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Synthesis and structural characterization of new weakly coordinating anions. Crystal structure of Ag(1-CH_3–$CB_{11}H_5X_6$) (X = H, Cl, Br, I)

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Abstract

New weakly coordinating anions 1-CH_3–$CB_{11}H_5X_6^-$ (X = Cl, Br, I) have been prepared in high yield by either *C*-methylation of hexahalocarborane anions $CB_{11}H_6X_6^-$ or direct halogenation of 1-CH_3–$CB_{11}H_{11}^-$. The lithiation of $CB_{11}H_6X_6^-$ works just as well as that of the parent anion $CB_{11}H_{12}^-$, which offers a convenient method for the preparation of *C*-alkylated carborane anions of the type 1-R–$CB_{11}H_5X_6^-$. The useful silver(I) reagents of these new anions not only showed increased solubility in various organic solvents but also demonstrated the subtlety and diversity of their solid state structures. They are all one-dimensional coordination polymers in the solid state. The coordination details are, however, unique to each structure. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Hexahalocarborane; Lithiation; Weakly coordinating anions

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1. Introduction

As a new class of weakly coordinating anions [1], monocarborane anions $CB_{11}H_6X_6^-$ (X = Cl, Br, I) have played a very important role in stabilizing coordinatively unsaturated cations such as the silylium ion (R_3Si^+) [2–4], the four-coordinate tetraphenylporphyrinatoiron(III) ion (Fe(tpp)$^+$) [5], fullerene cation (C_{76}^+) [6], hydronium ion ($H_9O_4^+$) [7], and in enhancing the reactivity of organolanthanide cations [8]. However, due to the poor solubility of these anions in less polar organic solvents such as benzene and toluene, they have limited applications. With the ultimate goal of making more bulkier, more soluble and less coordinating anions, we have explored the *C*-derivatization of $CB_{11}H_6X_6^-$. On the other hand, silver(I) salts of carborane anions are very useful halide metathesis reagents for introducing weakly coordinating anions into various kinds of compounds [1–9]. They are also of structural interest in their own right because they illustrate the subtlety and diversity of coordination chemistry when anions have comparable donor ability to solvent molecules [10]. As part of our attempt to prepare new weakly coordinating anions and to understand the systematics of silver–carborane structural chemistry, we now report the syntheses and structures of new weakly coordinating anions 1-CH_3-7,8,9,10,11,12-$CB_{11}H_5X_6^-$ (X = Cl, Br, I) as well as their silver(I) salt reagents.

2. Results and discussion

2.1. Synthesis

2.1.1. C-Derivatization of $CB_{11}H_6X_6^-$

Reaction of Li[$CB_{11}H_6X_6$] (X = Cl, Br, I) with excess ^{n}BuLi in THF gave $Li_2[CB_{11}H_5X_6]$, after addition of hexane, as a white precipitate in a quantitative yield according to ^{11}B-NMR. This dilithium salt is a very important intermediate for the preparation of *C*-substi-

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tuted derivatives. Treatment of this lithio species with freshly distilled CH_3I in THF led to the *C*-methylated product Li[$1\text{-}CH_3\text{–}CB_{11}H_5X_6$] in a good yield (Scheme 1). In principle, *C*-alkylated products of the type $1\text{-R-}CB_{11}H_5X_6^-$ could be prepared in the same manner.

2.1.2. *Halogenation of $1\text{-}CH_3\text{–}CB_{11}H_{11}^-$*

New weakly coordinating anions $1\text{-}CH_3\text{–}CB_{11}H_5X_6^-$ can also be synthesized by an alternate method. As shown in Scheme 2, direct chlorination of $1\text{-}CH_3\text{–}CB_{11}H_{11}^-$ (**1**) with Cl_2 gas in glacial acetic acid at 45°C gave **2** in an 85% yield. This reaction should be well-monitored by ^{11}B-NMR otherwise higher chlorination products would be formed [11] resulting in difficulty in the purification of the desirable hexachlorocarborane compound. Since this direct chlorination reaction involves the toxic chlorine gas which is not easily handled and such a reaction is sometimes difficult to control, another method using *N*-chlorosuccinimide (NCS) as a chlorinating reagent was developed. Treatment of **1** with excess NCS in $CHCl_2CHCl_2$ at 150°C in a sealed tube for 2 days gave $1\text{-}CH_3\text{–}CB_{11}H_5Cl_6^-$ in an 80% yield. It should be noted that NCS can introduce only two chlorine atoms onto the carborane cage to give the 7,12-dichlorocarborane anion under normal reaction conditions [12]. Reaction of **1** with an excess of liquid bromine in glacial acetic acid at 80°C for 12 h afforded **3** in an 80% yield. Treatment of **1** with an excess of ICl in dimethoxyethane (DME) at 70°C overnight produced **4** in a 70% yield.

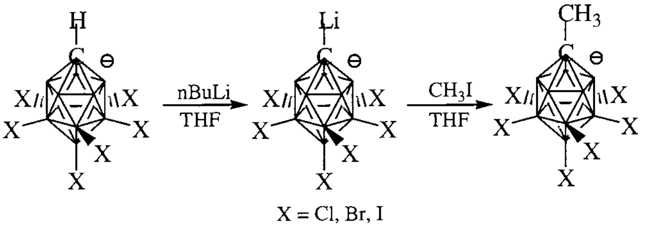
2.1.3. *Silver(I) salts*

The preparation of silver(I) salts of the anions **1**–**4** is readily achieved via $AgNO_3$ metathesis in aqueous solution as shown in Eq. (1).

