

appear to have a measurable effect on the relative intensities or energies of the two prominent \bar{z} -polarized features. The relative intensity of the lower-energy feature is less pronounced in complexes which have enhanced p_z π -bonding capabilities of the in-plane ligands. Both observations are consistent with a $4p_z \leftarrow 1s$ assignment to the lower-energy feature. Enhanced intensity of this feature results from less ligand interaction and, thus, more purely atomic Cu p character in the p_z final state.

For polarization in the ligand plane, the X-ray absorption edge is characterized by broad or split continuum resonance transitions at energies higher than those observed for the $\bar{z}||\bar{e}$ features. The energies of the principal maxima are influenced largely by the Cu-ligand bond distance (r) along the direction of polarization. Consistent with theoretical predictions for true continuum shape resonances, these energies are related inversely to r , which indicate delocalized final states much more sensitive to the in-plane Cu-ligand distances than the more localized $\bar{z}||\bar{e}$ final states.

The single-electron multiple-scattered wave X α method has proven successful in reproducing the qualitative features in the dichroic experimental edge spectra, including both the prominent $\bar{z}||\bar{e}$ features and the shifts in the $\bar{z} \perp \bar{e}$ principal maxima observed in response to Cu-ligand bond distance changes. The errors in

the energies and intensities of calculated transitions reflect the limitations of the muffin-tin model in treating highly anisotropic molecular potentials. There is, however, no indication that multielectron transitions are required to interpret any of the prominent edge features. An extension of this work to take into account the full nonspherical corrections to the molecular potential and to include more distant scatterers in the unit cell is planned.

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η^1 -Benzene Coordination: The Synthesis and X-ray Crystal Structure of a Novel Silver Salt of the Weakly Coordinating Carborane Anion B₁₁CH₁₂⁻

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Abstract: The silver salt of B₁₁CH₁₂⁻ has been synthesized and crystallized from benzene and its X-ray crystal structure determined. Crystal data for AgB₁₁CH₁₂·2C₆H₆: orthorhombic, space group *Pb*2₁*a*, *Z* = 4, *a* = 10.211 (3) Å, *b* = 20.806 (3) Å, *c* = 9.146 (1) Å; $\rho_{\text{calcd}} = 1.392 \text{ g/cm}^3$, $\rho_{\text{obsd}} = 1.39 \text{ g/cm}^3$. Diffraction data were collected by the θ - 2θ scan method. A total of 2010 reflections were used in the final structure determination; final discrepancy indices are $R_1 = 0.047$ and $R_2 = 0.059$. The structure reveals that two carborane anions are associated with each silver ion via terminal B-H bonds from the *closo*-carborane coordinated to the metal. Two molecules of benzene crystallize with the salt, one of which is coordinated to silver in a η^1 fashion with an Ag-C distance of 2.400 (7) Å, the shortest such contact ever observed. These modes of bonding support the idea that B₁₁CH₁₂⁻ is a poorer σ donor than most anionic spectator ions in common use and portend its use as a novel noncoordinating anion.

Coordination chemistry has made extensive use of "noncoordinating" anions. Their large size frequently aids the stabilization of complex cations,³ and their weak coordination allows the introduction of weak ligands⁴ or the creation of vacant sites.⁵ However, the usually noncoordinating anions of aqueous solution (ClO₄⁻, SbF₆⁻, CF₃OSO₂⁻, etc.) frequently become coordinating in low dielectric solvents,^{6,7} and the borates (BF₄⁻,

BPh₄⁻) can be too reactive, either by coordination^{7,8} or cleavage to form fluoride⁹ or phenyl⁶ containing products. A large, chemically inert anion which more nearly approaches the ideality of a truly noncoordinating anion could have wide utility in the preparative chemistry of cationic species.

Some 20 years ago a new class of counterions was synthesized.¹⁰ These were the dinegatively charged polyhedral boranes B₁₀H₁₀²⁻, B₁₂H₁₂²⁻, and their halogenated analogues. These species exhibit remarkable chemical and thermal stability. To date, however, there has been very little exploration of their possible roles as

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gegenions for complex cations. They have been usefully exploited to introduce acetonitrile ligands into the coordination sphere of nickel and palladium and stabilize their cationic complexes.¹¹

Our interest in weakly coordinating anions and in synthetic routes to coordinatively unsaturated complexes has led us to begin an investigation of the uninegative carborane anion $B_{11}CH_{12}^-$. It has a number of properties which give it great promise as a noncoordinating anion. Its large size and near spherical shape may stabilize complex cations or prevent its ligation to hindered cations. Finally, its pseudo-icosahedral structure is a representative of one of the most thermodynamically stable groups of *closo*-carboranes and this confers an attractive chemical inertness upon the anion.

