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Registry No. $H_3(sal)_3tach$, 53535-00-5; $Co((sal)_3tach)$, 53516-69-1; $Fe((sal)_3tach)$, 53516-70-4; $Ni_3((sal)_3tach)_2$, 53586-50-8; *cis,cis*-tach, 26150-46-9; salicylaldehyde, 90-02-8.

Supplementary Material Available. Table III, a listing of structure factors, will appear following these pages in the microfilm edition of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number AIC40544O. Crystallographic data tables, for this paper only, are also available in microfiche for \$2.00 from the Chemistry Library, Indiana University, Bloomington, Ind. 47401. Request Molecular Structure Center Report No. 7401.

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Transition Metal Hydroborate Complexes. VIII.[1] Structure of $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}\cdot CHCl_3$. Bonding Analogies between Boron Hydrides and *nido*-Metalloboranes

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The synthesis of the complex μ-decahydrodecaborato-tetrakis(triphenylphosphine)dicopper(I) is reported. The compound crystallizes from chloroform as the solvated species $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}\cdot CHCl_3$, the crystal and molecular structures of which have been determined in a single-crystal X-ray diffraction study. The colorless complex crystallizes in the triclinic space group $P\bar{1}$ with two formula units per unit cell. Lattice parameters are $a = 21.189$ (3) Å, $b = 13.438$ (2) Å, $c = 13.207$ (2) Å, $\alpha = 102.61$ (1)°, $\beta = 92.92$ (1)°, and $\gamma = 88.41$ (1)°. From 3405 unique observed reflections collected by diffractometer, the structure was solved and refined with the phenyl rings constrained as rigid groups to a final value for the discrepancy index R_F of 0.061. The $B_{10}H_{10}^{2-}$ cage ligand binds two crystallographically unique copper atoms by means of $\overset{\frown}{Cu-H-B-B-H}$ chelate rings along two apical edges related to each other by an approximate S_8 operation. Each quasitetrahedral copper atom is further bonded to two triphenylphosphine ligands. Boron–boron distances within the $B_{10}H_{10}^{2-}$ cage agree well with those published for $Cu_2B_{10}H_{10}$ [B_a–B_e(av) = 1.68 (3) Å, B_e–B_e(av) = 1.81 (3) Å (a = axial, e = equatorial)]. The geometry about the copper coordination spheres is similar to that of $[(C_6H_5)_3P]_2Cu(B_3H_8)$. The average Cu–P and Cu–B distances are 2.28 (1) and 2.30 (2) Å, respectively. The mean Cu–H_a distance of 2.08 (7) Å is notably longer than the value of 1.86 (6) Å found for the mean Cu–H_e distance, a result that is rationalized from the geometry of the $B_{10}H_{10}^{2-}$ cage by assuming equivalent Cu–B interactions in the three-center Cu–H–B bridge bonds. The molar conductivity of the compound in dichloromethane indicates strong covalent interaction between bis(triphenylphosphine)copper(I) and the cage ligand in solution. The bonding in $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}$ is discussed with reference to the geometries and electronic requirements known or postulated for other *nido*-metalloboranes.

Introduction

Earlier papers in this series have reported the molecular structures of $[(C_6H_5)_3P]_2CuX$ complexes, where $X^- = BH_4^-$, $B_3H_8^-$, or $NCBH_3^-$.[2] In each case the hydroborate anion was found to be coordinated to the copper atom through three-center Cu–H–B bridge bonds of the kind well-known in boron hydride chemistry.[3] The present study was undertaken to determine whether bis(triphenylphosphine)copper(I) would bond in a similar manner to a higher boron hydride anion. In particular, we chose to examine a complex with the decahydrodecaborate dianion,[4] since the adduct $Cu_2B_{10}H_{10}$ is known.[5,6] A number of related coinage metal derivatives of borane anions have been reported.[7] Of these, only $[(C_6H_5)_3P]_3Au^+B_9H_{12}S^-$ appears to have been characterized structurally, and in this case the anion is not coordinated.[7a]

Experimental Section

Synthesis. Decahydrodecaboratotetrakis(triphenylphosphine)dicopper(I)–chloroform was prepared by adding a solution containing 0.109 g (0.34 mmol) of triethylammonium decahydrodecaborate[4] in 10 ml of methanol to a solution of 0.593 g (0.67 mmol) of tris(triphenylphosphine)copper(I) chloride[8] dissolved in 15 ml of chloroform, both maintained at ~60°. A white precipitate formed immediately, and the mixture was allowed to stand at 25° overnight. Recrystallization from chloroform–methanol produced clear plates, some of which were suitable for X-ray work. Microchemical analysis, performed by Galbraith Laboratories, Knoxville, Tenn., revealed the presence of a chloroform molecule of solvation. *Anal.* Calcd for $C_{73}H_{71}P_4B_{10}Cl_3Cu_2$: C, 62.06; H, 5.06; B, 7.65; P, 8.76. Found (on a sample dried *in vacuo* for 1 hr at 25°): C, 62.36; H, 5.12; B, 7.99; P, 9.07.

Physical Measurements. Electrical conductance measurements were carried out a 25.0 ± 0.1° using an Industrial Instruments, Inc., Model RC16B2 conductivity bridge and a cell with platinized platinum electrodes standardized with 0.02 *M* aqueous KCl. Infrared spectra were obtained with Perkin-Elmer 137 and 621 instruments in the ranges 4000–670 and 3800–400 cm^{-1}, respectively. Samples were mulled in Nujol and spread between either NaCl or KBr plates. Polystyrene was used as a calibrant.

Collection and Reduction of X-Ray Data. All measurements were performed at 23 ± 1° on a clear prism of approximate dimensions 0.10 × 0.15 × 0.20 mm mounted on a glass fiber along b^*. Using a precession camera and Cu $K\bar{\alpha}$ radiation, the Laue symmetry was found to be $\bar{1}$. The space group $P\bar{1}$ was assumed, a choice that appears to be justified based on the successful refinement of the structure.

The crystal was then transferred to a Picker FACS-I-DOS diffractometer. Using graphite-monochromatized Cu $K\alpha_1$ (λ 1.54041 Å) radiation, 21 reflections were centered, 12 of which were used to compute an orientation matrix and lattice parameters for data collection. The full set of 21 reflections was later refined by a least-squares method[9] to yield the following unit cell constants: a = 21.189 (3) Å, b = 13.438 (2) Å, c = 13.207 (2) Å, α = 102.61 (1)°, β = 92.92 (1)°, and γ = 88.41 (1)°. This cell is reduced and was used in all subsequent calculations. A systematic search using TRACER[9] revealed no higher symmetry. The conventional reduced cell parameters are a = 13.207 Å, b = 13.438 Å, c = 21.189Å, α = 88.41°, β = 87.08°, γ = 77.39°. The calculated density for two formula units per unit cell is 1.281 g/cm³, which agrees well with the value of 1.279 (6) g/cm³ measured by suspension in aqueous potassium carbonate.

Open-counter ω scans showed the mosaic spread of the crystal to be acceptable ($\Delta\omega_{1/2}$ approximately 0.15°). The b^* reciprocal lattice vector was offset by about 15° from the spindle axis to minimize effects of secondary extinction, and data collection was initiated. A total of 4742 intensities were collected using a symmetric scan range of 1.25° for $5° \leq 2\theta \leq 40°$ and 1.50° for $40° < 2\theta \leq 80°$, plus the $K\alpha_1$–$K\alpha_2$ dispersion. The takeoff angle at the X-ray tube was 2.0°, which gave about 80% of the maximum intensity. A 4 × 4 mm aperture was positioned in front of the scintillation counter about 31 cm from the crystal. Stationary-crystal, stationary-counter background counts were recorded at the beginning and end of the scan range for 10-sec periods at $5° \leq 2\theta \leq 40°$ and for 20 sec at $40° < 2\theta \leq 80°$. Three standard reflections were monitored after every 97 data points; these showed insignificant fluctuations in intensity $[\Delta(F^2)/\sigma(F^2) \approx \pm 0.8]$.

The data were then reduced in the usual manner,[1] using a value of 0.04 for ϵ and the Lorentz–polarization correction of $(Lp)^{-1} = [(1 + \cos^2 2\theta_m)(\sin 2\theta)/(\cos^2 2\theta_m + \cos^2 2\theta)]$.[10] An absorption correction was made,[9] the linear absorption coefficient being 28.6 cm^{-1}. The calculated transmission coefficients ranged from 0.683 to 0.782. A total of 180 ($0kl$) and ($0\bar{k}\bar{l}$) Friedel pairs were averaged to an agreement factor

$$\left(\sum_{i=1}^{180}\sum_{j=1}^{2}|F_{ij}{}^2 - \overline{F_i^2}|\right)/\sum_{i=1}^{180}\overline{F_i^2}$$

of 0.038. The data were then placed on an approximately absolute scale using a modification of Wilson's method.[9,11] A total of 3410 reflections had $F^2 > 3\sigma(F^2)$, and these were used in the refinement of the structure.

Determination and Refinement of the Structure. An origin-removed sharpened Patterson map was computed and solved for the positions of the two copper and four phosphorus atoms in the asymmetric unit. A difference Fourier map, phased on these atoms using neutral atom scattering factors,[12] revealed the locations of 72 phenyl carbon and 10 boron atoms. Refinement of the 12 phenyl rings as 11-atom rigid groups[9,13] (C–C and C–H distances were taken to be 1.392 and 0.96 Å, respectively), along with the copper, phosphorus, and boron atoms, resulted in discrepancy factors[14] of R_1 = 15.6% and R_2 = 23.8%. Anisotropic thermal parameters of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ were assigned to the nongroup atoms.