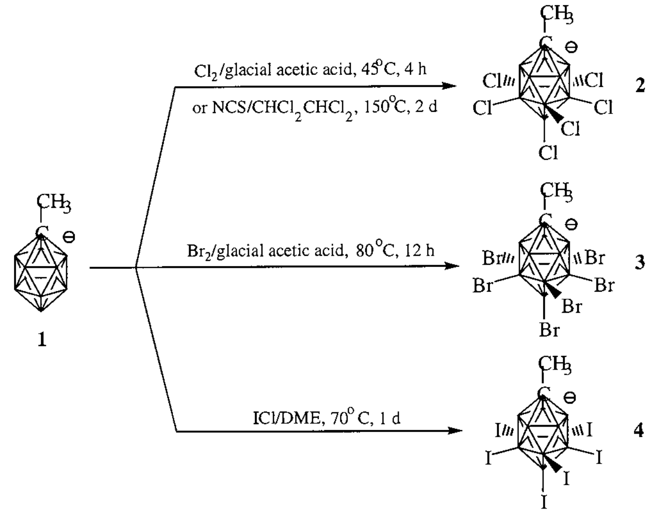
$$M[1\text{-}CH_3\text{–}CB_{11}H_5X_6] + AgNO_3 \rightarrow Ag(1\text{-}CH_3\text{–}CB_{11}H_5X_6) + MNO_3 \qquad (1)$$

$M = Li, Na; X = H, Cl, Br, I$

Only in the case of the $1\text{-}CH_3\text{–}CB_{11}H_5I_6^-$ anion, was it necessary to add a small amount of acetone for the synthesis due to poor solubility of its lithium or sodium salts in water. These silver(I) salts are light-sensitive and the color gradually turns from white to grey. Their solubility in various solvents decreases in the order Ag[**1**] > Ag[**2**] > Ag[**3**] > Ag[**4**]. In general, they are quite soluble in polar organic solvents such as acetone, acetonitrile and ethers, and insoluble in nonpolar organic solvents. The compounds Ag[**1**] and Ag[**2**] are soluble in arenes like benzene, toluene, xylene, mesitylene, and slightly soluble in CH_2Cl_2 and hot water. The compounds Ag[**3**] and Ag[**4**] are slightly soluble in arenes and insoluble in hot water.



Scheme 1.



Scheme 2.

2.2. ^{11}B-NMR

^{11}B-NMR is an extremely useful technique for the characterization of boron compounds. Fig. 1 shows the proton-coupled ^{11}B-NMR spectra of the compound $Ag(1\text{-}CH_3\text{–}CB_{11}H_5X_6)$ (X = H, Cl, Br, I) in d_6-acetone. Due to the electron-donating effect of the substituted methyl group at the C position, the chemical shift of six boron atoms at 7–12 positions in **1** become almost identical. Anions **2**–**4** all exhibit typical 1:5:5 splitting pattern which is consistent with C_{5v} symmetry and 7,8,9,10,11,12 regioselective pattern of electrophilic substitution of **1**.

2.3. *Crystal structures of (η^2-benzene)Ag[**1**], (η^1-mesitylene)Ag[**2**], Ag[**3**], and Ag[**4**]*

The coordination geometries of the silver(I) salts of anions **1**–**4** are shown in Fig. 2. Fig. 3 shows the stereoscopic views of their crystal packing. Selected bond distances are listed in Table 1. Similar to other known silver salts of carborane anions, a common feature of all four compounds is that the carborane acts as a bridging ligand to give an alternating cation–anion zigzag chain which is maintained in one-dimension throughout the lattice. The silver(I) salts of **1** and **2** are

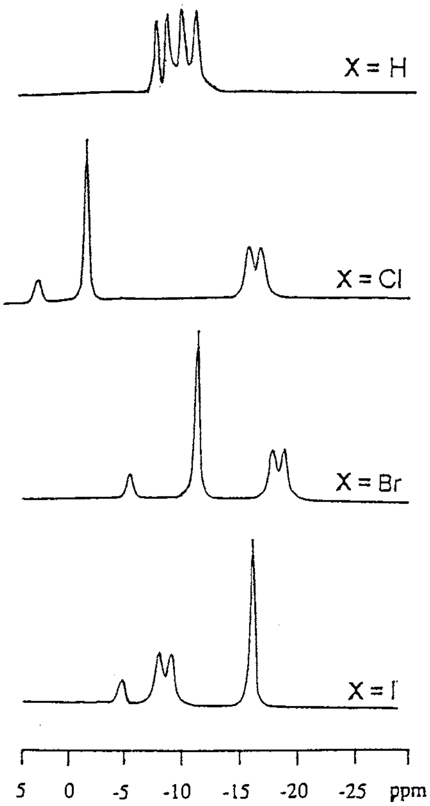


Fig. 1. ^{11}B-NMR spectra of Ag(1-CH_3–$CB_{11}H_5X_6$) in d_6-acetone.

coordinated with arene molecules, while those of **3** and **4** are unsolvated although they were crystallized from toluene and benzene, respectively. The coordination details are unique to each structure.