We have prepared the silver salt of $B_{11}CH_{12}^-$ in anticipation of using it as a metathesis reagent for introducing this anion to complexes via metal halides. Preliminary results show that it can be used this way and suggest that $B_{11}CH_{12}^-$ is more weakly coordinating than any other anion in common use.¹² In this paper we report the synthesis and crystal structure of the silver salt as isolated from benzene in which it has excellent solubility. An unusual, essentially η^1 mode of benzene coordination is observed which may reflect the ionic character of the silver carborane bonding.

Experimental Section

All reagents were used as commercially available. Decaborane was obtained from Dexsil Chemical Co. **CAUTION:** Decaborane is a cumulative poison which can be inhaled or absorbed through the skin. It may undergo violent oxidation with air at high temperature or form shock-sensitive mixtures with halogenated hydrocarbons. $CsB_{11}CH_{12}$ was prepared by slight modifications of published procedures.^{13,14} All intermediates were identified by comparison of their infrared spectra to those in the literature.

$B_{10}H_{12}CN(CH_3)_3$ was synthesized by the published procedure¹⁴ except that the intermediate $B_{10}H_{12}CNH_3$ was not isolated. The product was recrystallized from CH_3CN to give $B_{10}H_{12}CN(CH_3)_3$ in 60% yield (from decaborane) as sparkling white crystals.

$CsB_{10}CH_{13}$ was made as previously described¹⁴ and recrystallized from water to give white crystals in 84% yield.

$CsB_{11}CH_{12}$. Triethylamine-borane (80 mL) containing 20 g (75 mmol) of the above cesium salt was heated under nitrogen to 170–180 °C for 15 h. Excess Et_3NBH_3 was recovered by vacuum distillation and the residue vacuum dried. The crude $CsB_{11}CH_{12}$ was recrystallized twice from hot water to give 15.1 g (73%) of a white powder.

$AgB_{11}CH_{12}$. Five grams (18 mmol) of $CsB_{11}CH_{12}$ was dissolved in 120 mL of water and the mixture cooled to 0 °C. Silver nitrate (3.1 g, 18 mmol) was dissolved in 10 mL of water and the mixture cooled. In the dark, the two solutions were mixed and immediately filtered through a coarse fritted funnel. The resulting precipitate was vacuum dried at room temperature with minimum exposure to light to give a fine tan powder. This was recrystallized under normal benchtop conditions from 40 °C benzene to yield clear, colorless crystals. Vacuum drying resulted in 3.7 g (82%) of a white solid. Microanalysis was performed by Canadian Microanalytical Service, Vancouver, B.C. Anal. Calcd for $AgB_{11}CH_{12}$: C, 4.79, H, 4.82; Ag, 42.99. Found: C, 4.97; H, 5.00; Ag, 42.60. The dry silver salt exhibits an infrared spectrum (KBr disc) almost identical with that of the cesium salt: 3027 (w), 2550 (s, br), 1090, 1065, 1025 (m), 715 (s).

X-ray Structure Determination. Crystals of $AgB_{11}CH_{12} \cdot 2C_6H_6$ were grown from a mixture of benzene and hexane inside an inert atmosphere glovebox. Crystals handled in the usual way changed from transparent to white over short periods of time with a concomitant loss of crystallinity. We presume that this is the result of loss of benzene from the lattice. Several different attempts to protect the crystal were unsuccessful, although these preliminary examinations did establish a four-molecule orthorhombic unit cell. Satisfactory retention of crystallinity was finally achieved by wedging a rather large crystal (approximate dimensions of $0.65 \times 0.65 \times 1.1$ mm) into a thin-walled glass capillary along with a drop of mother liquor. Most of the mother liquor was separated from the crystal, but a small amount did adhere to the crystalline specimen. Intensity data and final cell constants were measured by using this sample