A difference Fourier map at this stage revealed the presence of several peaks in the region expected for the chloroform molecule. A careful examination of the electron density suggested that the chloroform resides in two orientations of partial occupancy *ca.* 50% each. Six chlorine and two carbon atoms were therefore introduced into the structure with multipliers of 0.5 for atoms at each site, both of which were anisotropically refined independently to test the possibility that the total chloroform content of the asymmetric unit differed from 1. The multipliers refined to values of 0.48 and 0.54 for the two sites. Although the geometry of the refined molecules was less than ideal, this model appeared to describe satisfactorily the electron density in the region of the chloroform molecules. A difference Fourier map at this stage allowed the location of the hydrogen atoms of the decaborate ligand as 10 of the 13 strongest peaks. The average electron density of these atoms was about 0.45 e/Å³, compared to the average value of *ca.* 2.5 e/Å³ for a phenyl carbon atom. Subsequent isotropic refinement of these boron hydrogen atoms proceeded well except for the thermal parameter of HB1. In the last cycles of refinement the nine successfully refined boron–hydrogen thermal parameters were fixed at their final values, while that for HB1 was arbitrarily assigned a value of 1.1 Å². The refined boron hydrogen positions agreed well with those determined from the Fourier map.

Final refinement, including all atoms of the asymmetric unit except the chloroform hydrogen atoms, based on a total of 393 variable parameters, converged at R_1 = 0.061 and R_2 = 0.073. Two reflections having tape-write errors, ($7\bar{3}\bar{1}$) and ($9\bar{1}\bar{1}$), and the five data suffering from $\Delta(F)/\sigma(F_o) > 8.0$ were rejected. The latter, (001), ($10\bar{2}$), ($1\bar{3}1$), ($1\bar{3}5$), and ($4\bar{5}\bar{3}$), appeared not to be suffering from secondary extinction. Inspection of the function $w\Delta^2$ for reflections ordered according to $|F_o|$ and $(\sin\theta)/\lambda$ showed satisfactory consistency.[15] The weighting scheme was therefore deemed adequate, although the value of the standard deviation of an observation of unit weight was 2.27, compared to the ideal value of 1.0.[15] A final difference Fourier map showed only slight residual electron density, ≤0.45 e/Å³, in the vicinity of the group-refined phenyl carbon atoms.

Results

Table I contains the final positional, thermal, and (for chloroform atoms) occupancy parameters for all except phenyl hydrogen atoms, which are available as Table Ia,[16] the standard deviations of which are derived from the inverse matrix of the last least-squares cycles. Table II includes pertinent interatomic distances and angles in the decahydrodecaborate(2–) ligand,[17] while Table III deals with those in proximity to the copper coördination spheres, and Table IV lists structural details within the phosphine ligands and chloroform molecules. Table V notes the results of best-plane and dihedral angle calculations. On deposit are Tables VI and VII, which incorporate the root-mean-square amplitudes of thermal vibration for all anisotropically refined atoms and close inter- and intramolecular nonbonding distances, respectively.[16] Also available is Table VIII, listing final observed and calculated structure factor amplitudes.

The geometry of a full μ-decahydrodecaborato-tetrakis(triphenylphosphine)dicopper(I) molecule (omitting all hydrogen atoms for clarity) is shown in Figure 1. Figure 2 portrays the coordination geometry, and Figure 3 displays the contents of one unit cell.

The infrared spectra of $(NEt_3H)_2B_{10}H_{10}$ and $\{[(C_6H_5)_3$-

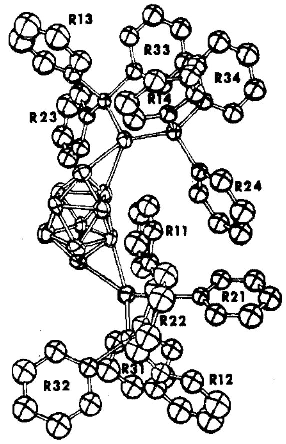


Figure 1. A view of one full μ-decahydrodecaborato-tetrakis(triphenylphosphine)dicopper(I) molecule. The shapes of all atoms represent 50% probability contours of thermal motion. All hydrogen atoms have been omitted for clarity.

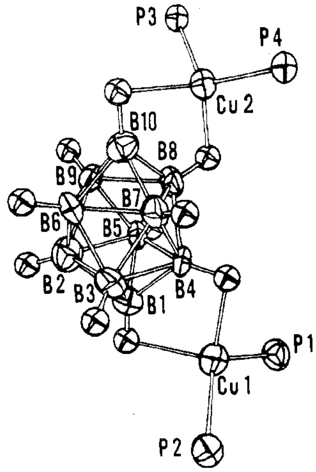


Figure 2. A view of the $P_4Cu_2B_{10}H_{10}$ coordination core of $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}$. Hydrogen atoms, each numbered like the directly attached boron atom, are given isotropic thermal parameters of 2.5 Å^2 here. All other atoms represent 50% probability ellipsoids.

$P]_2Cu\}_2B_{10}H_{10}\cdot CHCl_3$ were examined in the B–H stretching frequency region. Strong bands with high-frequency shoulders centered at 2450 (20) cm^{-1} for the anion and at 2490 (10) cm^{-1} for the complex are assigned to ν_{B-H_t} modes, the latter being weaker. In addition several weak broad bands appeared between 2150 and 2400 cm^{-1} in the copper complex, which are not present in the infrared spectra of $(Et_3NH)_2B_{10}H_{10}$, chloroform, or $[(C_6H_5)_3P]_3CuCl$. Similar absorptions are also seen in $Cu_2B_{10}H_{10}$.[18] We assign these bands to Cu–H–B bridging modes, although they are noticeably weaker and at higher energy here than for the corresponding bands of other bis(triphenylphosphine)copper(I) hydroborate complexes.[8,19] Also, "cage" bands of the free anion at 1015 (10) and 1070 (10) cm^{-1} disappear upon ligation to copper(I).[18] The molar conductance of $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}\cdot CHCl_3$ in CH_2Cl_2 was found to be 0.58 ohm^{-1} cm^2 mol^{-1} at 5.0×10^{-3} *M*, a value indicative of a nonelectrolyte in this solvent.[7b]

Discussion

As shown in Figure 1, the decahydrodecaborate anion is coordinated to two separate bis(triphenylphosphine)copper(I) units. A covalent interaction between copper(I) atoms and the $B_{10}H_{10}{}^{2-}$ cage has also been observed for $Cu_2B_{10}H_{10}$.[5] It is interesting to note that coordination of the copper atoms in both nido structures occurs along edges connecting apical with equatorial boron atoms associated with each decahydrodecaborate cage. The relationship of the four copper atoms to the $B_{10}H_{10}{}^{2-}$ cage in $Cu_2B_{10}H_{10}$ can be generated from the present structure by reflecting the two copper atoms through a mirror plane defined by boron atoms 1, 3, 5, and 10 (Figure 2). Assuming that each bis(triphenylphosphine)copper(I) unit will associate with two different edges of the $B_{10}H_{10}{}^{2-}$ cage and allowing for the possibility that two of these edges may share a common boron atom (as in $Cu_2B_{10}H_{10}$), there are a total of 25 possible isomers for $(L_2Cu)_2B_{10}H_{10}$, 17 of which are optically active. Of the two enantiomeric pairs having the copper atoms bonded to apical edges involving separate apical boron atoms, the present structure is the one in which the two Cu–H–B–B–H chelate rings are related approximately by an S_8 operation. The apical edges in the other isomer would be related by an $S_8{}^3$ operation.

The modes of attachment of the two crystallographically independent copper atoms to the $B_{10}H_{10}{}^{2-}$ cage are quite similar (Figure 2 and Table III). The four Cu–B contacts are equivalent, the average Cu–B distance being 2.30 (2) Å. This value is identical with that found for $[(C_6H_5)_3P]_2Cu(B_3H_8)$.[2b] The extent of M–B interactions[2a] in these *nido*-metalloborane structures is difficult to assess. In the cyanotrihydroborate-bridged dimer,[2c] the long Cu–B distances of 2.81 (1) and 3.01 (1) Å would appear to rule out any substantial amount of direct Cu–B orbital overlap. At the other extreme, recent synthetic and structural studies of *trans*-$Cl_2Pt(B_6H_{10})_2$,[20] $[(CH_3)_4N]_2Ni(B_{10}H_{12})_2$,[21] 2-$\{IrBr_2(CO)[(CH_3)_3P]_2\}(B_5H_8)$,[22] and related molecules[23-26] have shown that M–B σ bonding can occur in metalloboranes without appreciable involvement of the terminal hydrogen atoms. Compounds in the $[(C_6H_5)_3P]_2CuX$ series, $X^- = BH_4{}^-$, $B_3H_8{}^-$, or $^1/_2B_{10}H_{10}{}^{2-}$, are best viewed as intermediate, incorporating three-center Cu–H–B bonds in which the relative contributions of metal–boron and metal–hydrogen bonding cannot be evaluated solely from structural criteria.