In (η^2-benzene)Ag[**1**], silver is bound to one benzene molecule in η^2-fashion and two carborane anions via B(8)–H(8) and B(9A)–H(9A) bonds, respectively, in a trigonal geometry (Fig. 2(a)). The formal coordination number of silver is three. In contrast, the silver atom in (η^1-benzene)Ag($CB_{11}H_{12}$), a closely related analogue to (η^2-benzene)Ag[**1**], is η^1-bound to benzene and is coordinated to two B–H bonds from the 7-position of one cage and the 12-position of the other, respectively [13]. It should be pointed out that B(12), i.e. antipodal to the cage carbon, the so-called most electron-rich site in the icosahedral cage [13,14], does not coordinate to the silver in compound (η^2-benzene)Ag[**1**], suggesting the electronic effect of the methyl group. It is surprising that the methyl substituent at the carbon position of the icosahedral cage has such a large effect on the solid state structure of the silver(I) salt of the icosahedral carborane anion, which is also reflected in the ^{11}B-NMR of (η^2-benzene)Ag[**1**]. The asymmetric η^2 fashion of benzene bonding, with Ag–C bond distances of 2.460(1) and 2.698(1) Å, is typical of many silver–arene complexes [9a,15]. The 2.671(1) Å of the Ag(1)–B(8) distance and the 2.613(1) Å of the Ag(1)–B(9A) distance are close to the values of 2.682(5) and 2.581(6) Å found in (η^1-benzene)Ag($CB_{11}H_{12}$) [13].

The solid state structure of compound (η^1-mesitylene)Ag[**2**] is shown in Fig. 2(b). The asymmetrical unit in the unit cell is [(η^1-mesitylene)Ag[**2**]]$_2$ in which each of two five coordinate silver atoms are in a distorted square pyramidal arrangement of one η^1-mesitylene and two bidentate bridging 1-CH_3–$CB_{11}H_5Cl_6^-$ anions. The Ag–C bonds are not exactly perpendicular to the hexagonal ring planes, but tilted outward by 3.2° for Ag(1) and 0.7° for Ag(2), respectively. The Ag–C bond distances of 2.495(6) and 2.422(5) Å are typical of those found in many silver–arene π complexes [9a,15]. The Ag–Cl distances range from 2.683(2) to 2.874(2) Å which are comparable to those found in (η^2-*p*-xylene)Ag($CB_{11}H_6Cl_6$) [10] or in dichloroalkane complexes of silver(I) [16–19]. The average B–Cl distance, 1.795(7) Å, is similar to the 1.789(3) Å average in (η^2-*p*-xylene)Ag($CB_{11}H_6Cl_6$). It has noted that the bond distance between the silver(I) and the most electron-rich chlorine atom (Cl(12) or Cl(32)) is the longest rather than the shortest among all four Ag–Cl distances, and the coordination geometry of the silver atom in the *C*-methylated hexachlorocarborane salt differs from that in (arene)Ag($CB_{11}H_6Cl_6$) [10].

The solid state structure of Ag[**3**] is almost identical to that of Ag($CB_{11}H_6Br_6$) [10]. As shown in Fig. 2(c), the anion **3** occupies a site of symmetry *m*, and the silver atom sits at an inversion center. The six coordinate octahedral geometry about silver is very similar to that found in the complex ion [Ag($CB_{11}H_6Br_6$)$_2$]$^-$ [5], with the metal atom bonding to three bromine atoms from each of two bridging 1-CH_3–$CB_{11}H_5Br_6^-$ ions. The bromine atom attached to B(12) is shared by two silver ions. Both the average Ag–Br distance of 2.858 (1) Å and the average B–Br distance of 1.954 (14) Å are close to those found in Ag($CB_{11}Br_6H_6$). These results imply that unlike the previous two cases, the methyl group on the hexabromocarborane cage does not affect the coordination geometry of silver atom in the silver(I) salt of the hexabromocarborane anion.

In the solid state structure of Ag[**4**] the silver atom is complexed by four iodine atoms from two bidentate bridging anions **4** in a distorted tetrahedral arrangement (Fig. 2(d)). However, in the molecular structure of the closely related analogue, Ag($CB_{11}H_6I_6$), the silver atom is coordinated to five iodine atoms in a distorted square pyramidal geometry [10]. It again shows the effect of the methyl substituent on the solid state structure of the silver(I) salt of hexaiodocarborane anion. The bond formed from I(12) to silver is the longest, as opposed to the shortest among the four Ag–I bond distances. The Ag–I distances vary from 2.798(2) to 2.872(2) Å which fall in the range 2.777(4)–3.306(5) Å for Ag($CB_{11}H_6I_6$) and diiodoalkane complexes of silver(I) [20,21]. The average B–I distance of 2.178(11) Å is very close to that of 2.179(30) Å in Ag($CB_{11}H_6I_6$).

