo-Mo distances.¹⁸⁻²¹ In comparison of the cluster-substituted complexes with the acetates, a substituent effect is clearly

apparent. That of the carborane cluster might be interpreted in terms of an increased O-C-O angle (ν_s decreases while ν_{as} increases relative to the acetate); however, the metal cluster effect is qualitatively different (both ν_s and ν_{as} decrease relative to the acetate). Some idea of the steric contribution to the observed effect comes from a comparison of the molybdenum compounds with an adamantanecarboxylate derivative. That is, for $Mo_2(C_{10}H_{15}CO_2)_4(THF)_2$, $\nu_s = 1410$ and $\nu_{as} = 1485\text{ cm}^{-1}$ demonstrating just a slight shift of both modes to lower frequencies relative to acetate.²² Although there is no simple explanation of the observed differences, the data do establish a cluster substituent effect which depends on the nature of the cluster.

Solid-State Structures. Single-crystal X-ray diffraction studies of two of these complexes were carried out. The structure of $Cu_2(C_2B_{10}H_{11}CO_2)_4(THF)_2$ is shown in Figure 1 and the structural metrics are given in the supplementary material. The structure is not of high quality but is sufficient to show that the molecule is a dimer with bidentate-bridging carboxylates as in the known acetate structure²³ and contains two axially coordinated THF molecules. The Cu-Cu distance ($2.676(4)\text{ \AA}$) is similar to that in organic carboxylates ($2.583\text{--}2.645\text{ \AA}$).¹⁶

X-ray diffraction studies of two forms of the nickel compound, $Ni_2(C_2B_{10}H_{11}CO_2)_4(THF)_4(\mu-H_2O)\cdot 2THF$ and $Ni_2(C_2B_{10}H_{11}CO_2)_4(THF)_4(\mu-H_2O)\cdot EtOH\cdot H_2O$ were carried out. In so far as the nickel complex is concerned, they are the same. As shown by Figure 2, this derivative is also a dimer. Each nickel atom is in an approximately octahedral environment being coordinated to one bridging-bidentate and one monodentate carboxylate ligand, two THF molecules, and one bridging H_2O . The water molecule is hydrogen bonded to the uncoordinated oxygens of the monodentate ligands, and the Ni-Ni distance is similar to that observed for closely related compounds.

Many nickel carboxylates have been crystallographically characterized.¹⁶ Most are monomeric with unidentate carboxylate ligands. The nickel atom is in an octahedral environment with the coordination being completed with other bases, often solvent. While multifunctional carboxylic acids lead to multinuclear nickel salts,²⁴ the acetate and chloro- and fluoroacetates appear to be monomeric in solution.^{25,26} On the other hand, the same salts in the presence of tetramethylethylenediamine lead to binuclear complexes with structures very similar to that of $Ni_2(C_2B_{10}H_{11}CO_2)_4(THF)_4(H_2O)\cdot THF$. In our case the oxygen atoms of THF replace the nitrogen atoms in the coordination sphere of nickel in the previously characterized $Ni_2(C_6H_{16}N_2)(Cl_2HC_2O_2)_4H_2O$.²⁷ As no other carboxylate ligand gives such a binuclear complex, the formation of $Ni_2(C_2B_{10}H_{11}CO_2)_4(THF)_4(H_2O)\cdot THF$ is viewed as an expression of a cluster substituent effect.

Synthesis of Complexes of II. The complexes of II are also prepared in a straightforward manner. The IR spectrum of $Cu\{C_2B_{10}H_{10}(CO_2)_2\}\cdot 2.5H_2O$ in the carboxylate region is reminiscent of that of $Cu_2(C_2B_{10}H_{11}CO_2)_4(THF)_2$ and consistent with the presence of bidentate-bridging ligands. As a consequence, we suggest the molecular formula $Cu_2\{C_2B_{10}H_{10}(CO_2)_2\}_2$. As pointed out in the Experimental Section, in protic solutions $Cu\{C_2B_{10}H_{10}(CO_2)_2\}$ is unstable toward cage degradation to copper metal, $[1,2-C_2B_9H_{10}(COOH)_2]^-$ (isolated as the anhydride or ester), and boric acid. During the preparation of this manuscript a report of a similar degradation appeared.²⁸ In the absence of water, $Cu\{C_2B_{10}H_{10}(CO_2)_2\}$ is stable in THF solutions for at least 2 weeks.

(16) Mehrotra, R. C.; Bohra, R. *Metal Carboxylates*; Academic Press: New York, 1983; p 396.

(17) Grigorev, A. I. *Russ. J. Inorg. Chem.* **1963**, *8*, 409.

(18) Cotton, F. A.; Norman, J. G.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1971**, 967.

(19) Cotton, F. A.; Norman, J. G. *J. Coord. Chem.* **1971**, *1*, 161.

(20) Filippo, J. S., Jr.; Sniadoch, H. *J. Inorg. Chem.* **1976**, *15*, 2209.

(21) Bratton, W. K.; Cotton, F. A.; Debean, M.; Walton, R. A. *J. Coord. Chem.* **1971**, *1*, 121.

(22) Cotton, F. A.; Labella, L.; Shang, M. *Inorg. Chim. Acta* **1992**, *197*, 149.

(23) van Nieherk, J. N.; Schoening, F. R. L. *Acta Crystallogr.* **1953**, *6*, 227.

(24) Coronado, E.; Drillon, M.; Fuentes, A.; Beltran, D.; Mosset, A.; Galy, J. *J. Am. Chem. Soc.* **1986**, *108*, 900.