Despite the fact that the apical and equatorial Cu–B distances are equivalent, the Cu–H distances in both Cu–H–B–B–H chelate rings are different. The inequivalence of these Cu–H distances may be contrasted with the results obtained for the other bis(triphenylphosphine)copper(I) hydroborate

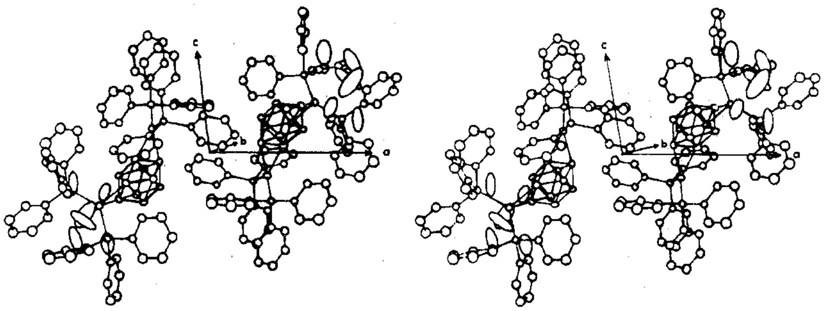


Figure 3. A stereoscopic packing diagram of $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}\cdot CHCl_3$, displaying the contents of one unit cell. Hydrogen and chloroform carbon atoms have been omitted for clarity. Atom shapes represent 20% probability contours.

Table I. Final Positional, Isotropic Thermal, and Occupancy Parameters of the Nongroup Atoms of $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}\cdot CHCl_3$[a,b]

Atom	x	y	z	B, Å^2 (or occ factor)
Cu1	0.29652 (6)	0.3835 (1)	0.2305 (1)	
Cu2	0.15573 (6)	0.1052 (1)	−0.1296 (1)	
P1	0.3767 (1)	0.4276 (2)	0.1401 (2)	
P2	0.2578 (1)	0.4897 (2)	0.3743 (2)	
P3	0.1825 (1)	−0.0397 (2)	−0.2427 (2)	
P4	0.0887 (1)	0.2252 (2)	−0.1747 (2)	
Cl11	0.3977 (5)	−0.0703 (8)	0.227 (1)	0.54 (1)[c]
Cl21	0.4599 (5)	0.0796 (9)	0.160 (1)	0.54
Cl31	0.439 (2)	0.103 (2)	0.357 (2)	0.54
Cl12	0.446 (1)	0.213 (2)	0.439 (3)	0.48 (1)
Cl22	0.3785 (8)	0.069 (1)	0.486 (2)	0.48
Cl32	0.454 (2)	0.021 (2)	0.340 (4)	0.48
C1	0.406 (2)	0.064 (3)	0.266 (5)	0.54
C2	0.418 (4)	0.122 (8)	0.448 (9)	0.48
B1	0.2753 (6)	0.216 (1)	0.2223 (9)	
B2	0.2430 (6)	0.101 (1)	0.213 (1)	
B3	0.1953 (6)	0.217 (1)	0.2368 (9)	
B4	0.2331 (6)	0.2571 (9)	0.1317 (8)	
B5	0.2829 (6)	0.1383 (8)	0.1075 (8)	
B6	0.1619 (6)	0.0999 (9)	0.1709 (8)	
B7	0.1535 (6)	0.209 (1)	0.1145 (9)	
B8	0.2143 (6)	0.1544 (9)	0.0223 (9)	
B9	0.2215 (6)	0.044 (1)	0.0823 (9)	
B10	0.1515 (6)	0.0904 (9)	0.0414 (9)	
HB1[d]	0.311 (3)	0.245 (5)	0.272 (5)	1.1[e]
HB2	0.265 (3)	0.051 (6)	0.257 (5)	2.8
HB3	0.174 (3)	0.257 (5)	0.310 (5)	1.2
HB4	0.243 (3)	0.327 (5)	0.115 (5)	1.7
HB5	0.330 (4)	0.120 (5)	0.061 (6)	3.9
HB6	0.125 (3)	0.062 (6)	0.217 (6)	4.1
HB7	0.116 (3)	0.267 (6)	0.111 (5)	2.8
HB8	0.227 (3)	0.160 (5)	−0.056 (6)	2.6
HB9	0.235 (3)	−0.033 (6)	0.050 (5)	2.1
HB10	0.113 (3)	0.042 (5)	−0.019 (5)	3.4
Derived Parameters for Ring Carbon Atoms[f]				
C111	0.4030 (3)	0.3308 (5)	0.0308 (4)	4.3 (2)
C211	0.4664 (3)	0.3024 (5)	0.0200 (5)	7.1 (3)
C311	0.4843 (3)	0.2277 (6)	−0.0649 (6)	9.2 (4)
C411	0.4390 (4)	0.1815 (5)	−0.1388 (5)	8.2 (3)
C511	0.3756 (3)	0.2100 (5)	−0.1279 (5)	6.7 (3)
C611	0.3576 (2)	0.2846 (5)	−0.0431 (5)	5.0 (2)
C121	0.3585 (4)	0.5364 (4)	0.0792 (5)	3.6 (2)
C221	0.3795 (4)	0.5421 (6)	−0.0174 (5)	5.1 (2)
C321	0.3638 (3)	0.6267 (6)	−0.0589 (4)	5.8 (3)
C421	0.3271 (4)	0.7057 (5)	−0.0037 (5)	6.7 (3)
C521	0.3060 (4)	0.7000 (6)	0.0929 (5)	6.8 (3)
C621	0.3217 (3)	0.6154 (6)	0.1344 (4)	5.3 (3)
C131	0.4485 (3)	0.4638 (6)	0.2190 (5)	4.4 (2)
C231	0.4841 (3)	0.5474 (5)	0.2127 (5)	5.7 (3)
C331	0.5370 (3)	0.5734 (5)	0.2793 (6)	7.0 (3)
C431	0.5542 (3)	0.5156 (6)	0.3522 (5)	7.2 (3)
C531	0.5186 (3)	0.4319 (5)	0.3585 (5)	7.8 (3)
C631	0.4657 (3)	0.4060 (5)	0.2919 (5)	6.0 (3)
C112	0.2941 (3)	−0.3858 (4)	0.3983 (5)	3.9 (2)
C212	0.2606 (2)	−0.2967 (6)	0.3922 (5)	5.4 (3)
C312	0.2925 (4)	−0.2058 (4)	0.4009 (5)	7.7 (3)
C412	0.3580 (4)	−0.2041 (5)	0.4158 (5)	8.2 (3)
C512	0.3915 (2)	−0.2933 (6)	0.4219 (5)	7.4 (3)
C612	0.3596 (3)	−0.3841 (5)	0.4132 (5)	5.2 (3)
C122	0.1727 (2)	0.5160 (6)	0.3664 (5)	3.9 (2)
C222	0.1411 (3)	0.4855 (6)	0.2701 (4)	4.7 (2)
C322	0.0760 (3)	0.5002 (4)	0.2604 (4)	6.3 (3)
C422	0.0425 (2)	0.5454 (6)	0.3471 (6)	6.3 (3)
C522	0.0741 (3)	0.5759 (6)	0.4434 (5)	6.8 (3)
C622	0.1392 (3)	0.5612 (4)	0.5431 (4)	6.1 (3)
C132	0.2706 (3)	0.4554 (5)	0.5010 (4)	4.0 (2)
C232	0.2773 (3)	0.3528 (5)	0.5043 (4)	5.3 (3)
C332	0.2850 (4)	0.3244 (4)	0.5995 (6)	6.2 (3)
C432	0.2859 (4)	0.3985 (6)	0.6914 (4)	6.3 (3)
C532	0.2792 (3)	0.5011 (5)	0.6881 (4)	6.5 (3)
C632	0.2715 (3)	0.5295 (4)	0.5929 (5)	5.3 (3)
C113	0.1290 (3)	−0.1400 (5)	−0.2304 (5)	4.1 (2)
C213	0.0655 (3)	−0.1114 (4)	−0.2226 (5)	5.5 (3)
C313	0.0205 (2)	−0.1839 (6)	−0.2190 (5)	7.4 (3)
C413	0.0389 (3)	−0.2849 (5)	−0.2234 (5)	8.3 (3)
C513	0.1024 (4)	−0.3134 (4)	−0.2312 (5)	8.3 (3)
C613	0.1474 (3)	−0.2410 (6)	−0.2348 (5)	6.7 (3)

Table I (*Continued*)

