Synthesis and Properties of Copper and Nickel Complexes of the General Formula $(B_{11}H_{11})_2M^{n-}$. Crystal Structure of $[(n\text{-Bu})_4N]_3[Cu(B_{11}H_{11})_2]$

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Reaction of $Me_3NH[B_{11}H_{14}]$ in aqueous NaOH with CuO or $NiCl_2$ formed the metallaborane anions $Cu(B_{11}H_{11})_2{}^{3-}$ and $Ni(B_{11}H_{11})_2{}^{4-}$, respectively. NMR, XPS, and cyclic voltammetry results on some of these compounds are reported. A single-crystal X-ray structure determination of $[N(n\text{-Bu})_4]_3[Cu(B_{11}H_{11})_2]$ has been completed (space group Pcnb, $a = 43.652(30)$ Å, $b = 23.221(13)$ Å, $c = 13.608(7)$ Å, $Z = 8$).

Introduction

In the 1970s, Union Carbide developed a high-yield synthesis of the $B_{11}H_{14}{}^-$ ion using sodium borohydride and boron trifluoride etherate as starting materials.[1,2] It is of interest to develop the synthetic methodology to convert this rather inexpensive higher boron hydride derivative into carboranes, heteroboranes, and metallaboranes. In this way, these at-present rather exotic chemicals will become readily available.

Previously, we have investigated the synthesis of several icosahedral heteroboranes using $B_{11}H_{14}{}^-$ as the starting material. Thus, reaction of $NaB_{11}H_{14}$ with excess $NaHSeO_3$ or solid TeO_2 in a water/heptane mixture at room temperature for 24 h formed $B_{11}H_{11}Se$ or $B_{11}H_{11}Te$ in 18% and 25% yields, respectively.[3] With an anhydrous protocol, $Me_3NH[B_{11}H_{14}]$ was reacted with excess butyllithium, followed by $SbCl_3$ or $BiCl_3$ to form $B_{11}H_{11}Sb^-$ or $B_{11}H_{11}Bi^-$ in 13% and 25% yields, respectively.[4,5] Similar results for these $B_{11}H_{11}E^-$ ions were reported by Frange and co-workers.[6]

We have found that the $B_{11}H_{14}{}^-$ ion reacts with As_2O_3 in aqueous KOH to form $Bu_{11}H_{11}As^-$ in 48% isolated yield.[7] Previously, the $B_{11}H_{11}As^-$ ion has been prepared by pyrolysis of $CsB_{10}H_{12}As$ at 350−370 °C (12.7% yield) or by treatment of $N(CH_3)_4(B_{10}H_{12}As)$ with $Et_3N\cdot BH_3$ in refluxing diglyme (52% yield).[8] However, the $B_{10}H_{12}As^-$ ion requires rather expensive $B_{10}H_{14}$ as the starting material for its synthesis. Thus, our aqueous route to the $B_{11}H_{11}As^-$ ion via the $B_{11}H_{14}{}^-$ ion is the best route at present to this heteroborane. Recently, we have found that the $B_{11}H_{11}E^{2-}$ ions (E = Ge, Sn, Pb) can be made in excellent yields from $B_{11}H_{14}{}^-$ employing nonaqueous (E = Ge, Sn) or aqueous (E = Pb) procedures.[14]

Several years ago, it was reported that $Ni(C_5H_5)_2$ reacted with $Na_2B_{11}H_{13}$ in the presence of sodium amalgam to form $(C_5H_5)Ni(B_{11}H_{11}).^-$ This is the first metallaborane with a $B_{11}H_{11}{}^{4-}$ η^5 ligand.[9] Alternately, reaction of closo-$B_{11}H_{11}{}^{2-}$ with $Ni(C_5H_5)_2$ or $[(C_5H_5)Ni(CO)]_2$ gave $(C_5H_5)Ni(B_{11}H_{11})^-$, but in lower yield.[10] More recently, it was reported that treatment of $Na_2B_{11}H_{13}$ with $Re(CO)_5Br$ produced Na-$[(OC)_5ReB_{11}H_{13}]$, a $B_{11}H_{14}{}^-$ metallaborane analog with a Re−B single bond.[11]

We believe that the transition metal−borane chemistry of the $B_{11}H_{14}{}^-$ ion can be significantly expanded. In this paper, we describe the syntheses and properties of metallaborane complexes of the general type $(B_{11}H_{11})_2M^{n-}$ where M = Cu or Ni. The single-crystal X-ray structure determination of the copper complex $[(n\text{-Bu})_4N]_3[Cu(B_{11}H_{11})_2]$ is also described.