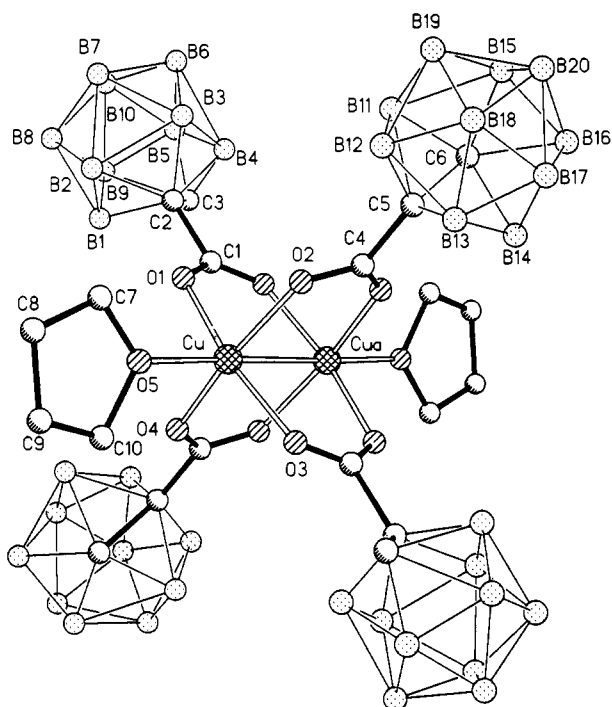
(25) Tsvadze, A. Y.; Tsvadze, G. V.; Kharitonov, Y. Y.; Gverdsitel, L. V. *Russ. J. Inorg. Chem.* **1978**, *23*, 248.

(26) Orrel, K. G. *Inorg. Chem. Acta* **1975**, *12*, 255.

(27) Ahlgrén, M.; Turpeinen, U.; Hämäläinen, R. *Acta Chem. Scand.* **1978**, *A32*, 189.

Table 1. Analytical and Selected Infrared Spectroscopic Data on $M(C_2B_{10}H_{11}CO_2)_2$, $M = Zn, Cu, Ni,$ and Mo , and $M\{C_2B_{10}H_{10}(CO_2)_2\}$, $M = Cu$ and Ni

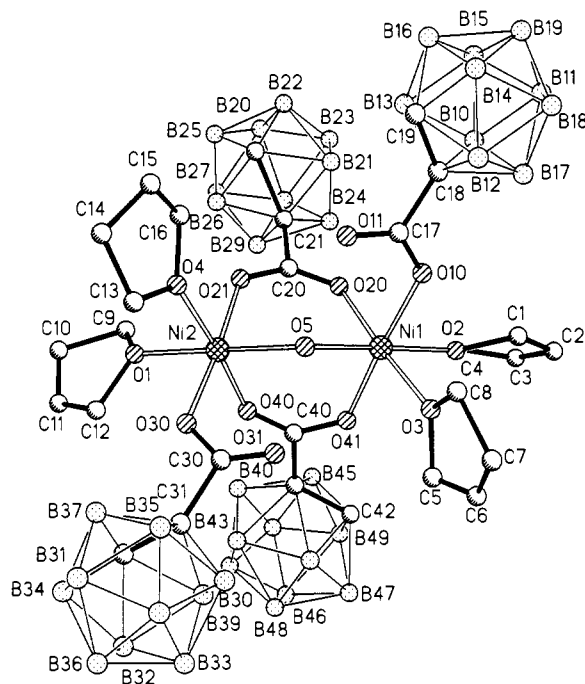
compd	wt % M: calcd, obsd	wt % B: calcd, obsd	$\nu(CO), cm^{-1}$		$\Delta\nu, cm^{-1}$
			antisym	sym	
$Zn(C_2B_{10}H_{11}CO_2)_2(THF)_2$	11.19, 10.9 ± 0.4	36.97, 33.6 ± 0.8	1675, 1655 sh	1377, 1395 sh	298
$Cu(C_2B_{10}H_{11}CO_2)_2THF$	12.46, 12.4 ± 0.4	42.34, 43.4 ± 0.5	1673	1402, 1385 sh	271
$Cu(C_2B_{10}H_{11}CO_2)(OH)THF$	18.68, 19.0 ± 1.0	31.77, 30.3 ± 0.8	1619, 1650 sh	1380, 1395	239
$Ni(C_2B_{10}H_{11}CO_2)_2(THF)_2 \cdot 1/2 H_2O \cdot THF$	8.91, 8.7 ± 0.3	32.79, 34 ± 1.4	1685, 1605 sh	1376, 1395 sh	309
$Mo(C_2B_{10}H_{11}CO_2)_{1.5}(CH_3CO_2)_{0.5}THF$	20.81, 19.8 ± 0.8	36.62, 37.2 ± 1.1	1570, 1561 sh	1402, 1380 sh	168
$Cu\{C_2B_{10}H_{10}(CO_2)_2\} \cdot 2.5 H_2O$	18.70, 18.3 ± 0.7	31.79, 32 ± 1	1617	1394	223
$Ni\{C_2B_{10}H_{10}(CO_2)_2\}(THF)_2 \cdot 3 H_2O$	12.02, 11.7 ± 0.6	22.13, 21.3 ± 0.5	1637, 1673	1382, 1370	255

**Figure 1.** Structure of $Cu_2(C_2B_{10}H_{11}CO_2)_4(THF)_2$.**Table 2.** Comparison of ν_s and ν_{as} (cm^{-1}) for Cluster-Substituted Metal Carboxylates and the Corresponding Acetates

	R group		
	CH ₃	C ₂ B ₁₀ H ₁₁	(CO) ₉ Co ₃ C
$Cu_2(RCO_2)_4(THF)_2$	1601, 1445, 1422 sh	1673, 1402, 1385 sh	1574, 1365
$Mo_2(RCO_2)_3(CH_3CO_2)(THF)_2$	1496, 1521, 1443, 1412 sh	1570, 1561 sh 1402, 1380 sh	1448, 1439 1388

Thermal Decomposition. The pyrolyses of the copper and nickel carboxylates $Cu_2(C_2B_{10}H_{11}CO_2)_4(THF)_2$ and $Ni_2(C_2B_{10}H_{11}CO_2)_4(THF)_4(H_2O) \cdot 2THF$ were studied as both compositions and structures are known. We have also studied the pyrolysis of $Cu\{C_2B_{10}H_{10}(CO_2)_2\}$ and $Ni\{C_2B_{10}H_{10}(CO_2)_2\}$ in order to assay the dependence of product type on precursor stoichiometry.