Atom	x	y	z	B, Å^2 (or occ factor)
C123	0.2622 (2)	−0.0910 (5)	−0.2351 (5)	3.6 (2)
C223	0.3020 (3)	−0.0501 (5)	−0.1500 (4)	4.5 (2)
C323	0.3634 (3)	−0.0880 (5)	−0.1427 (5)	5.8 (3)
C423	0.3851 (3)	−0.1669 (6)	−0.2206 (6)	7.0 (3)
C523	0.3454 (4)	−0.2078 (5)	−0.3057 (5)	8.0 (3)
C623	0.2839 (3)	−0.1699 (5)	−0.3130 (4)	6.5 (3)
C133	0.1715 (3)	−0.0364 (5)	−0.3794 (4)	3.8 (2)
C233	0.1349 (3)	−0.1066 (4)	−0.4496 (5)	4.7 (2)
C333	0.1287 (3)	−0.1002 (4)	−0.5535 (4)	5.8 (3)
C433	0.1591 (3)	−0.0236 (5)	−0.5870 (4)	6.0 (3)
C533	0.1958 (3)	0.0466 (4)	−0.5168 (5)	5.9 (3)
C633	0.2020 (3)	0.0402 (4)	−0.4130 (5)	5.2 (3)
C114	0.0059 (2)	0.2163 (5)	−0.1455 (5)	3.2 (2)
C214	−0.0081 (3)	0.1658 (6)	−0.0682 (4)	5.1 (3)
C314	−0.0708 (3)	0.1525 (4)	−0.0480 (4)	5.7 (3)
C414	−0.1194 (2)	0.1896 (6)	−0.1052 (5)	4.8 (2)
C514	−0.1054 (2)	0.2401 (6)	−0.1825 (4)	4.6 (2)
C614	−0.0427 (3)	0.2535 (4)	−0.2027 (4)	3.9 (2)
C124	0.1120 (3)	0.3545 (4)	−0.1123 (4)	3.3 (2)
C224	0.0686 (2)	0.4339 (5)	−0.0830 (5)	5.4 (3)
C324	0.0896 (3)	0.5320 (4)	−0.0402 (5)	6.5 (3)
C424	0.1541 (3)	0.5507 (4)	−0.0266 (5)	5.8 (3)
C524	0.1975 (2)	0.4713 (5)	−0.0559 (5)	5.1 (3)
C624	0.1765 (3)	0.3732 (4)	−0.0987 (4)	4.4 (2)
C134	0.0832 (3)	0.2292 (5)	−0.3128 (3)	3.5 (2)
C234	0.1120 (3)	0.3050 (4)	−0.3501 (5)	4.7 (2)
C334	0.1069 (3)	0.3052 (4)	−0.4555 (5)	5.5 (3)
C434	0.0730 (3)	0.2295 (5)	−0.5237 (4)	6.1 (3)
C534	0.0442 (3)	0.1536 (4)	−0.4865 (4)	5.6 (3)
C634	0.0493 (3)	0.1535 (4)	−0.3810 (5)	4.5 (2)

Rigid Group Parameters

Group	X_0[g]	Y_0	Z_0	ϕ	θ	ρ
R11	0.4210 (2)	0.2561 (4)	−0.0540 (4)	−1.518 (4)	−2.844 (4)	2.155 (4)
R21	0.3428 (2)	0.6211 (3)	0.0378 (3)	−0.070 (5)	2.307 (4)	−0.925 (5)
R31	0.5014 (2)	0.4897 (4)	0.2856 (3)	−0.180 (4)	2.696 (4)	−2.444 (4)
R12	0.3261 (2)	−0.2950 (4)	0.4070 (3)	1.059 (4)	3.069 (4)	−3.083 (4)
R22	0.1076 (2)	0.5307 (3)	0.3567 (4)	1.553 (4)	2.586 (4)	−1.807 (5)
R32	0.2783 (2)	0.4269 (4)	0.5962 (4)	−3.084 (4)	2.645 (4)	−1.481 (4)
R13	0.0839 (2)	−0.2124 (4)	−0.2269 (3)	0.808 (4)	−3.043 (4)	−0.065 (4)
R23	0.3237 (2)	−0.1289 (3)	−0.2278 (4)	−1.648 (4)	−2.671 (4)	2.169 (4)
R33	0.1653 (2)	−0.0300 (3)	−0.4832 (3)	2.502 (4)	−3.311 (4)	1.813 (4)
R14	−0.0567 (2)	0.2029 (3)	−0.1254 (3)	2.201 (4)	−2.556 (3)	2.506 (4)
R24	0.1330 (2)	0.4526 (3)	−0.0694 (3)	1.270 (4)	−3.014 (4)	−2.747 (4)
R34	0.0781 (2)	0.2293 (3)	−0.4183 (3)	−0.589 (4)	−3.001 (4)	1.384 (4)

Final Anisotropic Thermal Parameters of the Nongroup Atoms

Atom	β_{11}[h]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu1	2.39 (5)	5.2 (1)	5.7 (1)	−0.58 (6)	0.27 (6)	1.48 (9)
Cu2	2.87 (5)	4.7 (1)	4.7 (1)	−0.31 (6)	−0.04 (6)	1.69 (9)
P1	2.11 (9)	6.0 (2)	5.7 (2)	−0.5 (1)	0.2 (1)	2.0 (2)
P2	2.10 (8)	5.3 (2)	5.0 (2)	−0.2 (1)	0.1 (1)	1.3 (2)
P3	2.58 (9)	4.1 (2)	4.4 (2)	−0.6 (1)	−0.1 (1)	1.5 (2)
P4	2.21 (8)	4.4 (2)	4.7 (2)	−0.3 (1)	0.1 (1)	1.7 (2)
Cl11	8.2 (4)	10.4 (9)	41 (2)	1.8 (4)	8.1 (7)	9 (1)
Cl21	4.7 (4)	28 (2)	71 (4)	−2.4 (5)	0.1 (9)	25 (2)
Cl31	26 (2)	22 (2)	48 (4)	0.1 (2)	−28 (3)	−1 (2)
Cl12	12.8 (9)	42 (3)	72 (5)	−16 (1)	−16 (2)	40 (4)
Cl22	9.2 (7)	16 (1)	66 (4)	−0.7 (7)	4.3 (1)	−3 (2)
Cl32	25 (3)	30 (3)	94 (10)	10 (2)	35 (5)	17 (4)
C1	4 (1)	11 (4)	41 (7)	−1 (2)	1 (2)	1 (4)
C2	14 (4)	49 (14)	85 (22)	−5 (5)	31 (8)	9 (13)
B1	2.6 (5)	6 (1)	5 (1)	−0.9 (6)	−0.8 (5)	1 (1)
B2	2.8 (5)	5 (1)	7 (1)	0.6 (6)	0.1 (6)	2.0 (9)
B3	2.9 (5)	6 (1)	3 (1)	−0.7 (6)	0.4 (5)	1.0 (9)
B4	3.0 (4)	3 (1)	5 (1)	−0.6 (5)	0.2 (5)	2.0 (9)
B5	2.7 (4)	4 (1)	4 (1)	−0.4 (5)	0.5 (5)	2.1 (8)
B6	2.7 (4)	6 (1)	3 (1)	−0.5 (5)	−0.2 (5)	2.4 (8)
B7	2.4 (4)	6 (1)	5 (1)	−0.7 (5)	0.4 (5)	2.4 (9)
B8	2.9 (4)	5 (1)	4 (1)	−0.1 (5)	0.7 (5)	1.9 (9)
B9	4.0 (5)	3 (1)	4 (1)	−1 (1)	0.6 (6)	0.7 (9)
B10	1.8 (4)	5 (1)	6 (1)	−0.5 (5)	0.3 (5)	1.3 (9)

[a] See Figures 1 and 2 for nongroup atom and group labeling scheme. [b] Standard deviations, in parentheses beside each entry, occur in the last significant figure(s) for each parameter. [c] Occupancy factors. [d] HB*n* is always directly bonded to B*n*. [e] Fixed isotropic thermal parameters. [f] Carbon atom labeling proceeds in order around each ring, C1*xy* being that carbon of ring *x* bonded directly to phosphorus *y*. [g] X_0, Y_0, and Z_0 are the fractional coordinates of the center of gravity of the rigid-body constrained phenyl rings, and ϕ, θ, and ρ are the orientational angles given in radians. These parameters are defined in ref 13a. [h] β's are defined in the text; values reported are ×10^3.

Table II

Interatomic Distances within the Decahydrodecaborate(2–) Ligand (Å)[a]

$B_{e_1}-B_{e_1}$[b]		$B_{a_1}-B_{e_1}$		$B_{e_2}-B_{e_2}$		$B_{a_2}-B_{e_2}$		$B_{e_1}-B_{e_2}$		B–HB	
2–3[c]	1.81 (2)	1–2	1.68 (2)	6–7	1.78 (2)	10–6	1.69 (2)	2–6	1.78 (2)	1–1	1.01 (6)
3–4	1.82 (2)	1–3	1.72 (2)	7–8	1.84 (2)	10–7	1.67 (2)	2–9	1.78 (2)	2–2	1.07 (7)
4–5	1.87 (2)	1–4	1.64 (2)	8–9	1.83 (2)	10–8	1.66 (2)	3–6	1.77 (2)	3–3	1.11 (6)
2–5	1.83 (2)	1–5	1.66 (2)	9–6	1.80 (2)	10–9	1.70 (2)	3–7	1.78 (2)	4–4	1.04 (7)
								4–7	1.81 (2)	5–5	1.20 (7)
								4–8	1.80 (2)	6–6	1.20 (8)
								5–8	1.83 (2)	7–7	1.11 (7)
								5–9	1.81 (2)	8–8	1.11 (7)
										9–9	1.07 (7)
										10–10	1.21 (7)

Interatomic Angles within the Decahydrodecaborate(2–) Ligand (deg)

$B_{e_1}-B_{a_1}-B_{e_1}$		$B_{e_2}-B_{a_2}-B_{e_2}$		$B_{e_1}-B_{e_1}-B_{e_1}$		$B_{e_2}-B_{e_2}-B_{e_2}$		$B_{e_1}-B_{e_1}-B_{a_1}$		$B_{e_2}-B_{e_2}-B_{a_2}$	
4–1–5	69.0 (7)	6–10–7	64.0 (7)	2–3–4	89.4 (8)	6–7–8	89.5 (8)	2–3–1	56.8 (7)	6–7–10	58.5 (7)
3–1–4	65.7 (7)	7–10–8	67.1 (7)	3–4–5	91.0 (8)	7–8–9	89.2 (8)	3–2–1	58.7 (7)	7–6–10	57.5 (6)
2–1–5	66.7 (7)	8–10–9	65.8 (7)	4–5–2	87.3 (8)	8–9–6	89.4 (8)	3–4–1	59.1 (7)	7–8–10	56.7 (7)
2–1–3	64.5 (7)	6–10–9	64.1 (7)	5–2–3	92.3 (8)	9–6–7	92.0 (8)	4–3–1	55.1 (6)	8–7–10	56.2 (7)
2–1–4	100.6 (9)	7–10–9	99.6 (9)					4–5–1	55.1 (6)	8–9–10	56.1 (7)
3–1–5	102.6 (9)	6–10–8	99.1 (9)					5–4–1	55.9 (7)	9–8–10	58.1 (7)
								5–2–1	56.0 (7)	6–9–10	57.6 (7)
								2–5–1	57.3 (7)	9–6–10	58.2 (6)