Table I. Fractional Atomic Coordinates in the Unit Cell of $AgB_{11}CH_{12} \cdot 2C_6H_6^a$

atom	x	y	z
Ag	0.63388 (4)	0.5045	0.37940 (6)
B(1)	0.3312 (6)	0.4378 (3)	0.8014 (6)
B(2)	0.3851 (6)	0.3905 (3)	0.6489 (7)
B(3)	0.4309 (7)	0.3691 (3)	0.8321 (7)
B(4)	0.4595 (6)	0.4406 (4)	0.9336 (6)
B(5)	0.3893 (5)	0.4761 (3)	0.6409 (6)
B(6)	0.4329 (5)	0.5080 (4)	0.8160 (6)
B(7)	0.6495 (5)	0.4349 (3)	0.7022 (6)
B(8)	0.5495 (4)	0.5038 (3)	0.6736 (5)
B(9)	0.5225 (6)	0.43117 (29)	0.5701 (6)
B(10)	0.5489 (6)	0.3649 (3)	0.6879 (7)
B(11)	0.5947 (6)	0.4796 (3)	0.8517 (6)
C(1)	0.5848 (6)	0.39869 (29)	0.8526 (6)
C(2)	0.4395 (11)	0.5799 (4)	0.2599 (11)
C(3)	0.5666 (11)	0.5874 (4)	0.2131 (7)
C(4)	0.6443 (7)	0.6339 (5)	0.2749 (11)
C(5)	0.5918 (10)	0.6737 (5)	0.3825 (9)
C(6)	0.4689 (9)	0.6666 (4)	0.4288 (9)
C(7)	0.3941 (8)	0.6204 (5)	0.3672 (10)
C(8)	0.4503 (9)	0.7966 (4)	0.7767 (9)
C(9)	0.5801 (9)	0.7900 (4)	0.7370 (8)
C(10)	0.6502 (7)	0.7389 (5)	0.7886 (9)
C(11)	0.5929 (9)	0.6958 (4)	0.8790 (8)
C(12)	0.4644 (8)	0.7035 (4)	0.9220 (8)
C(13)	0.3943 (7)	0.7537 (5)	0.8706 (9)

^a The estimated standard deviations of the least significant digits are given in parentheses.

on a CAD4 automatic diffractometer. All measurements were made with use of graphite-monochromated Mo $K\alpha$ radiation (λ 0.71069 Å). Least-squares refinement of the setting angles of 25 reflections with $2\theta < 29.78^\circ$ led to the cell constants $a = 10.211$ (3) Å, $b = 20.806$ (3) Å, and $c = 9.146$ (1) Å. For a cell content of $AgCB_{11}H_{12} \cdot 2C_6H_6$ and $Z = 4$, the calculated density was 1.392 g/cm³; the experimental density was 1.39 g/cm³.

Intensity data were measured with use of graphite-monochromated Mo $K\alpha$ radiation and θ - 2θ scans; the scan rate was chosen after a prescan of each reflection. Three standard reflections were measured after every 1 h of exposure time to monitor the stability of the crystal. A small decline in intensities was observed (4%). The decrease in intensity was corrected by using the program CHORT.¹⁵ An empirical absorption correction was applied ($\mu = 1.02$ mm⁻¹ Mo $K\alpha$). A total of 2010 reflections having $(\sin \theta)/\lambda < 0.649$ Å⁻¹ and $F_o > 3\sigma(F_o)$ were retained as observed after correction for Lorentz and polarization factors. These data were used in the solution and refinement of the structure.

The structure was solved in the space group $Pb2_1a$ ¹⁶ by the Patterson method and the direct methods program DIRDIF.¹⁷ The Patterson map was used to obtain the coordinates of the silver atom, one cycle of DIRDIF located the remaining heavy atoms. After a few cycles of least-squares refinement,¹⁸ the position of the carbon atom in the carborane anion could be assigned from the interatomic distances (C-B = 1.701 (11) Å, B-B = 1.780 (13) Å) and a difference Fourier map showed the position of some hydrogen atoms. All hydrogen atoms were included in subsequent cycles of least-squares refinement as fixed idealized contributors (C-H = 0.95 Å and B-H = 1.04 Å, $B(H) = B(X) + 1.0$ Å²). Final cycles of full-matrix least-squares refinement were carried to convergence with anisotropic temperature factors for all heavy atoms. The final discrepancy indices were $R_1 = 0.047$ and $R_2 = 0.05$ ¹⁹ with an error of

(15) The program CHORT is part of the VAXSDP package and was written by B. A. Frenz and associates.

(16) The group $Pb2_1a$ is a non-standard setting of $Pca2_1$ (Hahn, T., Ed. "International Tables for Crystallography"; D. Reidel Publishing Co.; Dordrecht, Holland, 1983; Vol. A).