Experimental Section

Physical Measurements. Boron (^{11}B) NMR spectra were recorded at 115.8 MHz using a Nicolet NT-360 spectrometer and were externally referenced to $BF_3\cdot O(C_2H_5)_2$ (positive values downfield). Proton (^{1}H) NMR spectra were obtained on the same instrument and were referenced to the protio solvent impurities. Proton chemical shift values were reported relative to tetramethylsilane. Infrared spectra were determined by using KBr wafers with a Perkin-Elmer 283 spectrometer or a Nicolet 510P FTIR spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY. Samples for elemental analysis were heated to 80 °C under vacuum before being submitted. Ultraviolet/visible (UV/vis) spectra were obtained on a Hewlett-Packard Model 4450A spectrophotometer in acetonitrile or DMSO. Cyclic voltammograms were recorded on an IBM Model EC225 voltammetric analyzer in acetonitrile or DMSO containing Bu_4NPF_6.

X-ray photoelectron spectra were obtained on a Hewlett-Packard 5950B instrument operating at 1×10^{-9} mm base pressure during data

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Table 1. Crystallographic Data for [(*n*-Bu)$_4$N]$_3$[Cu(B$_{11}$H$_{11}$)$_2$]

chem formula	C$_{48}$H$_{130}$B$_{22}$N$_3$Cu	space group	*Pcnb*
a, Å	43.652(30)	*T*, °C	−155
b, Å	23.221(13)	λ, Å	0.710 69
c, Å	13.608(7)	ϱ_{calcd}, g cm^{-3}	1.012
V, Å^3	13794.19	μ(Mo Kα), cm^{-1}	3.474
Z	8	*R*	0.1134
fw	1050.94	*R*$_w$	0.1070

collection and employing a monochromatized Al Kα$_{1,2}$ radiation source operated at 800 W emissive power. Resolution for an 83.95 eV Au(4f$_{7/2}$) reference line was ±0.10 eV with a fwhm of 0.80 eV. Samples were mounted on Scotch Brand 665 double-coated tape. Surface charging was controlled by use of a low-energy electron flood gun operated at 0.4 mA current and 2 eV voltage. Charge-corrected binding energies are expressed relative to the background C(1s) line at 285.0 eV.

Materials. All reactions were carried out under an atmosphere of prepurified nitrogen unless noted. Tetrahydrofuran (THF) and pentane were distilled from sodium benzophenone ketyl. Pure (CH$_3$)$_4$NB$_{11}$H$_{14}$ was prepared by the literature method.[2]

[(*n*-Bu)$_4$N]$_3$[*commo*-1,1′-Cu[(B$_{11}$H$_{11}$)$_2$Cu]] (1). To a 50-mL, single-neck, round-bottom flask, equipped with a magnetic stir bar and nitrogen inlet, was added 20 mL of 2.5 M NaOH (50 mmol of NaOH), followed by Me$_3$NHB$_{11}$H$_{14}$ (1.01 g 5.23 mmol). The flask was lightly evacuated and flushed several times with N$_2$. The material in the flask was stirred for 30 min; then CuO (1.23 g, 15.5 mmol) was added. The contents turned dark green/black immediately. The flask contents were then stirred for 24 h, during which gas evolution was observed. Multiple filtrations with a Büchner funnel were required to remove the insoluble solids, with the last filtration using Celite. The dark green filtrate was treated with a saturated, aqueous solution of *n*-Bu$_4$NI until no more precipitate had visibly formed. The mixture was filtered through a medium-porosity glass frit to yield 0.763 g of dark green precipitate and a bright orange filtrate. The filtrate was treated with more *n*-Bu$_4$NI to obtain an orange precipitate, which was filtered off with a fine-porosity glass frit. The procedure was repeated a second time to precipitate any remaining orange compound. A total of 1.73 g of crude orange solid was obtained. Recrystallization from warm acetone/H$_2$O yielded 1.27 g (46.7%) of X-ray-quality plates of **1**, mp 201−203 °C. The ^{11}B, ^{1}H, and ^{1}H{^{11}B} NMR data are presented in Tables 4 and 5. Infrared spectrum of **1** (KBr, cm^{-1}): 3000 (w), 2961 (m), 2934 (m), 2874 (m), 2475 (s), 1480 (m), 1383 (w), 1007 (s), 895 (m), 738 (w). UV/vis (CH$_3$CN): 308 nm (ε = 57 400), 403 nm (ε = 1046). Anal. Calcd for C$_{48}$H$_{130}$B$_{22}$N$_3$Cu: C, 54.86; H, 12.47. Found: C, 54.88; H, 12.51.