$B_{e_1}-B_{e_1}-B_{e_2}$		$B_{e_2}-B_{e_2}-B_{e_1}$		$B_{e_1}-B_{e_2}-B_{e_1}$		$B_{e_2}-B_{e_1}-B_{e_2}$	
2–3–6	59.6 (7)	6–7–3	59.6 (6)	2–6–3	61.3 (7)	6–3–7	60.1 (7)
3–2–6	59.1 (7)	7–6–3	60.3 (7)	3–7–4	60.9 (6)	7–4–8	61.3 (7)
3–4–7	58.9 (6)	7–8–4	59.5 (6)	4–8–5	61.8 (6)	8–5–9	60.3 (7)
4–3–7	60.2 (6)	8–7–4	59.2 (6)	5–9–2	61.5 (7)	9–2–6	60.8 (7)
4–5–8	58.4 (6)	8–9–5	60.4 (6)				
5–4–8	59.8 (6)	9–8–5	59.3 (6)				
2–5–9	58.3 (6)	6–9–2	59.7 (6)				
5–2–9	60.2 (6)	9–6–2	59.5 (7)				

$HB_{e_1}-B_{e_1}-B_{e_1}$		$HB_{e_2}-B_{e_2}-B_{e_2}$		$HB_{e_1}-B_{e_1}-B_{e_2}$		$HB_{e_2}-B_{e_2}-B_{e_1}$	
2–2–3	138 (4)	6–6–7	131 (4)	2–2–6	125 (4)	6–6–2	118 (4)
2–2–5	122 (4)	6–6–9	131 (4)	2–2–9	115 (4)	6–6–3	117 (4)
3–3–4	135 (3)	7–7–8	131 (4)	3–3–6	118 (3)	7–7–3	117 (4)
3–3–2	128 (3)	7–7–6	135 (4)	3–3–7	121 (3)	7–7–4	115 (4)
4–4–5	127 (4)	8–8–9	129 (4)	4–4–7	121 (4)	8–8–4	119 (4)
4–4–3	135 (4)	8–8–7	137 (4)	4–4–8	117 (4)	8–8–5	113 (4)
5–5–2	140 (4)	9–9–6	133 (4)	5–5–8	113 (3)	9–9–5	117 (4)
5–5–4	130 (4)	9–9–8	130 (4)	5–5–9	118 (4)	9–9–2	121 (4)

$HB_{a_1}-B_{a_1}-B_{e_1}$		$HB_{a_2}-B_{a_2}-B_{e_2}$		$HB_{e_1}-B_{e_1}-B_{a_1}$		$HB_{e_2}-B_{e_2}-B_{a_2}$		$HB_{a_m}-B_{a_m}-B_{a_n}$	
1–1–2	126 (4)	10–10–6	129 (3)	2–2–1	119 (4)	6–6–10	121 (4)	1–1–10	176 (3)
1–1–3	131 (4)	10–10–7	135 (3)	3–3–1	121 (3)	7–7–10	123 (4)	10–10–1	175 (3)
1–1–4	134 (4)	10–10–8	131 (3)	4–4–1	120 (4)	8–8–10	122 (4)		
1–1–5	126 (4)	10–10–9	126 (3)	5–5–1	126 (4)	9–9–10	119 (4)		

[a] See footnotes *a* and *b* of Table I. [b] In the headings here, the subscript e stands for equatorial, a for axial, 1 for the tetragonal pyramid comprised of boron atoms 1–5, and 2 for that pyramid of borons 6–10. [c] Atom number designations relate to the respective heading and are in corresponding order.

complexes studied in this laboratory.[2a,b] The difference is not surprising since the decahydrodecaborate(2–) anion is the only ligand that coordinates using chemically nonequivalent B–H bonds. The mean Cu–H_e distance of 1.86 (6) Å compares favorably with the corresponding values of 1.87 (9) Å in μ-bis(cyanotrihydroborato)-tetrakis(triphenylphosphine)dicopper(I),[2c] 1.85 (5) Å in octahydrotriboratobis(triphenylphosphine)copper(I),[2b] and 1.82 (3) Å in tetrahydroboratobis(triphenylphosphine)copper(I).[2a] The value quoted for the last structure resulted from continued refinement (*cf.* ref 2c), using a further improved weighting scheme, the full details of which are available as Table IX.[16,27] In the present structure, the mean apical Cu–H distance of 2.08 (7) Å, while barely distinguishable statistically from these values, is probably significant since the observed lengthening occurs at the apical hydrogen atom in two crystallographically independent sites. This result suggests that the apical Cu–H interaction is weaker than the equatorial one. It is interesting that this inequivalence is not the one expected on the basis of charge distribution calculations for the free $B_{10}H_{10}^{2-}$ ion, which indicate that the apical positions have more negative charge than the equatorial ones.[3,28] A similar effect has also been reported in the structure of 2-{$IrBr_2(CO)[(CH_3)_3P]_2$}(B_5H_8), in which only the equatorial position of pentaborane is coordinated to the iridium atom,[22] contrary to the charge density calculations for B_5H_9,[29] which indicate the apical position to have more negative charge. It would appear that charge density distribution calculations for the free polyhedral borane ions do not necessarily apply when they are coordinated to a metal atom (*cf.* also the discussion in ref 30).

Alternatively, the difference between the apical and equatorial Cu–H distances in the present structure may be rationalized on purely geometric grounds in the following manner. Assuming equivalent Cu–B distances of 2.30 Å, a B_a–B_e bond length of 1.68 Å, H_a–B_a–B_e and H_e–B_e–B_a angles of 129 and 121°, respectively (average values from nonchelated apex edges in the present structure), and a B–H distance of 1.11 Å, we compute the Cu–H_a and Cu–H_e distances to be

Table III. Interatomic Distances (Å) and Angles (deg) about the Copper Coordination Spheres[a]

Atoms	Distance	Atoms	Angle	Atoms	Angle
Copper 1		Copper 1		Copper 2	
Cu1-P1	2.289 (3)	P1-Cu1-P2	123.0 (1)	P3-Cu2-P4	122.7 (1)
Cu1-P2	2.286 (3)	P1-Cu1-HB1	114 (2)	P3-Cu2-HB10	99 (2)
Cu1-HB1	2.06 (6)	P1-Cu1-B1	120.7 (3)	P3-Cu2-B10	115.0 (3)
Cu1-B1	2.29 (1)	P1-Cu1-B4	113.1 (3)	P3-Cu2-B8	119.4 (3)
Cu1-B4	2.32 (1)	P1-Cu1-HB4	97 (2)	P3-Cu2-HB8	109 (2)
Cu1-HB4	1.88 (6)	P2-Cu1-HB1	105 (2)	P4-Cu2-HB10	108 (2)
		P2-Cu1-B1	112.7 (3)	P4-Cu2-B10	114.6 (3)
Copper 2		P2-Cu1-B4	119.7 (3)	P4-Cu2-B8	116.3 (3)
Cu2-P3	2.258 (3)	P2-Cu1-HB4	122 (2)	P4-Cu2-HB8	113 (2)
Cu2-P4	2.276 (3)	HB1-Cu1-HB4	93 (3)	HB10-Cu2-HB8	102 (3)
Cu2-HB10	2.09 (7)	B1-Cu1-B4	41.7 (4)	B10-Cu2-B8	42.4 (4)
Cu2-B10	2.32 (1)	HB1-Cu1-B4	68 (2)	HB10-Cu2-B8	73 (2)
Cu2-B8	2.28 (1)	HB4-Cu1-B1	67 (2)	HB8-Cu2-B10	71 (2)
Cu2-HB8	1.84 (6)	Cu1-HB1-B1	89 (4)	Cu2-HB10-B10	85 (4)
		Cu1-HB4-B4	101 (5)	Cu2-HB8-B8	98 (4)
		Cu1-B1-B4	70.1 (6)	Cu2-B10-B8	67.8 (5)
		Cu1-B4-B1	68.1 (6)	Cu2-B8-B10	69.9 (6)

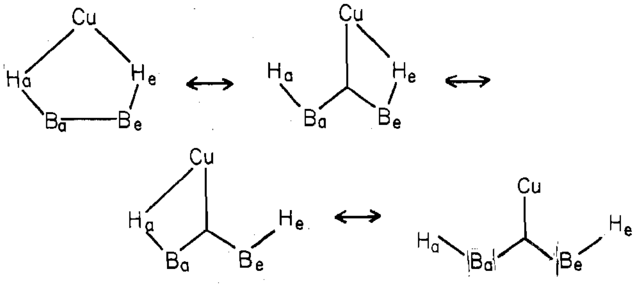
[a] See footnotes *a* and *b*, Table I.