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(18) Programs used in this study included local modifications of Jacobson's ORTEP2. Atomic form factors were from the following: Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321–323. Real and imaginary corrections for anomalous dispersion in the form factor of the silver atom were from the following: Cromer, D. T.; Liberman, D. J. *J. Chem. Phys.* **1970**, *53*, 1891–1898. Scattering factors for hydrogen were from the following: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *Ibid.* **1965**, *42*, 3175–3187. All programs were run on a VAX 11/730.

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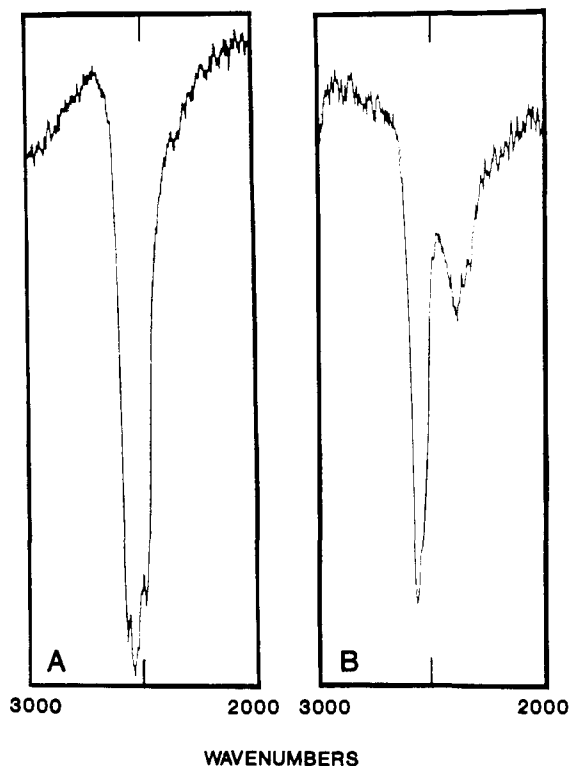


Figure 1. Infrared B-H stretching frequencies for $\text{AgB}_{11}\text{CH}_{12}$: (A) KBr disc, (B) benzene solution.

fit of 2.23. There were no significant features on the final electron density difference map; the highest peak was $0.33 \text{ e}/\text{\AA}^3$.

Final values for all refined atomic coordinates are listed in Table I. Anisotropic thermal parameters (\AA^2) are listed in Table A of the supplementary material. The atomic coordinates and the isotropic thermal parameters of the fixed hydrogen atoms are listed in Table B of the supplementary material. Bond angles not mentioned in the text are listed in Table C of the supplementary material.

Results and Discussion

Synthesis and Properties. The icosahedral borane $\text{B}_{12}\text{H}_{12}^{2-}$ and the isostructural carborane $\text{B}_{10}\text{C}_2\text{H}_{12}$ have received much attention due to their unusual stability and the scope of their derivative chemistry.²⁰ The link in this series, $\text{B}_{11}\text{CH}_{12}^-$, exhibits similar chemical properties to its analogues.¹⁴ While this carborane anion has been synthesized previously, its utility outside of carborane chemistry has not been investigated to any great extent. We have prepared the silver salt for use in metathesis reactions. Although we have found it most convenient to prepare this salt in aqueous solution from the cesium salt, rapid isolation from the reaction mixture appears to be critical. Wet $\text{AgB}_{11}\text{CH}_{12}$ is prone to discoloration and decomposition upon standing or heating. Fortunately, as with other silver salts of strong acids, it has good solubility in benzene. This has proved to be a suitable solvent for crystallization and for reactivity studies which will be reported in subsequent publications.¹²

The silver carborane crystallizes from benzene as clear, brittle crystals containing two molecules of the solvent. Removal from the mother liquor results in rapid loss of solvent and crystallinity, yielding white, amorphous $\text{AgB}_{11}\text{CH}_{12}$. This analytically pure dry material appears to be indefinitely stable in air when stored in the dark.