Preliminary data were obtained by conventional thermal gravimetric analysis (TGA) and are compiled in Table 3. For $Cu_2(C_2B_{10}H_{11}CO_2)_4(THF)_2$ a single, large weight loss was observed and its magnitude suggests the loss of carborane moieties as well as THF and CO₂. For $Cu\{C_2B_{10}H_{10}(CO_2)_2\}$ a vigorous decomposition occurred at about 175 °C and material was physically ejected from the holder. Hence, the TGA results could not be interpreted. For $Ni_2(C_2B_{10}H_{11}CO_2)_4(THF)_4(H_2O) \cdot 2THF$ in the low-temperature range the TGA results were in accord with our initial expectations in that several distinct mass losses were observed corresponding to the loss of all THF and H₂O moieties (34% observed, 34% calculated). In the case of the

**Figure 2.** Structure of $Ni_2(C_2B_{10}H_{11}CO_2)_4(THF)_4(H_2O) \cdot 2THF$.**Table 3.** Summary of Thermal Gravimetric Analyses of Metal Carboranecarboxylates

compd	% weight loss (T, °C) ^a
$Cu_2(C_2B_{10}H_{11}CO_2)_4(THF)_2$	72 (235)
$Cu\{C_2B_{10}H_{10}(CO_2)_2\} \cdot 2.5 H_2O$	63 ^b (175)
$Ni_2(C_2B_{10}H_{11}CO_2)_4(THF)_4(H_2O) \cdot 2THF$	4.5 (80), 16.5 (160), 24.2 (250), 34.0 (340)

^a Heating rate 10 °C/min. ^b Physical ejection of some material from the sample tube observed.

copper compounds, the temperature of onset of mass loss is higher than that of $Cu_2\{(CO)_9Co_3CCO_2\}_4$.²⁹

In order to get usable thermal gravimetric data and to identify the major volatile products, larger samples were pyrolyzed under vacuum (base pressure $\approx 10^{-3}$ Torr) for 12 h at a constant temperature. The volatile products were trapped and identified spectroscopically, and the nonvolatile material was weighed. For the two copper compounds the two gravimetric procedures yielded consistent results. Coordinated solvent and carborane ligand are lost around 200 °C. In the case of $Cu_2(C_2B_{10}H_{11}CO_2)_4(THF)_2$, a mixture of C₂B₁₀H₁₁COOH (80%) and C₂B₁₀H₁₂ (20%) along with THF was produced. The ultimate weight loss was 75% in agreement with the preliminary TGA (Table 3). This suggests the loss of 2 THF, 1 CO₂, 4 H₂, and 3 C₂B₁₀H₁₁COOH (as C₂B₁₀H₁₁COOH and C₂B₁₀H₁₂ + CO₂) giving a calculated weight loss of 75%. Presumably the hydrogen atoms required for these products come from the carborane skeleton. At 900 °C copper metal sublimed away.

(28) Teixidor, F.; Viñas, C.; Abad, M.; Lopez, M.; Casabó, J. *Organometallics* 1993, 12, 3766.

(29) Lei, X. Unpublished data.

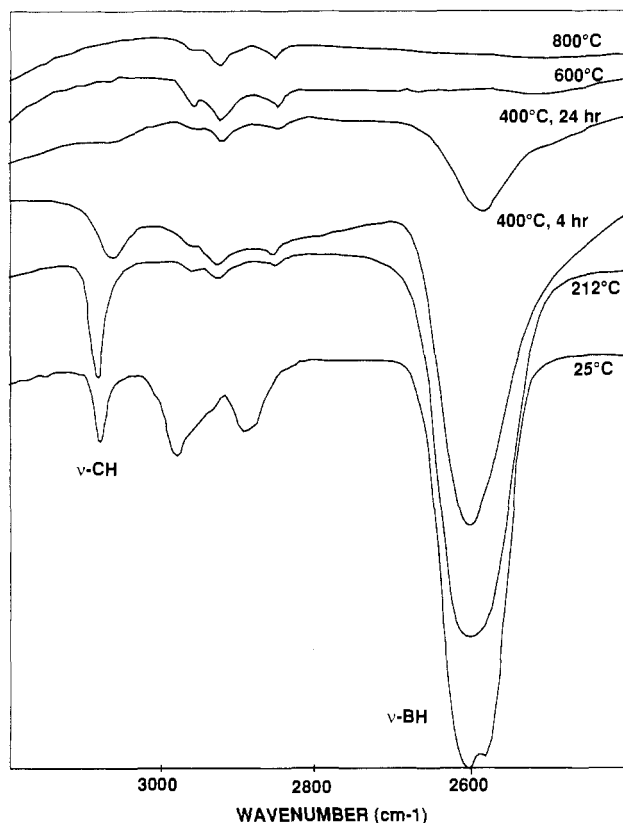


Figure 3. IR spectra in the CH and BH regions of $\text{Ni}_2(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_4(\text{THF})_4(\text{H}_2\text{O})\cdot 2\text{THF}$ before and after heating for 5 h (except where noted otherwise) at the indicated temperatures.

In the pyrolysis of $\text{Cu}\{(\text{C}_2\text{B}_{10}\text{H}_{10}(\text{CO}_2)_2)\}$, a mixture of $\text{C}_2\text{B}_{10}\text{H}_{10}(\text{COOH})_2$ (30–70%) and $\text{C}_2\text{B}_{10}\text{H}_{11}(\text{COOH})$ (70–30%) was observed, depending on the preparation time of the precursor (See Experimental Section). No $\text{C}_2\text{B}_{10}\text{H}_{12}$ was found as a volatile product in this case. The ultimate weight loss was $\approx 50\%$, but because of material losses due to the vigorous decomposition occurring at $\approx 160^\circ\text{C}$, this measurement is not sufficiently accurate to be useful.