Table IV. Interatomic Distances (Å) and Angles (deg) within the Phosphine Ligands and Chloroform Molecules[a]

Atoms	Distances	Atoms	Angles
	Phosphine 1		
P1-C111	1.819 (7)	Cu1-P1-C111	116.4 (3)
P1-C121	1.839 (7)	Cu1-P1-C121	114.8 (2)
P1-C131	1.814 (7)	Cu1-P1-C131	113.7 (2)
		C111-P1-C121	102.0 (3)
		C111-P1-C131	104.1 (3)
		C121-P1-C131	104.3 (3)
	Phosphine 2		
P2-C112	1.817 (7)	Cu1-P2-C112	111.1 (2)
P2-C122	1.831 (6)	Cu1-P2-C122	114.9 (2)
P2-C132	1.836 (6)	Cu1-P2-C132	118.9 (2)
		C112-P2-C122	104.9 (3)
		C112-P2-C132	101.8 (3)
		C122-P2-C132	103.5 (3)
	Phosphine 3		
P3-C113	1.824 (7)	Cu2-P3-C113	108.7 (2)
P3-C123	1.812 (6)	Cu2-P3-C123	119.2 (2)
P3-C133	1.819 (5)	Cu2-P3-C133	115.6 (2)
		C113-P3-C123	107.0 (3)
		C113-P3-C133	102.4 (3)
		C123-P3-C133	102.5 (3)
	Phosphine 4		
P4-C114	1.826 (5)	Cu2-P4-C114	115.9 (2)
P4-C124	1.822 (6)	Cu2-P4-C124	112.3 (2)
P4-C134	1.835 (5)	Cu2-P4-C134	116.2 (2)
		C114-P4-C124	105.7 (3)
		C114-P4-C134	102.4 (3)
		C124-P4-C134	102.8 (3)
	Chloroform 1		
Cl11-Cl21	2.76 (1)	Cl21-Cl11-Cl31	56.9 (9)
Cl11-Cl31	2.72 (2)	Cl31-Cl21-Cl11	60.7 (8)
Cl21-Cl31	2.61 (4)	Cl11-Cl31-Cl21	62.4 (6)
C1-Cl11	1.77 (5)	Cl11-C1-Cl21	97 (3)
C1-Cl21	1.91 (5)	Cl21-C1-Cl31	104 (3)
C1-Cl31	1.37 (5)	Cl31-C1-Cl11	119 (3)
	Chloroform 2		
Cl12-Cl22	2.62 (2)	Cl22-Cl12-Cl32	57.5 (8)
Cl22-Cl32	2.53 (3)	Cl32-Cl22-Cl12	61 (1)
Cl32-Cl12	2.63 (4)	Cl12-Cl32-Cl22	61 (1)
C2-Cl12	1.40 (9)	Cl12-C2-Cl22	153 (8)
C2-Cl22	1.29 (6)	Cl22-C2-Cl32	102 (7)
C2-Cl32	1.91 (10)	Cl32-C2-Cl12	104 (3)

[a] See footnotes *a* and *b*, Table I.

2.00 and 1.85 Å, respectively. The difference of 0.15 Å is nearly as large as the observed one of 0.22 Å. Again we stress that the relative strengths of the Cu–H and Cu–B interactions cannot be definitively assessed from geometric criteria alone, and we depict the bonding here in the manner



As in $[(C_6H_5)_3P]_2Cu(B_3H_8)$, the five-membered Cu–H–B–B–H chelate rings are slightly puckered about the line joining the hydrogen atoms. Here the bridging hydrogen atoms lie at an average distance of 0.15 (4) Å above the plane defined by the copper and two boron atoms. The corresponding value in the octahydrotriborate complex is *ca.* 0.4 Å. The internal angles in the chelate rings of both structures are similar, except for minor differences that result from the lengthening of the Cu–H_a distance.

The geometry of the decaborate(10) cage (Tables II and V) is only slightly distorted from that required by D_{4d} symmetry. The atoms 2–3–4–5 and 6–7–8–9 deviate by only a few hundredths of 1 Å from their calculated best mean planes. The dihedral angle between these two planes is 0.72°, indicating that they are very nearly parallel. Dihedral angles between planes formed by an apical and two adjacent trans equatorial boron atoms closely approach the ideal values of 45, 90, and 135°. The boron–boron distances compare favorably with those reported for $Cu_2B_{10}H_{10}$[5b] and $[(CH_3)_4N]_2B_{10}H_7Cl_3$.[31] Those of $Cu_2B_{10}H_{10}$ are consistently 0.02–0.05 Å longer, possibly because hydrogen atoms were not included in the refinement. The average apical-to-equatorial B–B distance is 1.68 (3) Å. Of the eight separate distances, the shortest two, 1.64 (2) and 1.66 (2) Å, occur between boron atoms in the Cu–H–B–B–H chelate rings. Chelation of a metal ion by adjacent boron–hydrogen bonds in $[(C_6H_5)_3P]_2Cu(B_3H_8)$ and $[(OC)_4Cr(B_3H_8)]^-$ also resulted in a shortening of the boron–boron distance by 0.04 (1) and 0.02 (1) Å, respectively, from the value found in the free ligand.[2b,32] The mean boron–boron distance along the 16 equatorial edges is 1.81 (3) Å, which is significantly longer (*ca.* 0.13 Å) than the mean value for the eight remaining edges. This inequivalence was also observed in the structure of $Cu_2B_{10}H_{10}$, in which the corresponding average edge lengths

Table V. Distances of Atoms from Best Planes and Dihedral Angles within the Copper Coordination Spheres and Decahydrodecaborate(2−) Ligand[a]

Atoms defining best plane	Distance (Å) of atom		Atoms defining best plane	Distance (Å) of atom		Dihedral angles		
						Plane 1	Plane 2	Angle, deg
Cu1–B1–B4	B3	1.41	B1–B2–B4–B10	B1	−0.03 (1)	P1–Cu1–P2	B1–Cu1–B4	79.4 (6)
	B5	−1.20		B2	0.02 (1)		HB1–Cu1–HB4	78 (2)
	HB1	−0.12		B4	0.02 (1)		Cu1–P2–HB1	132 (2)
	HB4	−0.19		B10	−0.01 (1)		Cu1–P2–B1	158.6 (4)
Cu2–B8–B10	B7	1.32		Cu1	0.26		Cu1–P2–B4	−155.3 (4)
	B9	−1.25		B3	1.31		Cu1–P2–HB4	−125 (3)
	HB8	−0.13		B5	−1.32	B1–Cu1–B4	HB1–Cu1–HB4	7 (2)
	HB10	−0.15		HB1	−0.08	P3–Cu2–P4	B8–Cu2–B10	88.3 (6)
B2–B3–B4–B5	B2–B5	0.00 (1)		HB4	−0.05		HB8–Cu2–HB10	87 (2)
	B6	−1.48	B1–B6–B8–B10	B1, B6, B8, B10	0.00 (1)		Cu2–P4–HB8	134 (2)
	B7	−1.50		Cu2	0.11		Cu2–P4–B8	165.1 (4)
	B8	−1.52		B7	1.29		Cu2–P4–B10	−147.8 (4)
	B9	−1.50		B9	−1.29		Cu2–P4–HB10	−115 (2)
B6–B7–B8–B9	B6–B9	0.00 (1)		HB8	−0.09	B8–Cu2–B10	HB8–Cu2–HB10	6 (2)
	B2	1.49		HB10	−0.10	B2–B1–B4	B3–B1–B5	90.5 (5)
	B3	1.49				B6–B10–B8	B7–B10–B9	90.6 (5)
	B4	1.51				B2–B1–B4	B7–B10–B9	134.5 (5)
	B5	1.51				B2–B1–B4	B6–B10–B8	134.6 (5)
						B3–B1–B5	B7–B10–B9	44.6 (5)
						B3–B1–B5	B6–B10–B8	134.9 (5)

[a] See Figure 2 for atom labeling scheme. See also footnote *b*, Table I.

differed by 0.11 Å. Comparable B–B distances of nonahydropentaborane, derived from various structural determinations, are 1.69 Å for the apical and 1.80 Å for the equatorial edges (*cf.* ref 3, p 4, and references therein), in quantitative agreement with the present structure. In addition, the equatorial B–B distances within the tetragonal pyramids are slightly larger than those within the equatorial belt. Although this difference is statistically insignificant here, it has been observed in structural determinations of other decaborate(2−) derivatives.[5b,31] The average B–H distance is 1.11 (8) Å, a value which is reasonable for an X-ray structural determination.[33] Further details of the geometry of the $B_{10}H_{10}^{2-}$ cage are summarized in Table II.