[(CH$_3$)$_4$N]$_3${*commo*-1,1′-Cu[(B$_{11}$H$_{11}$)$_2$Cu]} (2). This salt was prepared in the same way as compound **1**. The final product was precipitated from aqueous solution with a saturated aqueous solution of [(CH$_3$)$_4$N]Br. Compound **2** is sparingly soluble in most solvents. IR (KBr): 3020 (w), 2480 (s), 1485 (s), 1280 (w), 1010 (s), 945 (m), 895 (m) cm^{-1}. Anal. Calcd for C$_{12}$H$_{58}$B$_{22}$N$_3$Cu: C, 26.40; H, 10.71. Found: C, 26.21; H, 10.87.

Cs$_4$[*commo*-1,1′-Ni[(B$_{11}$H$_{11}$)$_2$Ni]] (3). To a 100-mL, single-neck, round-bottom flask equipped with a magnetic stir bar and nitrogen inlet, was added 40 mL of 2.5 M NaOH (99 mmol NaOH), followed by Me$_3$NHB$_{11}$H$_{14}$ (2.01 g, 10.4 mmol). The flask was lightly evacuated and flushed several times with N$_2$. The content were stirred for 30 min; then finely powdered NiCl$_2$·6H$_2$O (9.41 g, 39.6 mmol) was added. The contents turned dark gray within 1 min. The reaction mixture was stirred for 24 h and then filtered through a Büchner funnel to remove a large amount of green insoluble solid. The resulting olive green filtrate was treated with a saturated aqueous solution of CsCl to obtain 3.61 g of crude microcrystalline yellow solid. Recrystallization from warm H$_2$O yielded 3.53 g (79.9%) of **3**. The ^{11}B and ^{1}H{^{11}B} NMR data are presented in Tables 4 and 5, respectively. Infrared spectrum of **3** (KBr): 2463 (s), 2389 (s), 1040 (m), 912 (m), 739 (w), 717 (w) cm^{-1}. Anal. Calcd for B$_{22}$Cs$_4$H$_{22}$Ni: B, 27.97; H, 2.61. Found: B, 28.31; H, 2.67.

[Ph$_3$PMe]$_4${*commo*-1,1-Ni[(B$_{11}$H$_{11}$)$_2$Ni]} (4). The salt Cs$_4$[Ni-(B$_{11}$H$_{11}$)$_2$] was dissolved in hot water, the solution was treated with a saturated aqueous solution of [Ph$_3$PMe]Br, the solid filtered off to
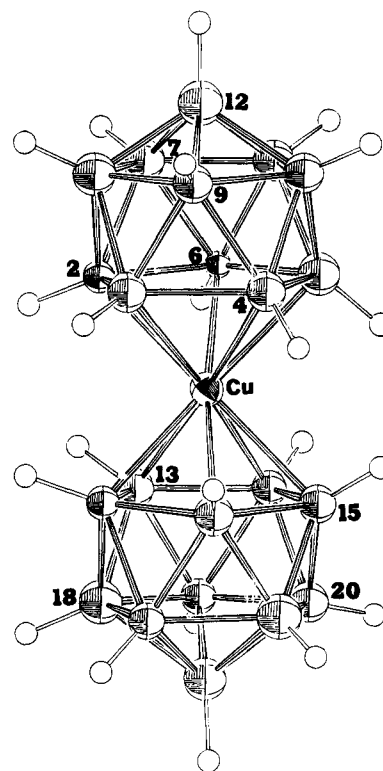
Figure 1. ORTEP diagram of the (B$_{11}$H$_{11}$)$_2$Cu^{3-} ion.