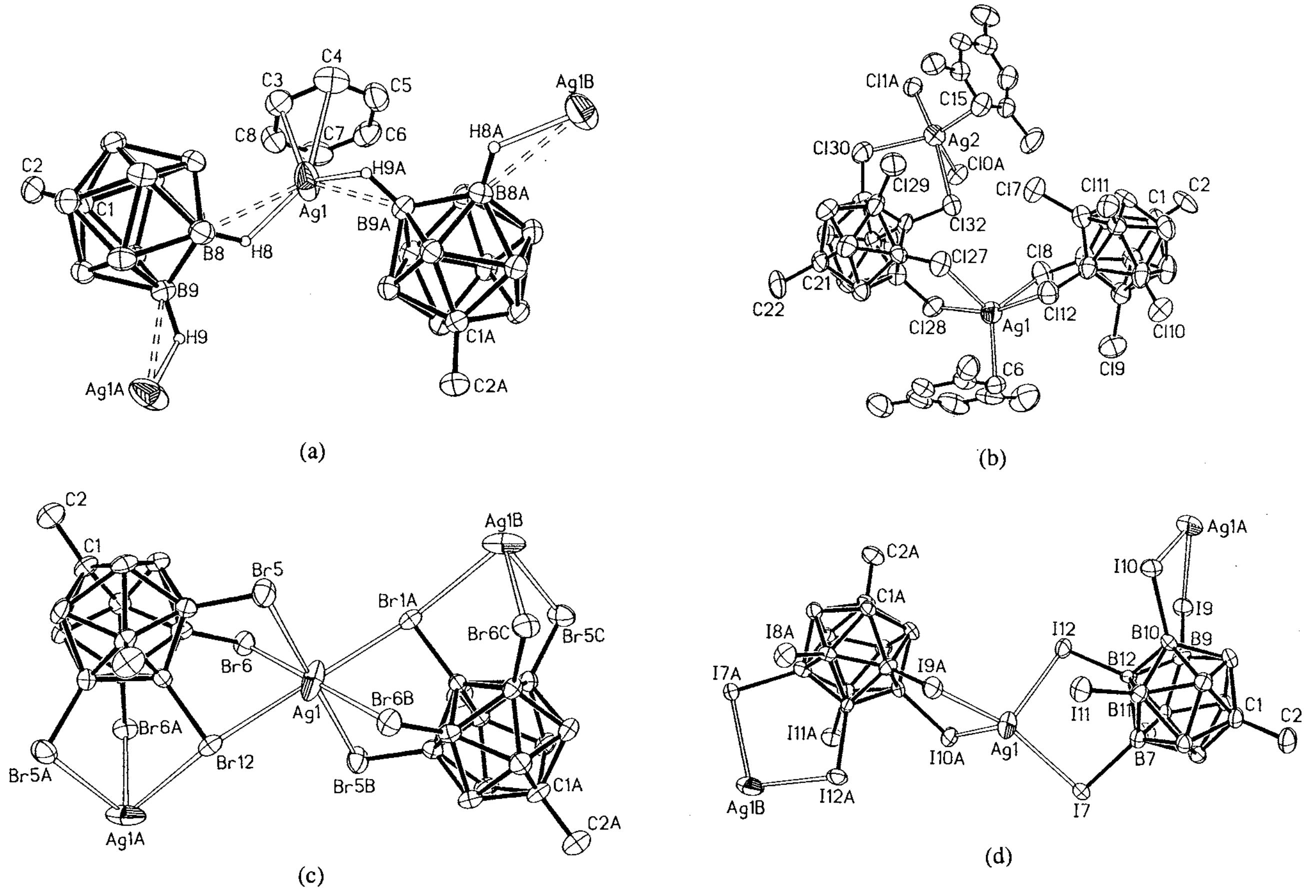


Fig. 2. Perspective view of the coordinating sphere around the silver atom in Ag[anion] showing a portion of the infinite Ag···[anion]···Ag···[anion] polymeric chain: (a) (η^2-benzene)Ag(1-CH_3–$CB_{11}H_{11}$); (b) (η^1-mesitylene)Ag(1-CH_3–$CB_{11}H_5Cl_6$); (c) Ag(1-CH_3–$CB_{11}H_5Br_6$); (d) Ag(1-CH_3–$CB_{11}H_5I_6$).

In conclusion, *C*-methylation of the icosahedral carborane anions can result in a change not only in the solubility but also in the molecular structure of silver(I) salts of carborane anions.

3. Experimental section

3.1. General procedure

All carborane anions prepared are air and moisture stable. However, some reagents used are moisture sensitive. Therefore, Schlenk and high vacuum techniques were employed whenever necessary. Compounds $CB_{11}H_{12}^-$ [22], 1-CH_3–$CB_{11}H_{11}^-$ [11], 7,8,9,10,11,12-$CB_{11},H_6X_6^-$ (X = Cl [23], Br [23], I [4]) were prepared according to the literature methods. All other chemicals were purchased from Aldrich Chemical Company and used as received unless otherwise noted. IR spectra were obtained from a KBr pellet on a Nicolet Magna 550 Fourier transform spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker 300 MHz DPX spectrometer at 300.13 and 75.47 MHz, respectively. ^{11}B-NMR spectra were recorded on a Bruker ARX-500 spectrometer at 160.46 MHz. All chemical shifts are reported in δ units with reference to the residual protons of d-solvent or external TMS (0.00 ppm) for proton and carbon chemical shifts, to external BF_3·OEt_2 (0.00 ppm) for boron chemical shifts.

3.2. Preparation of Ag(1-CH_3–$CB_{11}H_{11}$) Ag[**1**]

An aqueous solution of Cs(1-CH_3–$CB_{11}H_{11}$) (0.10 g, 0.34 mmol) was treated with a solution of $AgNO_3$ (0.088 g, 0.52 mmol) in water (2 ml) to give a white precipitate (Ag[**1**]) which was filtered off and washed with cold water. The aqueous solution was then extracted with benzene (3 × 5 ml). The benzene solutions were combined and concentrated to afford the second crop of product. Total yield of the white solid was 0.08 g (90%). X-ray quality crystals were grown from slow evaporation of a benzene solution at room temperature (r.t.). ^{1}H-NMR (d_6-acetone): δ 1.5 (s, 3H, CH_3). ^{13}C-NMR (d_6-acetone): δ 66.4 (s, cage carbon), 26.5 [q, CH_3, $^1J(^{13}C–^1H) = 134.8$ Hz]. ^{11}B-NMR (d_6-acetone): δ −9.1 (d, 5B), −10.8 (d, 6B). IR (KBr, cm^{-1}): 2961