The solid-state infrared spectrum of $\text{AgB}_{11}\text{CH}_{12}$ (after recrystallization from benzene and vacuum drying) is virtually identical with that of the cesium salt. The strong broad band at 2550 cm^{-1} is assigned to the family of terminal B-H stretching modes (Figure 1A). However, the solution spectrum (benzene) shows a new B-H band at lower frequency (2380 cm^{-1}), indicating

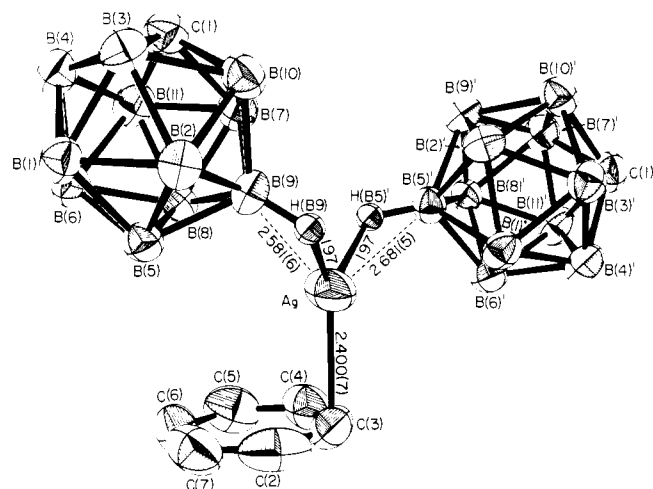


Figure 2. ORTEP drawing of the coordination group of the silver ion in $\text{AgB}_{11}\text{CH}_{12}\cdot 2\text{C}_6\text{H}_6$. The atom-labeling scheme is shown. Primed atoms are related to unprimed by the a glide symmetry operator.

Table II. Interatomic Distances (\AA) for $\text{AgB}_{11}\text{CH}_{12}\cdot 2\text{C}_6\text{H}_6^a$

Ag-C(2)	2.756 (9)	B(6)-B(8)	1.767 (7)
Ag-C(3)	2.400 (7)	B(6)-B(11)	1.786 (8)
Ag-C(4)	2.858 (9)	B(7)-B(8)	1.780 (8)
Ag-B(1)'	2.953 (6)	B(7)-B(9)	1.774 (8)
Ag-B(5)'	2.681 (5)	B(7)-B(10)	1.787 (9)
Ag-B(8)	2.826 (5)	B(7)-B(11)	1.745 (9)
Ag-B(9)	2.581 (6)	B(7)-C(1)	1.701 (8)
B(1)-B(2)	1.794 (8)	B(8)-B(9)	1.804 (9)
B(1)-B(3)	1.777 (9)	B(8)-B(11)	1.766 (8)
B(1)-B(4)	1.784 (9)	B(9)-B(10)	1.771 (9)
B(1)-B(5)	1.773 (8)	B(10)-C(1)	1.702 (9)
B(1)-B(6)	1.798 (9)	B(11)-C(1)	1.686 (9)
B(2)-B(3)	1.796 (9)	C(2)-C(3)	1.375 (13)
B(2)-B(5)	1.783 (9)	C(2)-C(7)	1.374 (14)
B(2)-B(9)	1.790 (8)	C(3)-C(4)	1.372 (13)
B(2)-B(10)	1.791 (9)	C(4)-C(5)	1.394 (14)
B(3)-B(4)	1.776 (10)	C(5)-C(6)	1.333 (12)
B(3)-B(10)	1.788 (9)	C(6)-C(7)	1.351 (14)
B(3)-C(1)	1.698 (9)	C(8)-C(9)	1.381 (12)
B(4)-B(6)	1.789 (10)	C(8)-C(13)	1.364 (12)
B(4)-B(11)	1.768 (9)	C(9)-C(10)	1.366 (12)
B(4)-C(1)	1.716 (9)	C(10)-C(11)	1.352 (12)
B(5)-B(6)	1.789 (8)	C(11)-C(12)	1.379 (12)
B(5)-B(8)	1.760 (7)	C(12)-C(13)	1.351 (12)
B(5)-B(9)	1.773 (8)		

^a The numbers in parentheses are the estimated standard deviations. Primes refer to atoms related to the a glide plane.

a specific B-H-Ag interaction and lower overall symmetry of the carborane anion. This is illustrated in Figure 1B. Similar splittings of the strong B-H absorption have been observed in boranes and carboranes with terminal B-H bonds coordinated to metals (vide infra).