Table 2. Selected Interatomic Distances for [(*n*-Bu)$_4$N]$_3$[Cu(B$_{11}$H$_{11}$)$_2$]

Cu(1)−B(2)	2.157(21)	B(9)−B(12)	1.74(3)
Cu(1)−B(3)	2.175(22)	B(10)−B(11)	1.73(3)
Cu(1)−B(4)	2.180(22)	B(10)−B(12)	1.78(3)
CU(1)−B(6)	2.160(18)	B(11)−B(12)	1.78(3)
Cu(1)−B(14)	2.149(23)	B(13)−B(14)	1.850(24)
Cu(1)−B(15)	2.181(23)	B(13)−B(17)	1.91(3)
Cu(1)−B(16)	2.189(21)	B(13)−B(18)	1.75(3)
Cu(1)−B(17)	2.151(22)	B(13)−B(19)	1.74(3)
B(2)−B(3)	1.81(3)	B(14)−B(15)	1.80(3)
B(2)−B(6)	1.893(27)	B(14)−B(19)	1.78(3)
B(2)−B(7)	1.74(3)	B(14)−B(20)	1.70(3)
B(2)−B(8)	1.76(3)	B(15)−B(16)	1.83(3)
B(3)−B(4)	1.92(3)	B(15)−B(20)	1.75(3)
B(3)−B(8)	1.77(3)	B(15)−B(21)	1.68(3)
B(3)−B(9)	1.78(3)	B(16)−B(17)	1.80(3)
B(4)−B(5)	1.84(3)	B(16)−B(21)	1.74(3)
B(4)−B(9)	1.79(3)	B(16)−B(22)	1.75(3)
B(4)−B(10)	1.76(3)	B(17)−B(18)	1.74(3)
B(5)−B(6)	1.84(3)	B(17)−B(22)	1.76(3)
B(5)−B(10)	1.77(3)	B(18)−B(19)	1.76(3)
B(5)−B(11)	1.74(3)	B(18)−B(22)	1.75(3)
B(6)−B(7)	1.80(3)	B(18)−B(23)	1.79(3)
B(6)−B(11)	1.72(3)	B(19)−B(20)	1.76(3)
B(7)−B(8)	1.72(3)	B(19)−B(23)	1.75(3)
B(7)−B(11)	1.79(3)	B(20)−B(21)	1.72(3)
B(7)−B(12)	1.78(3)	B(20)−B(23)	1.82(3)
B(8)−B(9)	1.78(3)	B(21)−B(22)	1.83(3)
B(8)−B(12)	1.76(3)	B(21)−B(23)	1.81(3)
B(9)−B(10)	1.77(3)	B(22)−B(23)	1.81(3)

obtain compound **4**. UV/vis (DMSO): 298 nm (ε = 41 800), 352 nm (ε = 3500). Anal. Calcd for C$_{76}$H$_{100}$B$_{22}$P$_4$Ni: C, 61.59; H, 6.80. Found: C, 61.43; H, 6.74.

Electrochemistry. The cyclic voltammetry of [(*n*-Bu)$_4$N]$_3$[Cu-(B$_{11}$H$_{11}$)$_2$] was studied in acetonitrile solvent with 0.1 M Bu$_4$NPF$_6$ as solvent electrolyte. The working electrode was a platinum bead. No reductions for this compound were observed to −2.3 V *vs* SCE. Irreversible oxidation waves were observed at +0.78 and +1.14 V *vs* SCE. A more detailed description of the electrochemical procedures has been published.[12]

Table 3. Fractional Coordinates and Isotropic Thermal Parameters for $[(n\text{-}Bu)_4N]_3[Cu(B_{11}H_{11})_2]$[a,b]