Heating $\text{Ni}_2(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_4(\text{THF})_4\text{H}_2\text{O}\cdot 2\text{THF}$ to 210°C for 24 h under vacuum leads to a weight loss of 33% and the trapping of THF and H_2O only (34%, calcd). This is consistent with the TGA data (Table 3). At 300°C and above additional weight loss was observed and carboranes ($\text{C}_2\text{B}_{10}\text{H}_{11}\text{COOH}$ (40%) and $\text{C}_2\text{B}_{10}\text{H}_{12}$ (60%)) were trapped out. The final weight loss lay between 55 to 62% depending on sample annealing history with an average of 60%. This suggests the overall loss of 6 THF, 1 H_2O , 3 CO_2 , 16 H_2 , and 1 $\text{C}_2\text{B}_{10}\text{H}_{11}\text{COOH}$ (as $\text{C}_2\text{B}_{10}\text{H}_{11}\text{COOH}$ and $\text{C}_2\text{B}_{10}\text{H}_{12} + \text{CO}_2$) giving a calculated weight loss of 61% for the respective ligand losses.

For $\text{Ni}\{(\text{C}_2\text{B}_{10}\text{H}_{10}(\text{CO}_2)_2)\}$ in the range $25\text{--}400^\circ\text{C}$ the only volatile products were THF and H_2O . No products containing boron sublimed. The weight loss was 60% (calculated 58.6%), and the ultimate weight loss on heating up to 800°C was 68%.

In order to obtain information on the fate of the CH and BH bonds on pyrolysis and, by difference, on the H content of the solid product, the progress of the thermal decomposition was also followed by IR spectroscopy of the solid material. The change in one system is shown in Figure 3. After the initial weight loss and heating at 250°C , the IR still showed BH and CH stretches at approximately the original intensities. At 400°C these weakened (50% after 4 h, 10% after 24 h, and a trace after 90 h). After heating at 600°C they were absent. Similar behavior was observed for all four compounds. Thus, it is reasonably clear that the material remaining after annealing at 600°C and above is free from BH and CH bonds.

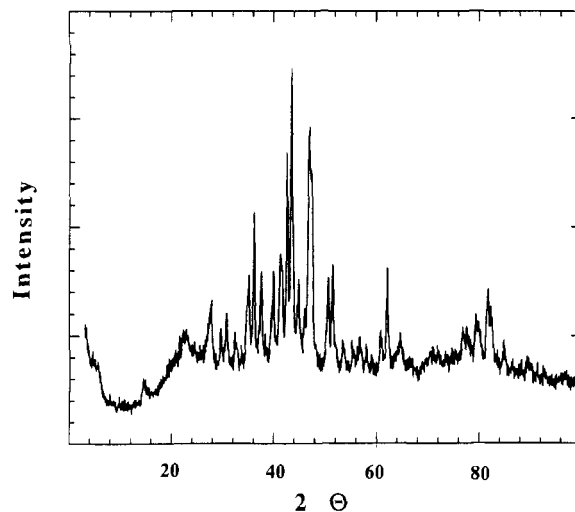


Figure 4. Powder X-ray diffraction pattern of the material formed on the pyrolysis of $\text{Ni}_2(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_4(\text{THF})_4(\text{H}_2\text{O})\cdot 2\text{THF}$ and annealing at 800°C for 5 h.

Nonvolatile Products. The gravimetric results suggest the compositions of the solid materials formed from the metal carborane carboxylates are as follows: $\text{Cu}_2\text{C}_2\text{B}_{10}$ from $\text{Cu}_2(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_4(\text{THF})_2$; $\text{Cu}(\text{C}_2\text{B}_{10})_x$ from $\text{Cu}\{(\text{C}_2\text{B}_{10}\text{H}_{10}(\text{CO}_2)_2)\}$; $\text{Ni}_2(\text{C}_2\text{B}_{10})_3$ from $\text{Ni}_2(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_4(\text{THF})_4\text{H}_2\text{O}\cdot 2\text{THF}$; $\text{NiC}_2\text{B}_{10}$ from $\text{Ni}\{(\text{C}_2\text{B}_{10}\text{H}_{10}(\text{CO}_2)_2)\}$. However, this information says nothing about the form of the nonvolatile material nor can it be taken as the composition of a compound.

Attempts to crystallize these amorphous products for diffraction studies led to ambiguous results. In the case of the copper compounds, examination by XRD after annealing showed the presence of copper metal and weak lines of another phase. The copper was extracted with HNO_3 , and the residual crystalline material (about 1–3% by weight of the original precursor) gave a weak diffraction pattern. The strongest diffraction lines suggest the presence of B_4C .³⁰ The XPS analysis showed the presence of boron (and carbon and oxygen), and chemical analysis gave 60% B and 1.2% Cu for the material from $\text{Cu}(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_2$ and 60% B and 1.0% Cu for the material from $\text{Cu}\{(\text{C}_2\text{B}_{10}\text{H}_{10}(\text{CO}_2)_2)\}$.

In the case of the nickel compounds, annealing resulted in an XRD powder pattern (Figure 4) that could not be identified with any known material (monoclinic, $a = 9.892(2)\text{ \AA}$, $b = 20.908(3)\text{ \AA}$, $c = 6.452(1)\text{ \AA}$, $\beta = 114.73(1)^\circ$; see supplementary material in which the similar but not identical XRD data from the two precursors are compared). In some samples, three additional lines were observed in the XRD which we assign to graphite. The XPS analysis of the polycrystalline material annealed at 800°C showed the presence of Ni (BE Ni $3\text{P}_{3/2} = 853.0\text{ eV}$), boron (BE B $2\text{p} = 188.3\text{ eV}$) (see Figure 5), carbon, and oxygen but no other elements. Bulk chemical analysis of samples containing some graphite by XRD showed $16.8 \pm 0.7\%$ Ni, $36.3 \pm 1.1\%$ B, 14.1% C, and 0.5% H by weight from the 1:2 precursor and $23 \pm 3\%$ Ni and $31 \pm 3\%$ B for the 1:1 precursor.

Clearly, none of these carborane-substituted carboxylates are suitable precursors for metal carborides.

Conclusions

This work suggests that the thermolysis of molecular solids composed of cluster-substituted metal coordination compounds will only yield complex, reproducible solids when the cluster-central metal link has greater thermal stability than the cluster itself. This is the situation for the metal cluster substituted carboxylates that yield active porous materials.⁹ It is not the situation for the analogous carborane-substituted complexes

(30) *Powder Diffraction Files*; Joint Committee on Powder Diffraction: Swarthmore, PA, 1975.