In addition to the two three-center Cu–H–B bridge bonds, the coordination sphere of each copper atom contains two triphenylphosphine ligands. The average Cu–P bond length, 2.278 (10) Å, and P–Cu–P bond angle, 122.9 (3)°, agree with expectations based on previous structural studies of bis(triphenylphosphine)copper(I) complexes.[34] The dihedral angles between planes defined by P1–Cu1–P2 with B1–Cu1–B4 and P3–Cu2–P4 with B8–Cu2–B10 are 79.4 (6) and 88.3 (6)°, respectively. This inequivalence reveals the coordination sphere of Cu1 to be substantially more distorted than that of Cu2 and probably has its origin in crystal-packing forces. The pronounced influence of these lattice forces on the geometries of triphenylphosphine copper(I) complexes, especially the dihedral angles of planes that intersect at the Cu atom, has considerable precedence in structural studies carried out both in this laboratory and elsewhere.[35]

Each of the four triphenylphosphine groups has a conformation well known for this ligand.[36–38] Three of these, ligands 1, 3, and 4 (Figure 3), are of the same chirality, which differs from that of ligand 2. This result is unusual for a bis(triphenylphosphine)copper(I) complex.[37] A careful inspection of the table of interatomic distances revealed only one graphitic stacking of phenyl rings, namely that between R33 and R34. The dihedral angle between these two rings is 3.66° and their separation is *ca.* 3.45 Å. Other features of the packing may be seen in Figure 3 and Table VII. The internal geometry of the triphenylphosphine ligands (Table IV) is normal.[38]

The chloroform geometry is summarized in Table IV.[39] The deviations from idealized C_{3v} symmetry in both chloroform half-molecules result largely from difficulty in locating carbon atoms in the presence of the diffuse electron density contributed by chlorine atoms of high thermal motion (Table VI). Optimization of geometry about the chloroform carbon atoms by means of fixed atomic coordinates or rigid-body treatments was briefly attempted. Since no improvement resulted, the chloroform electron density was approximated by unrestricted refinement of positional and thermal parameters of the eight atoms. No structural meaning can be attached to the interatomic distances and angles about carbon atoms (especially C2) of the chloroform molecules which are chemically unreasonable and a consequence of the disorder.

Bonding Patterns in *nido*-Metalloboranes

At a time when only limited information about the bonding modes in metalloboranes was available, there being relatively few compounds of this kind, the structure of octahydrotriboratobis(triphenylphosphine)copper(I) was postulated to contain a four-membered CuH_2B chelate ring by analogy to the known structure of tetrahydroboratobis(triphenylphosphine)copper(I).[40] This suggestion was of course later proved to be incorrect. When the crystal structure of the former complex was determined, the copper was found to coordinate to two separate terminal B–H bonds involving the two equivalent borons of the $B_3H_8^-$ anion.[2b] Subsequently, a number of studies of metalloboranes have been undertaken providing additional information about the structural features characteristic of this class of compounds.[41] Several bonding patterns can now be recognized in these compounds, and these will be reviewed as a prelude to a discussion of the bonding in $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}\cdot CHCl_3$.

It is useful in this context to consider the metal atom and its associated ligands as a Lewis acid which achieves an octet (or inert gas configuration) by complexation to a boron hydride ligand. In a formal sense, the partially complexed metal is analogous in its interaction with the boron hydride species to simple Lewis acids such as H^+, BR_2^+, or BR^{2+}, depending upon the number of electron pairs needed. Reference will be made to the formal construction of various boron hydride species from simple well-characterized compounds such as B_2H_6, B_4H_{10}, B_6H_{10}, and $B_{10}H_{14}$, by addition or elimination of H^+ or BH_2^+. Thus BH_4^- is generated from diborane and ammonia (loss of BH_2^+)[42] and $B_3H_8^-$, from B_4H_{10} and ammonia (loss of BH_2^+);[43] $B_6H_{11}^+$ is postulated to be the stable adduct of H^+ with B_6H_{10};[44] $B_{10}H_{12}^{2-}$ is the product of NaH and $B_{10}H_{14}$ (loss of two protons);[45] and $B_{10}H_{10}^{2-}$ is produced when triethylamine is allowed to react with $B_{10}H_{14}$

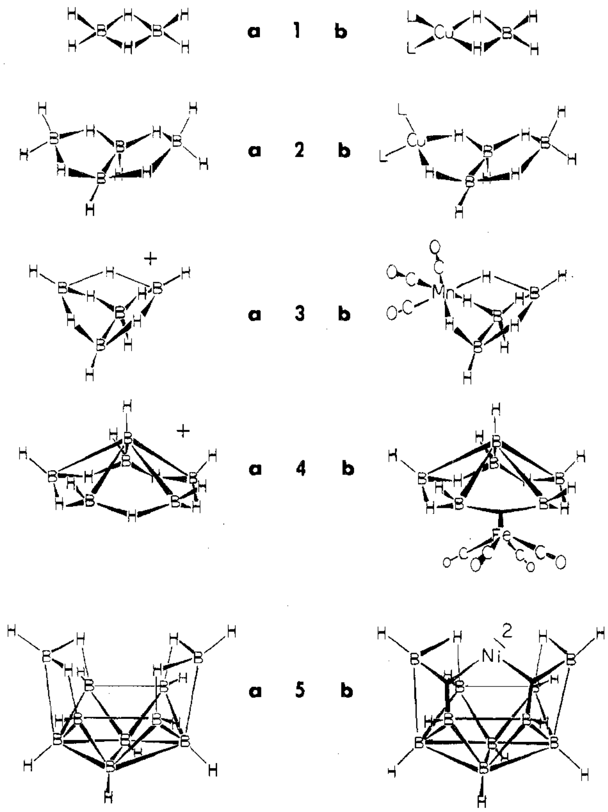


Figure 4. A comparison of several boron hydrides (a) with their structurally related *nido*-metalloboranes (b).

(loss of hydrogen gas and two H^+).[4] Analogy to chemistry of this kind has already been employed to rationalize the apparent difference between the mode of bonding of bis(triphenylphosphine)copper(I) with BH_4^-, $B_3H_8^-$, and $B_5H_8^-$ [7c,46] and will be used in the following more general discussion.

A correlation can be drawn between the known *nido*-metalloborane structures and those of related boron hydride compounds. In many instances it appears that formation of the metalloborane enables the hydroborate fragment to obtain stability inherent in a related higher boron hydride. Coordination of BH_4^- to bis(triphenylphosphine)copper(I) to form $[(C_6H_5)_3P]_2Cu(BH_4)$ in which there are two three-center Cu–H–B bridge bonds[2a] is a reaction electronically similar to that of BH_2^+ with BH_4^- to form diborane (structures **1a**, **b**; Figure 4). Various structural analogs containing bidentate BH_4^- groups exist.[47] Exceptions include $Zr(BH_4)_4$,[48] $Hf(BH_4)_4$,[49] and $U(BH_4)_4$,[50] molecules which are less stable thermally and which incorporate triply bridging hydroborate ligands. The boron hydride structural analog of these compounds would be the not completely unreasonable triply bridged $B_2H_5^+$ cation.

The octahydrotriborate ion, the asymmetrical cleavage product of B_4H_{10}, coordinates in a manner formally analogous to the reverse of the degradation reaction, assuming that the metal center requires two electron pairs as does the BR_2^+ cation. Examples include the structurally characterized compounds $[(C_6H_5)_3P]_2Cu(B_3H_8)$[2b] and $[(OC)_4Cr(B_3H_8)]^-$,[32] as well as other complexes of this anion (structures **2a**, **b**; Figure 4).[7a,b] The complex $HMn_3(CO)_{10}(BH_3)_2$,[51] an intriguing molecule that was the first metalloborane to be characterized by X-ray diffraction, may be viewed as incorporating the $B_2H_6^{2-}$ unit, a further degradation product of B_4H_{10} (loss of two BH_2^+ ions).[52] Recently, a novel tridentate mode of coordination was proposed for the $B_3H_8^-$ anion in the complex $Mn(CO)_3(B_3H_8)$,[53] involving the usual two three-center M–H–B bridge bonds and an additional such interaction with the B–H bond of the unique boron atom. Such a structure is reminiscent of that proposed for the adduct $B_4H_8\cdot C_2H_4$, if the bridging ethylene group were replaced by a proton (structures **3a**, **b**; Figure 4).[54] The $B_4H_9^+$ cation may be the unstable product of the reaction of B_4H_{10} with HCl.[55] Once again we note the analogy: $B_3H_8^- + BH^{2+} \approx B_3H_8^- + Mn(CO)_3^+$.

The B_6H_{10} molecule contains a single B–B bond in the basal plane. This compound is proposed to form a stable adduct, $B_6H_{11}^+$, in which the proton ostensibly bridges that basal bond.[44] The B_6H_{10} molecule has recently been found to coordinate to transition metals.[20,24] Coordination occurs at the basal B–B bond *via* a two-electron three-center B–M–B interaction which is similar to the proposed B–H–B bond in the $B_6H_{11}^+$ ion (structures **4a**, **b**; Figure 4). Metal complexes requiring a single pair of electrons coordinate to one B_6H_{10} molecule, *e.g.*, $Fe(CO)_4(B_6H_{10})$,[24] while those requiring two electron pairs bind two hexaborane(10) ligands, *e.g.*, *trans*-$Cl_2Pt(B_6H_{10})_2$.[20,24b] The crystal structure of the latter compound corroborates the existence of three-center B–M–B bonding.

The $B_{10}H_{12}^{2-}$ anion, obtained by double deprotonation of $B_{10}H_{14}$ at bridging positions of the open B_6 face, forms complexes with transition metals requiring four electrons (structures **5a**, **b**; Figure 4).[25] The structural determination of $[(CH_3)_4N]_2Ni(B_{10}H_{12})_2$ revealed the presence of two three-center B–M–B bonds per boron hydride ligand,[21] and it is reasonable to assume that the edges involved in this interaction are those deprotonated when $B_{10}H_{14}$ is converted to $B_{10}H_{12}^{2-}$.