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å²	atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å²
Cu(1)	8737(1)	439(1)	9262(2)	18	C(40)	1635(5)	1989(9)	4030(16)	37(5)
B(2)	9060(5)	−201(9)	8764(15)	15(4)	N(41)	9574(3)	514(7)	13064(10)	24(3)
B(3)	8751(6)	−64(10)	7913(16)	23(5)	C(42)	9510(4)	210(7)	12069(13)	18(4)
B(4)	8720(6)	755(10)	7754(16)	23(5)	C(43)	9703(4)	−316(7)	11906(13)	20(4)
B(5)	9018(6)	1095(10)	8515(18)	27(5)	C(44)	9663(4)	9503(9)	781(15)	33(4)
B(6)	9228(4)	517(8)	9141(14)	11(4)	C(45)	9835(5)	−1037(9)	10519(15)	40(6)
B(7)	9393(6)	55(11)	8214(18)	28(5)	C(46)	9898(4)	773(8)	13096(13)	22(4)
B(8)	9119(6)	−259(10)	7485(18)	29(6)	C(47)	9932(4)	1279(8)	12346(14)	28(5)
B(9)	8912(5)	304(10)	6887(17)	24(5)	C(48)	10265(5)	1500(9)	12366(14)	29(5)
B(10)	9071(5)	972(10)	7245(17)	25(4)	C(49)	10348(6)	1809(10)	13345(18)	53(6)
B(11)	9361(6)	821(11)	8072(18)	27(5)	C(50)	9568(5)	92(8)	13930(14)	29(5)
B(12)	9306(5)	359(11)	7047(18)	31(5)	C(51)	9252(5)	9794(9)	4065(15)	33(5)
B(13)	8735(6)	45(9)	10734(19)	23(4)	C(52)	9310(5)	−694(9)	14783(15)	35(5)
B(14)	8733(5)	841(9)	10684(17)	18(4)	C(53)	9002(5)	−1019(10)	15006(18)	50(6)
B(15)	8437(5)	1098(10)	9878(17)	22(5)	C(54)	9313(4)	965(8)	13165(13)	18(4)
B(16)	8237(5)	468(11)	9384(16)	24(5)	C(55)	9346(4)	1345(8)	14103(15)	31(5)
B(17)	8416(5)	−174(9)	9851(16)	17(5)	C(56)	9089(5)	1792(9)	14066(16)	38(5)
B(18)	8367(6)	−157(11)	11118(18)	29(6)	C(57)	9113(5)	2230(10)	14919(18)	48(6)
B(19)	8552(5)	440(11)	11642(15)	19(4)	N(58)	7977(3)	625(6)	5010(12)	24(3)
B(20)	8395(5)	1077(10)	11154(17)	24(5)	C(59)	8200(5)	1037(9)	5507(14)	31(5)
B(21)	8105(6)	877(11)	10369(18)	32(6)	C(60)	8049(5)	1471(9)	6221(15)	33(5)
B(22)	8071(5)	90(10)	10357(16)	21(5)	C(61)	8299(6)	1968(11)	6438(20)	58(7)
B(23)	8155(5)	464(12)	11489(17)	28(5)	C(62)	8205(6)	2231(11)	7381(20)	62(7)
N(24)	1322(4)	2046(6)	436(10)	26(4)	C(63)	7744(4)	925(7)	4363(14)	21(4)
C(25)	1108(4)	2578(8)	564(13)	23(4)	C(64)	7887(4)	1388(8)	3685(13)	18(4)
C(26)	797(4)	2430(8)	1049(14)	26(5)	C(65)	7624(5)	1582(9)	2955(15)	34(5)
C(27)	554(5)	2883(9)	689(17)	42(5)	C(66)	7722(5)	2093(10)	2344(17)	45(6)
C(28)	426(6)	2741(11)	−312(19)	63(7)	C(67)	8177(5)	189(9)	4453(15)	34(5)
C(29)	1181(4)	1622(8)	−322(13)	21(4)	C(68)	7989(5)	−296(8)	3973(14)	32(5)
C(30)	1168(5)	1881(9)	−1377(16)	35(5)	C(69)	8235(5)	−775(10)	3726(17)	47(6)
C(31)	921(5)	1570(10)	−1986(17)	45(6)	C(70)	8063(6)	−1297(11)	3218(19)	57(7)
C(32)	868(6)	1931(11)	−2930(18)	52(6)	C(71)	7771(4)	315(7)	5816(14)	19(4)
C(33)	1634(4)	2283(8)	138(14)	26(4)	C(72)	7951(4)	−85(8)	6487(14)	21(4)
C(34)	1868(5)	1805(9)	−63(15)	30(5)	C(73)	7712(4)	−297(8)	7248(14)	25(4)
C(35)	2179(5)	2100(10)	−302(15)	40(5)	C(74)	7838(5)	−805(9)	7868(15)	31(5)
C(36)	2433(6)	1643(10)	−536(17)	53(6)	X(75)	5000*	2500*	929(25)	48(8)
C(37)	1338(4)	1688(7)	1410(13)	19(4)	X(75)	4915(6)	3819(12)	913(21)	95(8)
C(38)	1498(4)	2039(8)	2222(14)	25(4)	X(76)	5000*	2500*	2317(29)	80(10)
C(39)	1446(5)	1699(8)	3204(15)	29(5)					
H(1)	907*	−60*	923*	30	H(12)	892*	−28*	1079*	30
H(2)	855*	−33*	769*	30	H(13)	897*	104*	1082*	30
H(3)	848*	94*	774*	30	H(14)	844*	146*	935*	30
H(4)	895*	146*	898*	30	H(15)	813*	45*	864*	30
H(5)	931*	44*	990*	30	H(16)	845*	−63*	960*	30
H(6)	961*	−19*	846*	30	H(17)	835*	−58*	1153*	30
H(7)	914*	−68*	712*	30	H(18)	866*	44*	1239*	30
H(8)	879*	24*	617*	30	H(19)	846*	147*	1154*	30
H(9)	905*	135*	673*	30	H(20)	788*	108*	1017*	30
H(10)	955*	115*	811*	30	H(21)	786*	−18*	1040*	30
H(11)	946*	34*	643*	30	H(22)	799*	50*	1212*	30