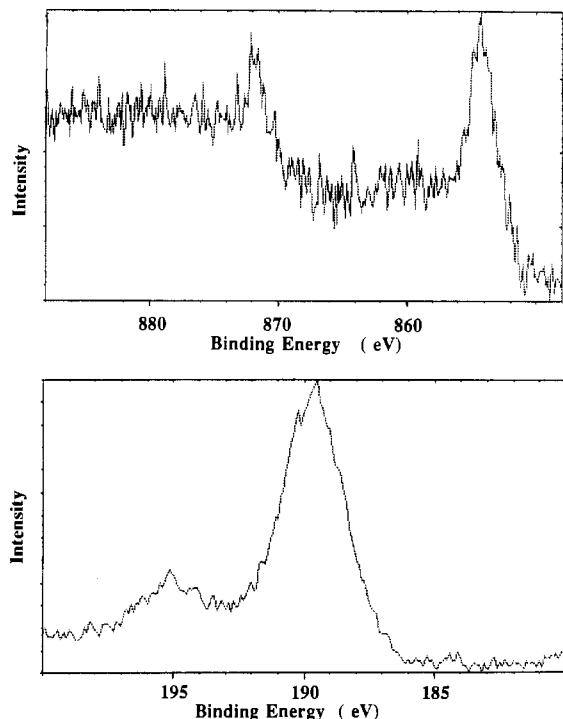


Figure 5. X-ray photoelectron lines for Ni 3p (top) and B 2p (bottom) of the material formed on the pyrolysis of $\text{Ni}_2(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_4(\text{THF})_4 \cdot (\text{H}_2\text{O}) \cdot 2\text{THF}$ and annealing at 800°C for 5 h.

studied here. In fact, although the nickel system initially looked promising, no useful route to carborides was found. The high stability of the carborane cage permits substantial cluster loss before temperatures high enough to cause cluster decomposition are reached. Further the high temperatures required to effect cluster decomposition result in significant contamination of the final solid products. We expect relative link-cluster stability to be as important a consideration for extended linked cluster systems as it is for these smaller molecular systems.

Experimental Section

General Methods. Reactions and manipulations were conducted under N_2 using standard Schlenk tube techniques. Glassware was oven-dried before use. Solvents were distilled from drying agents under nitrogen as follows: sodium benzophenone ketyl for hexane, diethyl ether, and tetrahydrofuran (THF); P_2O_5 for CH_2Cl_2 . CuSO_4 , CuCl_2 , NiCl_2 , $\text{Mo}(\text{CO})_6$, $n\text{-C}_4\text{H}_9\text{Li}$ (2.0 M solution in hexane), and Et_2Zn (1.0 M solution in hexane) were used as received from Aldrich. $1,2\text{-C}_2\text{B}_{10}\text{H}_{11}(\text{COOH})$ and $1,2\text{-C}_2\text{B}_{10}\text{H}_{10}(\text{COOH})_2$ were prepared from $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ by treatment with $n\text{-BuLi}$ and CO_2 in toluene and diethyl ether, respectively.^{31,32} Spectral data were obtained on the following instruments: ^1H and ^{13}C NMR, GN-300 and Varian 500; FT-IR, Nicolet 205. NMR shifts are referenced to residual solvent signals (δ): CD_2Cl_2 , 5.32; $(\text{CD}_3)_2\text{CO}$, 2.04. Mass measurements were obtained on a Finnigan-MAT 8400, with FAB matrix (50% *p*-nitrobenzyl alcohol and 50% glycerol). XPS measurements were conducted with a Kratos XSAM 800 spectrometer using a magnesium anode. Samples in the form of powders were examined. The reported binding energies were referenced to adventitious carbon at 285 eV. The X-ray powder patterns were measured with a Philips X-ray powder diffraction system APD 3520. Elemental analyses were performed by the Institute of Inorganic Chemistry, Czech Academy of Sciences, Prague, Czech Republic.

Preparation of $\text{M}(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_2$, $\text{M} = \text{Zn}, \text{Cu}, \text{Ni},$ and Mo .

The copper salt, $\text{Cu}(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_2 \cdot \text{THF}$, was prepared by the reaction of $[1,2\text{-C}_2\text{B}_{10}\text{H}_{11}(\text{CO}_2)][\text{Na}]$ with CuSO_4 in water-ethanol. In a typical reaction, 0.5 g (2.66 mmol) of $1,2\text{-C}_2\text{B}_{10}\text{H}_{11}(\text{COOH})$ in 2 mL of ethanol was neutralized by a 1 M water solution of NaOH with a phenolphthalein indicator at room temperature and immediately mixed with the solution of 0.37 g (2.92 mmol) of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ in 1.5 mL of water. The solution temperature gradually rose to 30°C . The color of the solution turned from blue to green and finally to olive green during a 10 min period. After 2 h the water-ethanol was removed under vacuum and was followed by repeated dissolution in THF and vacuum drying. Extraction by THF was followed by filtration to remove the Na_2SO_4 and crystallization by layering with hexanes. This crystallization was repeated once. The yield of green crystals of $\text{Cu}(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_2 \cdot \text{THF}$ was 80%. The compound is insoluble in diethyl ether and hydrocarbons, slightly soluble in CHCl_3 and CH_2Cl_2 , and soluble in alcohols, THF, and acetone (somewhat less than the first two). NMR: ^1H (acetone- d_6 , 20°C , δ) 2.5 br m, BH, 3.71 s, THF, 1.82 s, THF; ^{13}C (acetone- d_6 , 20°C , δ) 67.6 s, THF, 25.6 s, THF; ^{11}B (THF, 20°C , δ) 1.8 sh, -2.2 sh, -6.0 sh, -8.9 s, -17.4 s. IR (KBr pellet, cm^{-1}): 3423 w br, 3080 m, 2962 m, 2926 m, 2854 m, 2617 s, 2607 s, 2585 s, 1673 s, 1402 vs, 1385 sh, 1262 m, 1095 m, 1063 m, 1037 m, 1015 m, 822 w, 801 m, 784 m, 719 m, 631 w, 472 m.