Structure. The coordination structure of $\text{AgB}_{11}\text{CH}_{12}\cdot 2\text{C}_6\text{H}_6$ (1) and the atom numbering scheme used are shown in Figure 2. A stereoscopic view of the crystal packing (Figure 3) shows that the gross features of the structure show similarities to other known silver-arene complexes, consisting of sheets of ionic material separated by sheets of the aromatic molecules. In the present case, silver is complexed to one benzene molecule while the other appears only to fill space within the lattice. The carborane acts as a bridging ligand to give an alternating cation-anion chain which is maintained in one dimension throughout the lattice. Silver has a formal coordination number of three, bonding to two carborane anions and one benzene molecule.

Tables II and III list the individual bond distances and important bond angles. The complexed benzene ring (C(2)-C(7)) does not appear to be significantly different from the solvate (C(8)-C(13)). Some minor distortions from perfect hexagonality do occur, as is common for such complexes, but all C-C bond lengths and C-C-C bond angles are the same within three

(19) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$.

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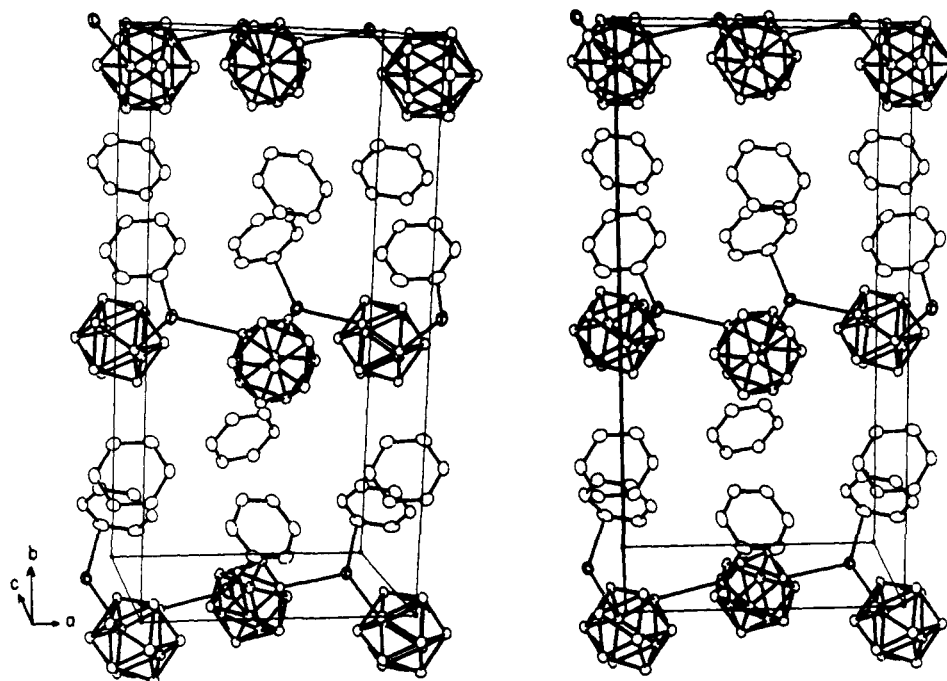


Figure 3. A stereoscopic view of the unit cell of $\text{AgB}_{11}\text{CH}_{12}\cdot 2\text{C}_6\text{H}_6$.

Table III. Interatomic Angles (deg) for $\text{AgB}_{11}\text{CH}_{12}\cdot 2\text{C}_6\text{H}_6^a$

C(2)AgC(3)	29.92 (29)	AgB(1)'B(3)'	149.0 (4)
C(2)AgB(1)'	122.45 (28)	AgB(1)'B(4)'	149.9 (4)
C(2)AgB(5)'	142.99 (27)	AgB(1)'B(5)'	63.47 (25)
C(2)AgB(8)	99.28 (27)	AgB(1)'B(6)'	93.1 (3)
C(2)AgB(9)	106.70 (27)	AgB(5)'B(1)'	80.25 (27)
C(3)AgC(4)	28.59 (29)	AgB(5)'B(2)'	101.5 (3)
C(3)AgB(1)'	100.28 (22)	AgB(5)'B(6)'	102.84 (29)
C(3)AgB(5)'	113.14 (29)	AgB(5)'B(8)'	147.6 (4)
C(3)AgB(8)	121.32 (22)	AgB(5)'B(9)'	146.8 (4)
C(3)AgB(9)	136.62 (29)	AgB(8)B(5)	97.07 (28)
C(4)AgB(1)'	103.30 (21)	AgB(8)B(6)	155.09 (27)
C(4)AgB(5)'	98.52 (19)	AgB(8)B(7)	88.24 (29)
C(4)AgB(8)	109.56 (25)	AgB(8)B(9)	63.33 (22)
C(4)AgB(9)	143.03 (22)	AgB(8)B(11)	143.1 (3)
B(1)'AgB(5)'	36.28 (16)	AgB(9)B(2)	153.7 (4)
B(1)'AgB(8)	137.63 (16)	AgB(9)B(5)	105.8 (3)
B(1)'AgB(9)	113.64 (18)	AgB(9)B(7)	96.5 (3)
B(5)'AgB(8)	111.19 (15)	AgB(9)B(8)	78.02 (26)
B(5)'AgB(9)	110.20 (19)	AgB(9)B(10)	143.6 (4)
B(8)AgB(9)	38.65 (19)	C(3)C(2)C(7)	118.1 (8)
AgC(2)C(3)	60.6 (4)	C(2)C(3)C(4)	119.9 (7)
AgC(3)C(2)	89.5 (5)	C(3)C(4)C(5)	119.1 (7)
AgC(3)C(4)	94.6 (5)	C(4)C(5)C(6)	121.4 (8)
AgC(4)C(3)	56.8 (4)	C(5)C(6)C(7)	118.6 (8)
AgB(1)'B(2)'	91.8 (3)	C(2)C(7)C(6)	122.9 (8)