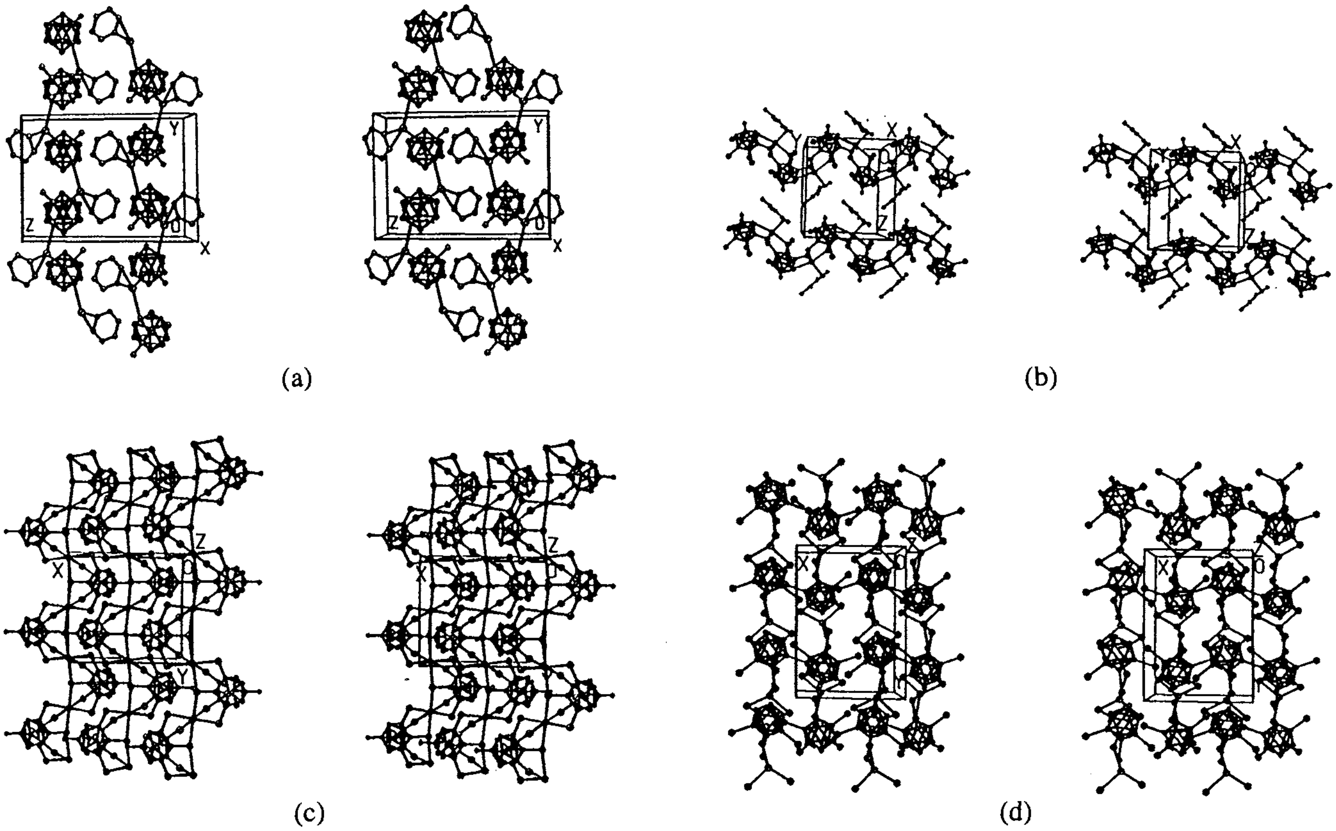


Fig. 3. Stereoscopic views of (a) (η^2-benzene)Ag(1-CH_3–$CB_{11}H_{11}$); (b) (η^1-mesitylene)Ag(1-CH_3–$CB_{11}H_5Cl_6$); (c) Ag(1-CH_3–$CB_{11}H_5Br_6$); (d) Ag(1-CH_3–$CB_{11}H_5I_6$).

(m), 2920 (m), 2850 (s), 2542 (br, s), 1463 (s), 1261 (m), 1095 (m), 1023 (m). Negative-ion MS (isotopic abundance): 155 (36), 156 (74), 157 (100), 158 (80); calc. for **1**: 155 (37), 156 (75), 157 (100), 158 (81).

3.3. Preparation of [Me_3NH][1-CH_3–$CB_{11}H_5Cl_6$] [Me_3NH][**2**]

3.3.1. Method A

To a thick-walled pyrex tube was charged with Cs[1-CH_3–$CB_{11}H_{11}$] (0.10 g, 0.34 mmol), *N*-chlorosuccinimide (0.68 g, 5.1 mmol) and 1,1,2,2-tetrachloroethane (2 ml). The tube was evacuated and sealed under liquid N_2, slowly warmed to r.t., then heated to 150°C (1°C min^{-1}), and kept at this temperature for 2 days. After slowly cooling to r.t., the tube was opened. The residue was dissolved in water and an aqueous solution of Me_3NHCl was added until no more precipitate was formed. The off-white solid was filtered off, washed thoroughly with water and then washed with a mixture of CH_2Cl_2/hexane (1:5) to give [Me_3NH][**2**] as a white solid (0.12 g, 80%). ^{1}H-NMR (d_6-acetone): δ 1.6 (s, 3H, CH_3), 3.2 [s, 9H, $(CH_3)_3NH$]. ^{13}C-NMR (d_6-acetone): δ 46.8 (s, cage carbon), 45.0 [q, $(CH_3)_3NH$, $^1J(^{13}C–^1H) = 144.8$ Hz], 25.3 [q, CH_3, $^1J(^{13}C–^1H) = 134.8$ Hz]. ^{11}B-NMR (d_6-acetone): δ −3.5 (s, 1B), −7.8 (s, 5B), −22.1 (d. 5B). IR (KBr, cm^{-1}): 3186 (m), 2953 (br, s), 2699 (s), 1475 (m), 1033 (m), 985 (m), 885 (m).