The temperature of the reaction is important. Lower reaction temperatures ($10\text{--}20^\circ\text{C}$) leads to a mixture of products containing little or no $\text{Cu}(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_2 \cdot \text{THF}$. Likewise, the stoichiometry of the reaction is important. With an excess of CuSO_4 the same procedure yields 40% of a hydroxo derivative, $\text{Cu}(\text{OH})(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2) \cdot \text{THF}$, as large pale olive-green crystals which are soluble in THF and acetone. NMR: ^1H (acetone- d_6 , 20°C , δ) 2.8 br, BH, 3.9 br, THF, 1.9 br, THF; ^{13}C (acetone- d_6 , 20°C , δ) 67 br, THF, 26 br, THF; ^{11}B (THF, 20°C , δ) 1.3 sh, -4.2 sh, -9.3 s, -17.2 sh. IR (KBr pellet, cm^{-1}): 3638 w, 3423 wbr, 3079 m, 2978 m, 2966 sh, 2948 sh, 2877 m, 2606 vs, 2582 vs, 1650 sh, 1619 vs, 1395 s, 1380 vs, 1262 w, 1183 w, 1127 sh, 1089 m, 1046 m, 1016 m, 925 w, 913 w, 886 w, 839 w, 778 m, 731 w, 718 m, 631 w, 581 w, 532 w, 493 sh, 464 w.

The preparation of $\text{Ni}(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_2(\text{THF})_2 \cdot \frac{1}{2}\text{H}_2\text{O} \cdot \text{THF}$ was carried out in the same manner as the Cu salt using a water solution of $\text{NiCl}_2 \cdot \text{H}_2\text{O}$ as the source of Ni(II). The yield of planar green crystals of the Ni derivative was 85%. NMR: ^1H (acetone- d_6 , 20°C , δ) 5 br, BH, 3.9 br, THF, 2.2 br, THF; ^{13}C (acetone- d_6 , 20°C , δ) 70 br, THF; $^{11}\text{B}\{^1\text{H}\}$ (THF, 20°C , δ) 12.6 s, 0.1 sh, -2.8 sh, -6.5 s, -19.0 sh. IR (KBr pellet, cm^{-1}): 3419 w br, 3081 m, 2983 m, 2968 sh, 2896 m, 2884 sh, 2855 sh, 2603 vs, 2578 vs, 1685 s, 1605 sh, 1459 w, 1395 sh, 1376 s, 1297 vw, 1262 m, 1182 vw, 1130 vw, 1086 m, 1062 sh, 1038 m, 1015 m, 909 w, 875 m, 841 w, 766 s, 746 vw, 729 sh, 717 m, 683 w, 629 m, 580 w, 498 w, 458 sh, 421 m.

The preparation of $\text{Zn}(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_2 \cdot 2\text{THF}$ was carried out by adding 1.9 mL of Et_2Zn (1 M in hexane) to a solution of $\text{C}_2\text{B}_{10}\text{H}_{11}\text{COOH}$ (0.36 g, 1.89 mmol) in Et_2O (10 mL) over the course of 1 min with stirring. After several minutes, a microcrystalline solid precipitated. The solid was collected on a filter, washed with Et_2O , and dried under vacuum. As with the copper derivative, it was crystallized twice from THF by layering with hexanes. The yield of colorless crystals was 70%. NMR: ^1H (acetone- d_6 , 20°C , δ) 4.15 s, 1H, CH, 3.63 s, THF, 2.3, $w_{1/2} = 360$ Hz, 10H, BH, 1.78 s, THF; ^{13}C (acetone- d_6 , 20°C , δ) 166.4 s, C-CO₂, 74.5 s, CCH, 68.1 s, THF, 63.4 d, $J_{\text{CH}} = 200$ Hz, CH-C, 26.1 s, THF; ^{11}B (THF, 20°C , δ) -3.4 s, -9.7 s, -12.0 s, -14.2 sh. IR (KBr pellet, cm^{-1}): 3425 w br, 3081 m, 2983 m, 2961 sh, 2937 w, 2929 w, 2904 w, 2605 vs, 2589 vs, 1675 vs, 1655 sh, 1395 sh, 1377 vs, 1160 vw, 1091 w, 1062 vw, 1043 m, 1016 m, 906 vw, 880 m, 839 w, 775 m, 731 sh, 719 m, 642 w, 590 w, 402 w.

(31) Zakhakin, L. I.; Grebenikov, V. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1967**, 1331.

(32) Hetler, W. R.; Wiltger, Y.; Clark, S. L.; Alexander, R. P.; Papetti, S.; Riedl, Y. I.; Trotz, S. I. *Inorg. Chem.* **1963**, *2*, 1097.

The preparation of $\text{Mo}(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_{1.5}(\text{CH}_3\text{CO}_2)_{0.5}\cdot\text{THF}$ was by ligand exchange which, apparently, does not proceed to completion. A 20-mL volume of THF was added to a mixture of 0.128 g (0.598 mmol) of $\text{Mo}_2(\text{CH}_3\text{CO}_2)_4^{33}$ and 0.225 g (1.197 mmol) of $\text{C}_2\text{B}_{10}\text{H}_{11}\text{COOH}$, and after 5 min with stirring, all the Mo compound had dissolved. Stirring was continued at room temperature for another 2 h after which the solution was evaporated to dryness. The residue was dissolved in 15 mL of Et_2O , and after the addition of 30 mL of toluene, it was filtered through a short column of silica gel. The resulting clear yellow solution was evaporated to dryness and crystallized from 2 mL of THF layered by 5 mL of hexane. In the daylight, the solution turns brown after several hours. The yield of yellow crystals was 60%. NMR: ^1H (acetone- d_6 , 20 °C, δ) 5.28 s, CH, 3.61 br, THF, 2.8 br, CH_3CO_2 , 2.0 v br, BH, 1.92 br, THF; ^{13}C (acetone- d_6 , 20 °C, δ) 169.7 s, C-CO₂, 71.2 s, CCH, 68.0 s, THF, 60.1 d, $J_{\text{CH}} = 200$ Hz, 36 s, CH_3CO_2 , CH-C, 26.1 s, THF; ^{11}B (THF, 20 °C, δ) -3.4 d, $J_{\text{BH}} = 130$ Hz, -9.6 d, $J_{\text{BH}} = 140$ Hz, -12.1 sh. IR (KBr pellet, cm^{-1}): 3433 w br, 3079 m, 2980 w, 2960 w, 2929 w, 2881 w, 2857 w, 2606 s, 2585 s, 1570 s, 1561 s, 1402 vs, 1385 sh, 1262 w, 1123 w, 1095 m, 1062 m, 1041 m, 1014 m, 878 w, 828 w, 781 s, 743 vw, 729 sh, 717 m, 669 vw, 575 vw, br, 467 m, 457 m, 404 w.