[a] Isotropic values for those atoms refined anisotropically were calculated using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, 12, 609. [b] Parameters marked by an asterisk were not varied.

X-ray Structure Determination for $[(n\text{-}Bu)_4N]_3[Cu(B_{11}H_{11})_2]$. Crystals of this copper complex were obtained by crystallization from acetone/water. A small, well-formed crystal was affixed to the end of a glass fiber on a goniometer head using silicone grease and transferred to the goniostat where it was cooled to −155 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with symmetry and systematic absences corresponding to the orthorhombic space group *Pcnb* (an alternate setting of *Pbcn*, No. 60). Subsequent solution and refinement of the structure confirmed this choice. Data were collected in the usual manner using a continuous $\theta-2\theta$ scan with fixed backgrounds. Data were reduced to a unique set of intensities and associated σ's in the usual manner. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. Because of the large a-axis dimension (43.65(3) Å), there was some overlap in data adjacent to some diffraction maxima with very large intensities. It was also noted that the data were quite low in intensity, with only about one-third (3129 of 9023 unique) being observed on the basis of a 2.33σ criteria. For this reason, it was not possible to

anisotropically refine the structure in its entirety. The copper atom was allowed to refine anisotropically, and all other atoms were refined isotropically. Three peaks, two lying on the $[\frac{1}{2}, \frac{1}{4}, z]$ axis at $z = 0.0929$ and $z = 0.2317$ and the third in the general position [0.4915, 0.3819, 0.0913], were located in a difference Fourier map. Since these atoms were well separated from either the anion or cations in the cell, it was assumed that they corresponded to solvent inclusions of some type. In subsequent refinement, they were assigned oxygen scattering factors (based on the peak size in the difference map) and allowed to refine isotropically. It is noted that the two peaks identified as X(75) and X(76) have quite large thermal parameters, but no attempt was made to vary their occupancy. A difference Fourier map phased on the non-hydrogen atoms was able to locate many of the hydrogen atoms associated with the boron atoms. When the 108 hydrogen atoms associated with the cations were included as fixed atom contributors, 21 of the 22 hydrogen atoms associated with the $CuB_{22}H_{22}{}^{3-}$ anion were located. Because of program limitations, it was not possible to include all 130 hydrogen atoms in the final cycles. Since the geometry of the anion is of most interest, the 22 (21 located and one calculated)

Table 4. ^{11}B NMR Data for $(B_{11}H_{11})_2M^{n-}$ (M = Cu, Ni) Salts

		chem shift, ppm ($J_{^{11}B-H}$, Hz)		
compd	solvent	B(12)	B(2–6)	B(7–11)
$[(n\text{-Bu})_4N]_3[Cu(B_{11}H_{11})_2]$ (1)	a	22.9 (114)	14.7 (103)	−6.2 (127)
$[(CH_3)_4N]_3[Cu(B_{11}H_{11})_2$ (2)	a	22.8 (122)	14.2 (126)	−6.5 (128)
$Cs_4[Ni(B_{11}H_{11})_2]$ (3)	b	6.9 (118)	2.5 (116)	−13.8 (121)
$[Ph_3PMe]_4[Ni(B_{11}H_{11})_2]$ (4)	c	6.0^d	2.5^d	−13.2 (104)

^{a} Acetone solvent. ^{b} Water solvent. ^{c} DMSO solvent. ^{d} Broad signal.

hydrogens associated with it were used in the final cycles. The final residuals were $R(F) = 0.1134$ and $R_w(F) = 0.1070$. When the 108 hydrogen atoms were included, the residuals were 0.0934 and 0.0902, respectively.