3.3.2. Method B

To a solution of Cs(1-CH_3–$CB_{11}H_{11}$) (0.50 g, 1.7 mmol) in glacial acetic acid was bubbled chlorine gas for 4 h at 45°C. The reaction was closely monitored by ^{11}B-NMR. After the reaction was completed, the acetic acid was removed under vacuum, leaving a white residue which was dissolved in 5% NaOH solution. This solution was extracted with diethyl ether (3 × 10 ml). The ether solutions were combined and solvent was removed under vacuum, leaving a brown residue. The residue was treated with aqueous solution of Me_3NHCl until no more precipitate was formed. The precipitate was filtered off and washed with water twice, affording [Me_3NH][**2**] as a white solid (0.59 g, 85%).

3.4. Preparation of Ag(1-CH_3–$CB_{11}H_5Cl_6$) Ag[**2**]

To a suspension of [Me_3NH][**2**] (0.59 g, 1.45 mmol) in water (15 ml) was added two equivalents of NaOH, and the mixture was heated at 90°C for 2 h. After removal of all trimethylamine under vacuum and neutralization of the resulting aqueous solution with 1 N HNO_3, an aqueous solution of $AgNO_3$ (0.29 g, 1.74

mmol) was added to give a milky solution with some white precipitate. The precipitate was collected by the filtration and the resulting solution was then extracted with benzene three times (20 × 3 ml). Concentration of the benzene solution afforded a white solid. Two crops of the solid were then combined and washed with cold water twice giving Ag[**2**] as a white solid (0.58 g, 85%). Recrystallization from a mixture solvents of mesitylene and acetone at r.t. gave X-ray quality colorless crystals. ^{1}H-NMR (d$_6$-acetone): δ 1.6 (s, 3H, CH_3). ^{13}C-NMR (d$_6$-acetone): δ 46.8 (s, cage carbon), 25.3 [q, CH_3, $^1J(^{13}C-^1H) = 134.8$ Hz]. ^{11}B-NMR (d$_6$-acetone): δ 3.1 (s, 1B), -1.0 (s, 5B), -15.2 (d, 5B). IR (KBr, cm^{-1}): 2937 (m), 2873 (m), 2599 (vs), 1701 (m), 1618 (s), 1451 (m), 1381 (m), 1035 (vs), 939 (s), 885 (s). Negative-ion MS (isotopic abundance): 361 (60), 362 (89), 363 (100), 364 (99), 365 (83); calc. for **2**: 361 (62), 362 (87), 363 (100), 364 (99), 365 (84).

Table 1
Selected bond distances (Å)

*Compound (η^2-benzene)Ag[**1**]*	
Ag(1)–B(8)	2.671(1)
Ag(1)–B(9A)	2.613(1)
Ag(1)–C(4)	2.698(1)
Ag(1)–C(3)	2.460(1)
*Compound (η^1-mesitylene)Ag[**2**]*	
Cl(7)–B(7)	1.757(5)
Cl(8)–B(8)	1.805(7)
Cl(9)–B(9)	1.796(7)
Cl(10)–B(10)	1.765(6)
Cl(11)–B(11)	1.798(6)
Cl(12)–B(12)	1.776(6)
Ag(1)–C(6)	2.495(6)
Ag(1)–Cl(8)	2.683(2)
Ag(1)–Cl(12)	2.874(2)
Ag(1)–Cl(27)	2.763(2)
Ag(1)–Cl(28)	2.732(2)
Cl(27)–B(27)	1.829(5)
Cl(28)–B(28)	1.806(6)
Cl(29)–B(29)	1.801(7)
Cl(30)–B(30)	1.819(6)
Cl(31)–B(31)	1.797(6)
Cl(32)–B(32)	1.802(7)
Ag(2)–C(15)	2.422(5)
Ag(2)–Cl(30)	2.729(2)
Ag(2)–Cl(32)	2.867(2)
Ag(2)–Cl(10)	2.745(2)
Ag(2)–Cl(11)	2.780(2)
*Compound Ag[**3**]*	
Br(4)–B(4)	1.951(12)
Br(5)–B(5)	1.958(9)
Br(6)–B(6)	1.952(8)
Ag(1)–Br(5)	2.852(1)
Ag(1)–Br(6)	2.733(1)
Ag(1)–Br(12)	2.990(1)
Ag(1)–Br(5A)	2.852(1)
Ag(1)–Br(6A)	2.733(1)
Ag(1)–Br(12A)	2.990(1)
*Compound Ag[**4**]*	
I(7)–B(7)	2.188(11)
I(8)–B(8)	2.184(9)
I(9)–B(9)	2.192(10)
I(10)–B(10)	2.177(10)
I(11)–B(11)	2.172(11)
I(12)–B(12)	2.160(9)
Ag(1)–I(7)	2.798(2)
Ag(1)–I(12)	2.872(2)
Ag(1)–I(9A)	2.822(2)
Ag(1)–I(10A)	2.848(2)