^aThe numbers in parentheses are the estimated standard deviations. Primes refer to atoms related by the *a* glide plane.

standard deviations. The bond distances and angles within the carborane cage are unremarkable and are within experimental error for the "free" anion.¹²

Silver-Carborane Bonding. Metallaborane chemistry has flourished in the last two decades, and today numerous examples of B-H-M bonding have been structurally characterized.²¹ However, with the large boron clusters, few examples exist where the bridge bond is the only link between the metal and the cluster. One notable example is $\{(\text{Ph}_3\text{P})\text{AgB}_8\text{C}_2\text{H}_{11}\}_2$.²² Although the

silver is primarily part of an *arachno*-metallacarborane cage, additional interaction with two terminal B-H bonds results in dimer formation. This represents the purest example of intermolecular B-H-M bonding and is, to our knowledge, the only example of silver-hydrogen bonding that has been structurally characterized.

Such bonding in *closo*-boranes and *closo*-carboranes is also rare. Muetterties and co-workers¹⁰ found that $\text{B}_{10}\text{H}_{10}^{2-}$ and $\text{B}_{12}\text{H}_{12}^{2-}$ formed water-insoluble salts with polarizing cations (Ag^+ , Cu^+ , Hg^{2+}). It was suggested that this was due to a specific interaction of the metal with an edge or face of the borane cage. This idea was borne out by the structure of $\text{Cu}_2\text{B}_{10}\text{H}_{10}$ ²³ and $\{(\text{Ph}_3\text{P})_2\text{Cu}\}_2\text{B}_{10}\text{H}_{10}\cdot\text{CHCl}_3$.²⁴ In these compounds, copper coordinates to an "edge" of the borane cage, in effect forming a Cu-H-B-B-H chelate ring.

The present structure appears to be the first example of a *closo*-carborane with a single terminal boron-hydrogen bond complexed to a metal. The interatomic distances, 1.968 Å for Ag-H(B5)' and 1.974 Å for Ag-H(B9), are slightly smaller than those for the examples cited above. In $\{(\text{Ph}_3\text{P})\text{AgB}_8\text{C}_2\text{H}_{11}\}_2$ the Ag-H distance is 2.19 Å, while in $\{(\text{Ph}_3\text{P})_2\text{Cu}\}_2\text{B}_{10}\text{H}_{10}\cdot\text{CHCl}_3$ the closest Cu-H contact is 1.84 Å (but account must be taken for the 0.3-Å difference in ionic radius for copper). This shorter distance may reflect the lack of other good ligands around the silver atom of **1**. The M-H-B angles, 121.0° about H(B5)' and 113.6° about H(B9), are normal for unbridged M-H-B interactions.²⁵ Two such interactions exist within the same cage but with different silver ions. Thus, the carborane behaves as a bridging ligand, producing an alternating cation-anion chain. The two borons involved in the bonding are B(5), directly opposite the carbon of the icosahedron, and B(9), which is adjacent to B(5). These two borons would be expected to have the most "hydridic" B-H bonds,²⁶ and therefore are the most capable of serving as ligands.