Preparation of $\text{M}\{\text{C}_2\text{B}_{10}\text{H}_{10}(\text{CO}_2)_2\}$, M = Cu and Ni. The reaction of a suspension of 0.7 g (7.2 mmol) of $\text{Cu}(\text{OH})_2$ in 10 mL of water with 1.04 g (4.5 mmol) of 1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}(\text{COOH})_2$ for 45 min at room temperature leads to a slurry of excess $\text{Cu}(\text{OH})_2$ in a pale green solution. Centrifugation followed by evaporation to dryness in vacuo leads to the isolation of a pale green solid which was identified as $\text{Cu}\{\text{C}_2\text{B}_{10}\text{H}_{10}(\text{CO}_2)_2\}_2\cdot 5\text{H}_2\text{O}$. NMR: ^1H (acetone- d_6 , 20 °C, δ) 2.4 br q, $J_{\text{BH}} = 180$ Hz; ^{11}B (THF, 20 °C, δ) -4.9 d, $J_{\text{BH}} = 145$ Hz (2B), -10.4 d, $J_{\text{BH}} \approx 140$ Hz (8B). IR (KBr pellet, cm^{-1}): 3409 m, br, 3222 s, br, 2592 s, 1720 w, 1617 vs, 1394 vs, 1262 w, 1129 w, 1109 w, 1010 w, 843 w, 780 m, 624 w, 582 vw, 471 w, br, 420 w, 403.

A similar reaction for 2 or 3 h leads to a brown product which, on the basis of the similarities in the ^{11}B NMR, the significant differences in the IR, and different elemental analysis, suggests that the expected carboxylate is metastable under the reaction conditions. Indeed, a reaction solution containing $\text{Cu}\{\text{C}_2\text{B}_{10}\text{H}_{10}(\text{CO}_2)_2\}$ on standing shows clear evidence of decomposition by the deposition of copper metal on the walls of the reaction flask over a period of time that depends strongly on the mode of preparation, temperature, solvent, and concentration. Complete reaction takes from 1 to 3 days. The reaction was monitored by ^{11}B NMR. Besides Cu, the principal products are $[\text{1,2-}\text{C}_2\text{B}_9\text{H}_{10}(\text{COOH})_2]^-$ ($\approx 80\%$ isolated yield as the anhydride) and $\text{B}(\text{OH})_3$ from reaction in H_2O , and the corresponding esters were found when the reaction was carried out in methanol or ethanol. Significant differences in the spectral properties of the carborane products are attributed to the very easy dehydration of the acid to the anhydride in the presence of acid. Separation of $[\text{1,2-}\text{C}_2\text{B}_9\text{H}_{10}(\text{COOH})_2]^-$ from $\text{B}(\text{OH})_3$ was achieved by repeated evaporation of methanol from the product resulting in the formation of volatile $\text{B}(\text{OMe})_3$ and $[\text{1,2-}\text{C}_2\text{B}_9\text{H}_{10}(\text{COOMe})_2]^-$. MS-FAB (m/e): p^+ , 249.2, 10 B. NMR: ^1H (D_2O , 20 °C, δ) 3.60 s, 3H, CH_3 , 1.8 br, BH, -2.2 br d, BHB; ^{13}C (D_2O , 20 °C, δ) 172.8 s, CO_2 , 58.7 br s, C_2B_9 , 53.4 s, CH_3 ; ^{11}B (THF, 20 °C, δ) -9.8 d, $J_{\text{BH}} = 134$ Hz (2B), -12.3 d, $J_{\text{BH}} \approx 140$ Hz (1B), -17.1 d, $J_{\text{BH}} = 131$ Hz (2B), -21.4 d, $J_{\text{BH}} = 141$ Hz (2B), -32.7 dd, $J_{\text{BH}} = 50$, 130 Hz (1B), -36.2 d, $J_{\text{BH}} = 139$ Hz (1B). IR (KBr pellet, cm^{-1}): 2966 m, 2890 w, 2569 vs, 2553 vs, 1719 s, 1628 sh, 1576 vs, 1460 vs, 1441 vs, 1351 vs, 1295 sh, 1215 sh, 1037 s, 1004 s, 997 s, 939 s, 918 s, 899 sh, 803 m, 702 s, 597 s.