3.5. Preparation of Li[1-CH_3–$CB_{11}H_5Br_6$] Li[**3**]

To a clear colorless THF solution (20 ml) of Li[$CB_{11}H_6Br_6$] (0.61 g, 0.98 mmol) was slowly added ^{n}BuLi (5.0 ml of 1.6 M in *n*-hexane, 8.0 mmol) in several portions while stirring. This reaction was exothermic and was monitored by ^{11}B-NMR. After the reaction was completed, 20 ml of *n*-hexane was added. The resulting white precipitate, $Li_2(CB_{11}H_5Br_6)$, was filtered off and washed with *n*-hexane three times to remove excess ^{n}BuLi [^{11}B-NMR (THF): δ -4.0 (s, 1B), -12.55 (s, 5B), -22.50 (d, 5B)]. To the suspension of this solid in THF (50 ml) was slowly added freshly distilled CH_3I (0.30 g, 2.11 mmol), and the reaction mixture was stirred at r.t. for 6 h to give a clear pale yellow solution. After removal of THF and recrystallization of the crude product from hot water, Li[**3**] was obtained as a white crystalline solid (0.47 g, 75%). ^{1}H-NMR (d$_6$-acetone): δ 1.6 (s. 3H, CH_3). ^{11}B-NMR (d$_6$-acetone): δ -3.4 (s, 1B), -9.1 (s, 5B), -16.3 (d, 5B).

3.6. Preparation of [Me_3NH][1-CH_3–$CB_{11}H_5Br_6$] [Me_3NH][**3**]

To a solution of Cs[1-CH_3–$CB_{11}H_{11}$] (0.20 g, 0.68 mmol) in glacial acetic acid (15 ml) was added bromine (0.55 ml, 10.6 mmol), and the reaction mixture was heated at 80°C for 12 h. After removal of excess bromine and glacial acetic acid, the residue was treated with 5% NaOH solution until the pH value of the solution reached about 7. The solution was then extracted with diethyl ether (20 × 3 ml). The ether portions were combined, concentrated and treated with aqueous solution of Me_3NHCl until no more precipitate was formed. The white precipitate was filtered off, washed with deionized water and dried under vacuum giving [Me_3NH][**3**] as a white solid (0.67 g, 80%). ^{1}H-NMR (d$_6$-acetone): δ 1.6 (s, 3H, CH_3), 3.2 [s, 9H, $(CH_3)_3NH$]. ^{13}C-NMR (d$_6$-acetone): δ 53.6 (s, cage carbon), 45.0 [q, $(CH_3)_3NH$, $^1J(^{13}C-^1H) = 144.8$ Hz], 24.9 [q, CH_3, $^1J(^{13}C-^1H) = 134.8$ Hz]. ^{11}B-NMR (d$_6$-acetone): δ -0.9 (s, 1B), -6.5 (s, 5B), -13.9 (d, 5B). IR (KBr, cm^{-1}): 3159 (m), 2955 (br, s), 2698 (s), 1474 (m), 1258 (w), 985 (m), 874 (m).

3.7. Preparation of Ag(1-CH_3–$CB_{11}H_5Br_6$) Ag[3]

The compound Li[**3**] (0.40 g, 0.63 mmol) was dissolved in 40 ml of hot water, and $AgNO_3$ (0.15 g, 0.88 mmol) was dissolved in cold water (2 ml). The two solutions were mixed at r.t. The resulting grey precipitate was filtered off, washed with cold water, and dried under vacuum for 2 days affording Ag[**3**] (0.40 g, 86%). Recrystallization from toluene/acetone solution gave X-ray quality crystals. ^{1}H-NMR (d_6-acetone): δ 1.6 (s, 3H, CH_3). ^{13}C-NMR (d_6-acetone): δ 53.6 (s, cage carbon), 24.9 [q, CH_3, $^1J(^{13}C-^1H) = 134.8$ Hz]. ^{11}B-NMR (d_6-acetone): δ −5.7 (s, 1B), −11.5 (s, 5B), −18.4 (d, 5B). IR (KBr, cm^{-1}): 2994 (m), 2939 (s), 2870 (m), 2613 (vs), 1450 (m), 1009 (vs), 929 (vs), 813 (vs). Negative-ion MS (isotopic abundance): 628 (61), 629 (81), 630 (97), 631 (100), 632 (90), 633 (77); calc. for **3**: 628 (64), 629 (83), 630 (97), 631 (100), 632 (92), 633 (75).

3.8. Preparation of Li[1-CH_3–$CB_{11}H_5I_6$] Li[4]

This compound was prepared in a similar manner to Li[**3**]. Yields: 72%. ^{1}H-NMR (d_6-acetone): δ 1.6 (s. 3H, CH_3). ^{11}B-NMR (d_6-acetone): δ −8.8 (s, 1B), −11.2 (d, 5B), −18.6 (s, 5B).

3.9. Preparation of [Et_3NH][1-CH_3–$CB_{11}H_5I_6$] [Et_3NH][4]

To a solution of Li[**4**] (0.60 g, 0.65 mmol) in a mixture solvents of water and ethanol (1:1) was added excess [Et_3NH][Cl] aqueous solution. The resulting white precipitate was filtered off, washed with warm water, and dried under vacuum for 2 days affording [Et_3NH][**4**] as a white solid (0.61 g, 92%). ^{1}H-NMR (d_6-acetone): δ 3.5 [q, 6H, $(CH_3CH_2)_3NH$], 1.6 (s, 3H, CH_3), 1.4 (t, 9H, $(CH_3CH_2)_3NH$). ^{11}B-NMR (d_6-acetone): δ −8.9 (s, 1B), −11.2 (d, 5B), −18.8 (s, 5B).