Results and Discussion

Deprotonation of $Me_3NH[B_{11}H_{14}]$ with excess aqueous sodium hydroxide, followed by a prolonged room-temperature reaction with a Cu(I) [Cu_2O or $CuCl$] or a Cu(II) [CuO or $CuCl_2$] salt, formed pure $[(n\text{-Bu})_4N]_3$ [$Cu(B_{11}H_{11})_2$] in 46% yield. The tetra-n-butylammonium and tetramethylammonium salts (compounds 1 and 2, respectively) have been fully characterized. In a similar type of aqueous base reaction, the $Ni(B_{11}H_{11})_2^{4-}$ ion was synthesized in 79% yield from $Me_3NH[B_{11}H_{14}]$ and $NiCl_2\cdot6H_2O$. The nickel complex was characterized as the cesium and triphenylmethylphosphonium salts (compounds 3 and 4, respectively). The ^{11}B NMR spectra (Table 4) of each of these salts exhibits three doublets with a 1:5:5 area ratio. This NMR data suggest that the metal atom is sandwiched between two $B_{11}H_{11}^{4-}$ ligands and lies on the 5-fold axis of each ligand.

The structure of 1 was determined by a single-crystal X-ray study and is illustrated in Figure 1. The copper atom is complexed in a symmetrical η^5 fashion to each of the two $B_{11}H_{11}^{4-}$ ligands. The Cu−B bond distances of 1 (Table 2) were found to be in the range 2.149(23)−2.189(21) Å. This is similar to the Cu−B distances of [*closo*-3-PPh₃-3,1,2-CuC₂B₉H₁₁]-PPN, which are in the range 2.116(7)−2.181(7) Å.[13] The three other copper−carborane complexes whose structures were reported recently have similar Cu−B bond distances.[13] There is also the expected lengthening of the B−B distances of the five atoms adjacent to the copper atoms (1.85 Å average) of each of the $B_{11}H_{11}^{4-}$ ligands relative to the B−B distances of $B_{12}H_{12}^{2-}$ (1.77 Å average).[14] A similar distortion of the $B_{11}H_{11}$ portion of the $B_{11}H_{11}SnCH_3^-$ ion was observed.[15] The B−B distances (1.90 Å average) of the five atoms adjacent to the Sn atom are larger than the other B−B distances (1.78 Å) of the $B_{11}H_{11}$ fragment of the stannaborane ion. The $Cu(B_{11}H_{11})_2^{3-}$ ion thus represents a symmetrically-bonded *closo* structure expected for a formal $Cu^{(5+)}(d^6)$ ion η^5-bonded to the open face of *two* $B_{11}H_{11}^{4-}$ ligands.

Molecular orbital calculations on this hypothetical trianion were reported some years ago.[16]

The stabilization of unusually large positive formal oxidation states of transition metals by borane, carborane, or heteroborane ligands with high negative charges has been known for some time (see Table 6).

The cyclic voltammetry of $[(n\text{-Bu})_4N]_3[Cu(B_{11}H_{11})_2]$ (1) showed no reduction in the potential range investigated, which extended to −2.3 V (*vs* SCE). There were two irreversible oxidation waves at +0.78 and +1.14 V (*vs* SCE). From this

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Table 5. ^1H NMR Data for $(B_{11}H_{11})_2M^{n-}$ (M = Cu, Ni) Salts

compd	δ, ppm	rel intens	assgnt
1^a	0.96 (6)	3H	$CH_3{}^d$
	1.43 (m)	2H	CH_2
	1.78 (m)	2H	CH_2
	3.38 (m)	2H	NCH_2
	1.91^b	5H	BH
	3.17^b	5H	BH
	3.88^b	1H	BH apex
3^c	1.22	5H	BH
	2.10	5H	BH
	2.93	1H	BH apex
4^e	3.13	3H	$CH_3{}^f$
	7.75 (m)	15H	C_6H_5

^{a} Acetone-d_6 solvent. ^{b} $^1H\{^{11}B\}$ NMR in acetone-d_6 solvent. ^{c} $^1H\{^{11}B\}$ NMR in D_2O solvent. ^{d} $J_{B-H} = 7.4$ Hz. ^{e} DMSO-d_6 solvent. ^{f} $J_{B-H} = 14$ Hz.