In the light of the foregoing discussion, we shall now attempt to understand the bonding in $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}\cdot CHCl_3$. The task here is more difficult, since no direct analog such as $B_{10}H_{12}$ or $B_{12}H_{14}$ exists among the known higher boron hydrides, let alone one in which the D_{4d} B_{10} cage remains intact. The choice of apical edges for coordination of the bis(triphenylphosphine)copper(I) moiety, however, can be rationalized by reference to known chemistry, namely, the reaction of $B_{10}H_{14}$ with triethylamine to form the $B_{10}H_{10}^{2-}$ ion. A possible mechanism for this reaction is outlined in Figure 5, in which collapse of the boron framework in the $B_{10}H_{12}L_2$ molecule to the closed cage of the $B_{10}H_{10}^{2-}$ ion may be followed. The reverse process would involve proton attack at apical edges of the polyhedral $B_{10}H_{10}^{2-}$ cage, and coordination of bis(triphenylphosphine)copper(I) to these edges seems reasonable.

As discussed previously, the geometry of the five membered rings formed by copper and the apical and equatorial boron and hydrogen atoms does not permit a definitive evaluation of the relative contributions of M–H and M–B interactions. Continuing our analogy between the species $[(C_6H_5)_3P]_2Cu^+$ and BR_2^+ (or two protons), the existence of the covalent compounds $B_{10}H_{12}$ (or $B_{12}H_{14}$) might be predicted. The great thermodynamic and kinetic stability of the $B_{10}H_{10}^{2-}$ ion,[56] however, could make their syntheses difficult, *viz.*, the known inability to convert the $B_{10}H_{10}^{2-}$ anion to neutral $B_{10}H_{12}$ in 3 *M* HCl.[18]

Finally we turn our attention briefly to the compounds $[(C_6H_5)_3P]_2CuX$, where $X^- = B_5H_8^-$, $B_6H_9^-$, or $B_{10}H_{13}^-$. The complex with $B_6H_9^-$, an anion that can formally be viewed as a doubly deprotonated $B_6H_{11}^+$ cation, could incorporate the $[(C_6H_5)_3P]_2Cu^+$ unit along the two available basal edges (possibly nonadjacent, as in the $[(CH_3)_4N]_2Ni(B_{10}H_{12})_2$ structure)[21], with the formation of two three-center B–Cu–B bonds. Interactions of this kind have in fact been suggested for this complex.[7c] Here, as previously, we have assumed the $[(C_6H_5)_3P]_2Cu^+$ unit to require four electrons. The possible modes of attachment of bis(triphenylphosphine)copper(I) to

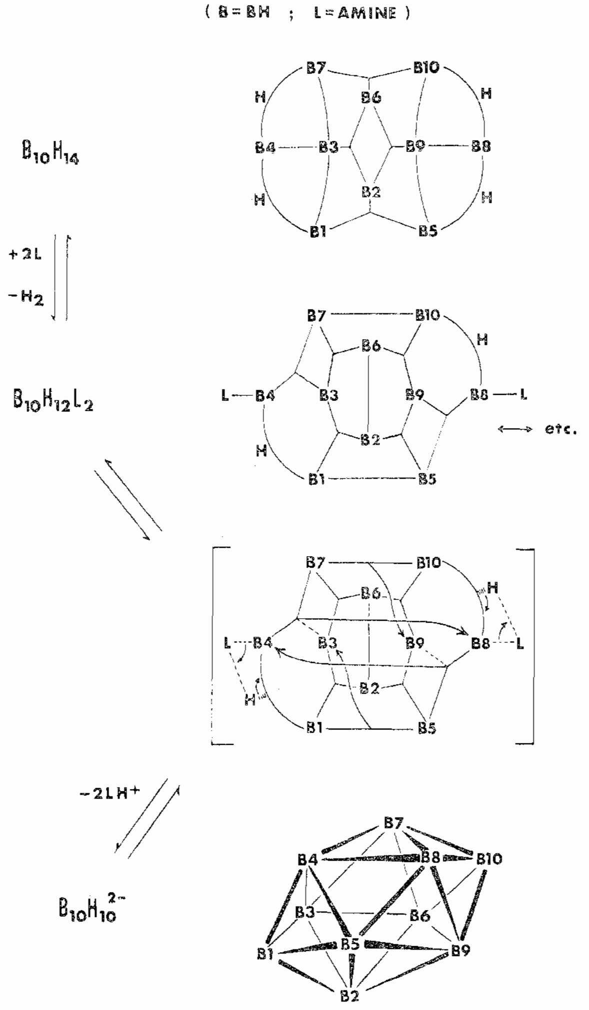


Figure 5. A feasible partial mechanism for the reaction of $B_{10}H_{14}$ with amine to form the $B_{10}H_{10}^{2-}$ ion based upon the discussion in Chapter 5 of ref 3.

the other two anions are more difficult to predict, since it is not obvious how they would supply four electrons without the involvement of Cu–H–B bridge bonds. As pointed out by Brice and Shore,[7c] insertion of dimethylboryl[57] into the unique basal B–B bond of octahydropentaborate(1–) suggests that bis(triphenylphosphine)copper(I) might behave similarly. The resultant structure would supply copper with only 16 electrons, however (*cf.* the electron-deficient boron in μ-dimethylboryl-pentaborane(9)[57]), for which there is some precedence in copper(I) chemistry,[37,58] but not yet in copper(I) hydroborate compounds. X-Ray crystallographic studies of these $[(C_6H_5)_3P]_2CuX$ complexes are clearly needed.

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Registry No. $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}\cdot CHCl_3$, 54020-27-8; tris(triphenylphosphine)copper(I) chloride, 15709-76-9.

Supplementary Material Available. Tables Ia and VI–VIII, showing positional and thermal parameters for phenyl hydrogens, rms amplitudes of thermal vibration, and structure factor amplitudes, and Table IX, showing full details of the final refinement of the $[(C_6H_5)_3P]_2Cu(BH_4)$ structure, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $5.00 for photocopy or $2.00 for microfiche, referring to code number AIC40590O.

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Electrolytic Reduction of *B*-Oxy Derivatives of 2,3-Dicarba-*closo*-undecaborane(11)

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Although the electrochemical reduction of 4,7-$(OH)_2$-2,3-$(CH_3)_2$-2,3-$C_2B_9H_7$ is a one-electron irreversible process, the reduction of the bis(oxy) derivatives 4,7-(ORO)-2,3-$(CH_3)_2$-2,3-$C_2B_9H_7$, R^1 = 1,2-ethanediyl, 1,2-phenyldiyl, or 1,3-dimethyl-1,3-propanediyl, consists of two one-electron wave reductions. The first electron reduction step is electrochemically reversible and produces a stable radical anion, which can be detected by electron spin resonance spectroscopy. Cyclic voltammetry and esr data indicate the addition of a second electron produces an unstable dianion species. A chemical reaction is associated with the addition of the second electron, which may involve an intramolecular rearrangement of the carborane dianion. The closo bis(oxy) derivatives, 4,7-(ORO)-2,3-$(CH_3)_2$-2,3-$C_2B_9H_7$, are regenerated by oxidation of the proposed dianion intermediates.

Introduction

The general reaction sequence involving the chemical reduction of a carborane followed by complexation with a transition metal to produce a monometallocarborane has led to the development of the polyhedral expansion reactions.[2a] The polyhedral expansion reaction has been extended to the metallocarboranes and is now an established procedure for producing bimetallocarboranes.[2b] The latter reaction is formally viewed as a M(III) → M(II) reduction followed by an additional two-electron reduction to form an anionic *nido*-metallocarborane species.[2b] The two-electron chemical reduction of the carboranes and the metallocarboranes has served as the basis for the polyhedral expansion reaction.

For the icosahedral carborane series, $B_{10}C_2H_{12}$, the reduction is accomplished by reaction with 2 equiv of an alkali metal[3–5] or by electrochemical methods.[6,7] The electrochemical reduction consists of a single two-electron irreversible process assuming the icosahedral carborane has no polarographically active substituents.[3] This reduction yields the dodecahydrodicarbadodecaborate(2−), $C_2B_{10}H_{12}{}^{2-}$, which then protonates to yield a stable tridecadicarba-*nido*-dodecaborate(1−), $C_2B_{10}H_{13}{}^{-}$, ion. Molecular orbital studies indicate retention of the cage structure for the dianion.[8] The structure of the *C,C′*-dimethyl-substituted *nido*-carborane anion has been published.[9] Prior publications on the electrochemical reductions of the carboranes have been concerned only with the icosahedral series.

This paper presents both electrochemical and spectroscopic data on the nature of the oxidation–reduction reactions of the octadecahedral carborane 2,3-$(CH_3)_2$-2,3-$C_2B_9H_{11}$ and its *B*-oxy derivatives. The electrochemical behavior of the octadecahedral derivatives is distinctly different from that described for the icosahedral carboranes.[6,7]

Experimental Section

Physical Measurements. The polarograms were obtained with a Heathbuilt Model EUA-19 dropping-mercury electrode. The constant-potential electrolyses were performed using a Wenking Electronic potentiostat, Model 68 FR 0.5, and a cell similar to the design described by Headridge.[10] The cyclic voltammograms were obtained with an instrument designed and built by Professor R. Reed[11] and by use of a cell described in the literature.[12] Esr spectra were recorded on a Varian Associates Model E-12 spectrometer operating on the X-band. Assignment of the splitting factor values were based on simultaneous calibration using the nmr signal of water.

Reagents. Acetonitrile was Spectrograde and distilled from calcium hydride prior to use. Monoglyme and tetrahydrofuran were distilled from potassium–benzophenone prior to use. Tetrabutylammonium perchlorate and tetraethylammonium bromide were obtained from Eastman Kodak. The tetrabutylammonium perchlorate was dried at 60° for 24 hr and the tetraethylammonium bromide was recrystallized from ethanol and dried prior to use.