3.10. Preparation of [Me_3NH][1-CH_3–$CB_{11}H_5I_6$] [Me_3NH][4]

The compound Cs[1-CH_3–$CB_{11}H_{11}$] (0.10 g, 0.34 mmol) was dissolved in dry dimethoxyethane (DME) (5 ml) and heated at 70°C with iodine monochloride (0.75 g, 4.62 mmol) for 1 day under N_2. After removal of most solvent and excess ICl, the residue was treated with 5% NaOH solution (10 ml), then extracted with diethyl ether three times (3 × 20 ml). The ether solutions were combined, concentrated and treated with an aqueous solution of Me_3NHCl until no more precipitate was formed. The precipitate was filtered off, washed with water twice and then a mixture of CH_2Cl_2/hexane (1:5) to give the compound [Me_3NH][**4**] as a pale yellow solid. (0.22 g, 70%). ^{1}H-NMR (d_6-acetone): δ 1.6 (s, 3H, CH_3), 3.2 [s, 9H, $(CH_3)_3NH$]. ^{13}C-NMR (d_6-acetone): δ 72.0 (s, cage carbon), 45.0 [q, $(CH_3)_3NH$, $^1J(^{13}C-^1H) = 144.8$ Hz], 26.4 [q, CH_3, $^1J(^{13}C-^1H) = 134.8$ Hz]. ^{11}B-NMR (d_6-acetone): δ −8.9 (s, 1B), −11.2 (d, 5B), −18.8 (s, 5B).). IR (KBr, cm^{-1}): 3165 (m), 2960 (br, s), 2697 (s), 1480 (m), 1258 (w), 990 (m), 875 (m).

3.11. Preparation of Ag(1-CH_3–$CB_{11}H_5I_6$) Ag[4]

This compound was prepared as a white solid in an analogous manner to Ag[**3**] except that the poor solubility of Li[**4**] in water required the addition of a small amount of acetone. Yield 86%. X-ray quality crystals were grown from a benzene/acetone solution at r.t. ^{1}H-NMR (d_6-acetone): δ 1.6 (s, 3H, CH_3). ^{13}C-NMR (d_6-acetone): δ 72.0 (s, cage carbon), 26.4 [q, CH_3, $^1J(^{13}C-^1H) = 134.8$ Hz]. ^{11}B-NMR (d_6-acetone): δ −4.9 (s, 1B), −8.5 (d, 5B), −15.8 (s, 5B). IR (KBr, cm^{-1}): 2925 (s), 2854 (s), 2593 (vs), 1728 (m), 1684 (m), 1383 (br), 1108 (m), 1029 (m). Negative-ion MS (isotopic abundance): 911 (35), 912 (78), 913 (100), 914 (78), 915 (31); calc. for **4**: 911 (37), 912 (75), 913 (100), 914 (81), 915 (31).

3.12. X-ray structure determination

All single crystals were sealed under N_2 and immersed in Paraton-N oil in a thin-walled glass capillary. Data were collected on a Rigaku AFC7R diffractometer for (η^1-mesitylene)Ag[**2**], and on an MSC/Rigaku RAXIS-IIC imaging plate for (η^2-benzene)Ag[**1**], Ag[**3**] and Ag[**4**] using Mo–K_α radiation from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. Absorption correction was applied by correlation of symmetry-equivalent reflections using the ABSCOR program [24], or using an empirical ψ-scan method. All four structures were solved by direct methods and subsequent Fourier difference techniques, and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares on F using the Siemens SHELXTL PLUS program package (PC version) [25]. All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinement are given in Table 2.

Tables of further details of X-ray crystal structure determinations, complete atomic coordinates, thermal parameters, bond lengths, bond angles and atom-numbering schemes for (η^2-benzene)Ag[**1**], (η^1-mesitylene)Ag[**2**], Ag[**3**] and Ag[**4**] are available from the authors.

Table 2
Crystal data and summary of data collection and refinement for (η^2-benzene)Ag[**1**], (η^1-mesitylene)Ag[**2**], Ag[**3**] and Ag[**4**]

	(η^2-Benzene)Ag[**1**]	(η^1-Mesitylene)Ag[**2**]	Ag[**3**]	Ag[**4**]
Empirical formula	$C_8H_{20}B_{11}Ag$	$C_{11}H_{20}B_{11}Cl_6Ag$	$C_2H_8B_{11}Br_6Ag$	$C_2H_8B_{11}I_6Ag$
Crystal size (mm)	0.18 × 0.26 × 0.40	0.40 × 0.40 × 0.62	0.30 × 0.38 × 0.40	0.08 × 0.38 × 0.40
Formula weight	343.0	591.75	738.3	1020.3
Crystal class	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$Pna2_1$	$Pnma$	$P2_1/n$
Unit cell dimensions				
a (Å)	9.781(1)	33.141(6)	12.602(3)	10.419(2)
b (Å)	10.709(1)	11.458(4)	11.160(2)	14.788(3)
c (Å)	14.905(1)	12.867(8)	12.471(2)	12.903(3)
β (°)	97.48(1)	90.00	90.00	92.98(3)
V (Å^3)	1548(1)	4886(4)	1754(1)	1985(1)
Z	4	8	4	4
$D_{calc.}$ (Mg m^{-3})	1.472	1.609	2.796	3.413
Radiation (λ) (Å)	Mo–Ko$_\alpha$ (0.71073)	Mo–Ko$_\alpha$ (0.71073)	Mo–Ko$_\alpha$ (0.71073)	Mo–Ko$_\alpha$ (0.71073)
2 θ range (°)	3.0–55.0	3.0–50.0	3.0–55.0	3.0–52.0
μ (mm^{-1})	1.276	1.480	14.792	10.324
F(000)	680	2320	1328	1760
No. of observed reflections	2403	4508	1326	3507
No. of parameters refined	229	524	118	182
Goodness-of-fit	2.55	0.989	1.92	1.87
R_f	0.0534	0.0548	0.0485	0.0462
R_w	0.0530	0.1442	0.0466	0.0644

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