Table 6. Examples of Borane, Carborane, or Heteroborane Metal Complexes with the Metal in an Unusual High Positive Formal Oxidation State: 4+

metal complex	ref	metal complex	ref
$(B_{10}H_{10}CH)_2Co^{2-}$	18	$(B_{10}H_{10}As)_2Co^{2-}$	22
$(B_7H_7CH)Co(C_5H_5)$	19	$(B_{10}H_{10}As)Co(C_5H_5)$	22
$(B_{10}H_{10}CH)Mn^{2-}$	20	$(B_{10}H_{10}P)Co(C_5H_5)$	22
$(B_{10}H_{10}CH)Ni(C_5H_5)$	21	$(B_9H_9C_2H_2)_2M$ (M = Ni, Pd)	23
$(B_{11}H_{11})Ni(C_5H_5)^-$	10		

Table 7. $Cu(2p_{3/2})$ Binding Energies

substance	Cu oxidn state	E_B, eV	ref
Cu	0	932.4	24
CuCl	1	932.2	25
CuCN	1	932.6	24
CuO	2	933.6	24
$CuCl_2$	2	933.8	25
CuO·ZnO	2	933.9	26
$CuBr_2$	2	934.6	25
$CuSO_4$	2	934.7	25
$CuSO_4\cdot5H_2O$	2	935.9	27
CuF_2	2	935.8	25
$[N(n\text{-Bu})_4]_3[(B_{11}H_{11})_2Cu]$ (1)	5	937.8	this work

Table 8. $Ni(2p_{3/2})$ Binding Energies (eV)

sample	$C(1s_{1/2})_{exp}{}^a$	$C(1s_{1/2})_{cor}{}^b$	$Ni(2p_{3/2})_{exp}$	$Ni(2p_{3/2})_{cor}{}^c$	lit.^{d}
Ni Foil	285.2	285.0	853.1	852.9	852.9
$(B_9C_2H_{11})_2Ni$	278.7	285.0	850.8	857.2	857.2
$Cs_4(B_{11}H_{11})_2Ni$	278.7	285.0	848.7	855.0	

^{a} The measured energy of the lowest binding energy component in the $C(1s_{1/2})$ photoelectron spectrum. This was the "adventitious hydrocarbon" peak on all three samples. ^{b} The hydrocarbon peak defined in footnote a was assigned a value of 285.0 eV to provide charge correction on each surface. ^{c} The $Ni(2p_{3/2})$ binding energy after charge correction relative to $C(1s_{1/2})$ at 285.0 eV. ^{d} Values obtained from the NIST ESCA database of photoelectron binding energies.

experiment, we did not determine the number of electrons involved in these oxidation processes. The +0.78 V oxidation state may be accessible using a chemical oxidant, and this detail is being investigated at present.

The X-ray photoelectron spectrum of the surface of a sample of compound 1 was obtained. All boron atoms were equivalent in this measurement [B(1s) = 186.7 eV] as there was no observed splitting of the B(1s) line. The $Cu(2p_{3/2})$ binding level of compound 1 is compared with the binding energies of other copper-containing substances in Table 7. The copper in compound 1 is in a high oxidation state, arguably 5+, for the following reasons. The $Cu(2p_{3/2})$ binding level is unusually high, 937.8 eV (referenced to C(1s) = 285.0 eV), and is inconsistent with Cu(I) or Cu(II). There is an absence of shake-

up satellites. These lower energy features are associated with d−d transitions in *paramagnetic* ions. Thus, one can exclude the Cu(III) oxidation state for compound **1**. Relatively large nickel $2p_{3/2}$ binding energies of carbollide and dicarbollide nickel complexes [Ni(III) and Ni(IV) materials] have been reported previously.[17] The results on the XPS study of compound **3** and related substances are given in Table 8. The variation of nickel

$2p_{3/2}$ binding energies for different formal oxidation states is not as large or consistent as observed for the copper complexes.

Supplementary Material Available: Tables of crystal data and intensity information, anisotropic thermal parameters, and bond distances and angles (8 pages). Ordering information is given on any current masthead page.

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