A solution of 1.09 g (4.7 mmol) of 1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}(\text{COOH})_2$ in 10 mL of CH_3OH was neutralized (phenolphthalein) with a 2 M solution of KOH in H_2O . This solution of the salt was

Table 4. Crystallographic Data for $\text{Cu}_2(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_4(\text{THF})_2$ and $\text{Ni}_2(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_4(\text{THF})_4(\mu\text{-H}_2\text{O})\cdot\text{EtOH}\cdot\text{H}_2\text{O}$

formula	$\text{C}_{20}\text{H}_{60}\text{B}_{40}\text{Cu}_2\text{O}_5$	$\text{C}_{30}\text{H}_{86}\text{B}_{40}\text{Ni}_2\text{O}_{15}$
fw	1020.2	1236.8
space group	$P2_1/n$	$Pca2_1$
a (Å)	10.327(2)	22.403(4)
b (Å)	13.428(2)	13.996(3)
c (Å)	19.605(6)	23.104(5)
β (deg)	90.58(2)	
V (Å ³)	2718.5(12)	7244(3)
Z	2	4
T (K)	235	235
λ (Å)	0.710 73	0.710 73
ρ_{calc} (g/cm ³)	1.246	1.134
$R(F)^a$	0.101	0.083
$R(wF)^a$	0.149	0.104

$$^a R(F) = \sum |F_o| - |F_c| / \sum F_o. \quad R(wF) = [w \sum (|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}.$$

immediately mixed with a solution of 1.12 g (4.7 mmol) of $\text{NiCl}_2\cdot\text{H}_2\text{O}$ in 8 mL of CH_3OH . After the mixture was stirred for 2 h, the solid KCl was precipitated by centrifugation. Removing the solvent from the resulting clear green solution led to the formation of a green oil which was subsequently extracted with 12 mL of THF. The undissolved solid was removed by centrifugation, and the extract was evaporated to dryness. After three such treatments the extract was a clear solution. Layering with hexanes gave pale green microcrystals of $\text{Ni}\{\text{C}_2\text{B}_{10}\text{H}_{10}(\text{CO}_2)_2\}$. NMR: ^1H (acetone- d_6 , 20 °C, δ) ≈ 5 vbr, BH + H_2O + CH_3OH , 13H, 4.8 br, THF, 4H, 2.9, br, THF, 4H, 2.81 s CH_3OH , 2H; ^{11}B (acetone- d_6 , 20 °C, δ) 6.5 br, -4.0 br. IR (KBr, cm^{-1}): 3409 s br, 2988 w, 2875 vw, 2573 vs, 1655 vs, 1380 vs, 1131 w, 1040 m, 892 w, 893 w 780 m, 723 m, 625 vw, 576 vw.

For all compounds reported, crystals for elemental analyses were separated from the mother liquor, washed with a small amount of hexanes, and dried for 1 min in a stream of dry nitrogen.

Structure Determinations. Crystallographic data for $\text{Cu}_2(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_4(\text{THF})_2$ (Cu) and $\text{Ni}_2(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_4(\text{THF})_4(\mu\text{-H}_2\text{O})\cdot\text{EtOH}\cdot\text{H}_2\text{O}$ (Ni) are collected in Table 4. Crystals were mounted in thin-walled capillary tubes. From photographic evidence Cu was found to have $2/m$ Laue symmetry, and Ni, mmm Laue symmetry. For Cu, systematic absences in the diffraction data allowed a unique assignment of space group. For Ni, both $Pca2_1$ and $Pcam$ were consistent with the observed absences; E statistics strongly favored the noncentrosymmetric alternative. Its choice was supported by the results of refinement.

All specimens of both complexes diffracted very diffusely with half-height line widths in excess of 1° . Also found are high thermal parameters, even at low temperatures, which is consistent with a low density and an assumed low lattice energy produced by the encasement of polar groups by the carborane cages.

In both cases the metal-atom positions were obtained by direct methods. For Cu all non-hydrogen atoms were anisotropically refined, and for Ni only the Ni and O atoms were similarly treated. In both cases hydrogen-atom contributions were ignored. The location of the 2-position carbon atoms in each cage was suggested by small differences in bond distances and thermal parameters; the certainty of these assignments is limited by high esd's and possible disorder among equivalent positions.

All calculations used the SHELXTL crystallography system (v. 4.2, G. Sheldrick, Siemens, Madison, WI).

Thermal Decomposition. In a typical reaction, 199 mg (0.302 mmol) of $\text{Ni}(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_2(\text{THF})_2\cdot\frac{1}{2}\text{H}_2\text{O}$ in a small glass bottle was dried in a Schlenk tube under vacuum at ambient temperature for 12 h. Low-boiling, volatile products produced on heating were condensed in a trap on the vacuum line cooled to -196°C . High-boiling, volatile products (carboranes) were condensed on a water-cooled finger inserted into the Schlenk tube. Periodically, the sample bottle was removed under nitrogen and weighed and a portion analyzed by IR (KBr pellet); the composition of the liquid volatile products was analyzed by ^1H

Table 5. Thermal Decomposition of $\text{Ni}_2(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_4(\text{THF})_4(\text{H}_2\text{O}) \cdot 2\text{THF}$

$T, ^\circ\text{C}$	t, h	vacuum, Torr	total % wt loss	vol prod
25	12	$\approx 10^{-3}$	9	THF
100	12	$\approx 10^{-3}$	24	THF
210	24	$\approx 10^{-3}$	33	THF + H_2O
410	5	$\approx 10^{-3}$	49	$\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2\text{H}$ (40%), $\text{C}_2\text{B}_{10}\text{H}_{12}$ (60%)
800	7	5×10^{-7}	55	not measd

NMR, and the material condensing on the cold finger was analyzed by IR (chloroform solution). In the last case, the ratio of $\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2\text{H}$ to $\text{C}_2\text{B}_{10}\text{H}_{12}$ was obtained using a previously determined calibration curve. This set of steps were repeated at several temperatures. A typical set of data are given in Table 5. For heating in the range 600–1000 $^\circ\text{C}$, the sample was placed in an alumina boat in a quartz tube heated by a tube furnace and

evacuated to a base pressure of 5×10^{-7} Torr. For powder XRD, XPS, and elemental analysis, the sample was crushed in an agate mortar. The copper carboranecarboxylate pyrolyses were carried out in like manner.

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Supplementary Material Available: Tables of crystal data, atomic positional and equivalent isotropic displacement parameters, anisotropic displacement parameters, and selected bond distances and bond angles for $\text{Cu}_2(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_4(\text{THF})_2$ and $\text{Ni}_2(\text{C}_2\text{B}_{10}\text{H}_{11}\text{CO}_2)_4(\text{THF})_4 \cdot \text{H}_2\text{O} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$ and an indexed powder XRD pattern for the nonvolatile product of the thermal decomposition of the nickel compounds (25 pages). Ordering information is given on any current masthead page.