Silver-Benzene bonding. Silver salts of strong acids have been known to form complexes with aromatics for a half-century. The gross geometric aspects of this interaction were predicted early in the 1950's by Mulliken²⁷ and by Dewar²⁸ before any structural

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(22) Colquhoun, H. M.; Greenough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1980**, 192. A similar compound with terminal B-H-M bonding, $\{(\text{Ph}_3\text{P})\text{RhB}_9\text{C}_2\text{H}_{11}\}_2$, has been structurally characterized, but in this case the dimer is also linked by a Rh-Rh bond; see: Baker, R. T.; King, R. E.; Knobler, C.; O'Con, C. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1978**, *100*, 8266.

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(26) The C-H bonds of a carborane contain the most acidic hydrogens; see ref 10.

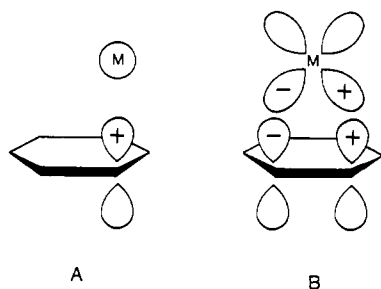


Figure 4. Bonding modes for a metal atom with a benzene ring: (A) metal acting as a σ electron acceptor; (B) metal back-donation in a π^* orbital of the ring.

results were known. Excluding a ferrocene-like structure, which has never been observed, two different positions of the metal with respect to the arene can be envisaged. First, if the metal behaves as an electron acceptor (Figure 4A), then regardless of what metal orbital or hybrid orbital is the acceptor, the metal may be expected to position itself directly above one carbon of the aromatic ring where the electron density is the highest.²⁹ However, with filled d orbitals as in the case of silver, the metal might back-donate into a π^* orbital of the arene (Figure 4B). In this case, the best overlap would occur with the metal positioned midway between two carbons of the aromatic ring.

In general, neither pure case is seen. Amma and co-workers have done extensive structural studies on a wide range of silver-arene complexes.³⁰ They found that silver nearly always coordinates to aromatic molecules in an unsymmetrical fashion, somewhere between case A and case B. But a common feature of all of these structures is a closest Ag-C distance of 2.45–2.49 Å. The next-nearest Ag-C contact varies from 2.6 to 2.9 Å. This suggests that it is more important for the arene to act as a σ donor of electron density than as a π acceptor. Corroborating evidence comes from complexes of substituted arenes where the silver is often, but not always, situated closest to the carbon with the highest electron density. The degree of back-donation and the distance to the next-nearest carbon apparently varies to accommodate crystal packing forces and the nature of the anions or other ligands

to silver. In the case of (naphthalene)tetrakis(silver perchlorate) tetrahydrate,³⁰ the σ electronic demand of the silver is apparently decreased by water ligands and the metal is better suited for back-donation. In this compound, the silver atom is positioned symmetrically between two carbon atoms of naphthalene.

In contrast, the silver ion of **1** is positioned directly above one carbon atom of the benzene ring with an unusually short Ag-C distance of 2.400 (7) Å. This is notable not only because it is the shortest silver-arene contact known but also because it is the first example of silver bound to an arene in an essentially η^1 mode. The bond distances to the next nearest carbon atoms are 2.756 (9) and 2.858 (9) Å for Ag-C(2) and Ag-C(4), respectively. We interpret this as being indicative of maximal σ -donation requirements of the silver atom. This in turn reflects the poor σ -donation properties of the carborane anion. The three-coordinate metal atom is left with a high demand for electron density and situates itself in the benzene π cloud where this is highest. This mode of silver-arene bonding is consistent with the idea of a high degree of ionic character to the silver-carborane bonding.

Conclusion

The unique observation of a short Ag-C distance and η^1 -benzene coordination in $\text{AgB}_{11}\text{CH}_{12}\cdot 2\text{C}_6\text{H}_6$ are interpreted as resulting from the poor ligation properties of the *closo*-carborane anion. It suggests that $\text{B}_{11}\text{CH}_{12}^-$ may find an important role as a non- or weakly-coordinating anion in coordination and organometallic chemistry.

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Note Added in Proof. Structurally related silver-arene bonding appears to be present in the silver triflate complex of deltaplane (see ref 31).

Supplementary Material Available: Anisotropic thermal parameters (Table A), fractional coordinates and isotropic thermal parameters for the hydrogen atoms (Table B), additional bond angles (Table C), and a listing of observed and calculated structure amplitudes ($\times 10$) (11 pages). Ordering information is given on any current masthead page.

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