APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organomet. Chem. 2003; **17**: 449–452
Main Group Metal Compounds **AOC**

Synthesis and crystal structure of silver and argentate complexes of mixed halocarborane anions, $(C_5H_5N)_2Ag(1\text{-}H\text{–}CB_{11}Br_5I_6)(C_5H_5N)$ and $[\{(CH_3CN)_4Ag_3\}\{Ag(CB_{11}I_5Br_6)_2\}]_n$[†]

Chi-Wing Tsang, Qingchuan Yang, Thomas C. W. Mak and Zuowei Xie*

Department of Chemistry, The Chinese University of Hong Kong, Shatin NT, Hong Kong, People's Republic of China

Received 12 December 2002; Revised 6 January 2003; Accepted 3 February 2003

The first argentate salt of carborane anion, $[\{(CH_3CN)_4Ag_3\}\{Ag(CB_{11}I_5Br_6)_2\}]_n$, was prepared from $K_2[CB_{11}I_5Br_6]$ and $AgNO_3$ followed by recrystallization from acetonitrile. Single-crystal X-ray analyses indicate that the $CB_{11}I_5Br_6^{2-}$ dianion has a significantly different coordination motif from that of the $CB_{11}Br_5I_6^{-}$ monoanion. This result suggests that the polarity of the CB_{11} cage can be changed after deprotonation of the cage C–H proton. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: argentate; carborane; cluster; silver; weakly coordinating anion; structure

INTRODUCTION

Icosahedral carboranes constitute a class of robust and weakly coordinating anions and have received much attention.[1–3] Their silver(I) salts are very useful halide metathesis reagents for introducing these anions into various kinds of complexes, and they are finding many applications in metathesis, catalysis and oxidation chemistry.[1–3] They have also been shown to possess a rich structural and coordination chemistry of their own. In fact, in all known crystallographically characterized silver(I) carborane complexes, each structure has a different coordination motif that could not be predicted from a knowledge of the constituent parts.[4–16]

Our previous work shows that in mixed and perhalocarborane anions, such as $1\text{-H–}CB_{11}Y_5X_6^{-}$ and $1\text{-H–}CB_{11}X_{11}^{-}$, the halogen atoms in the lower belt (positions 7–12) are more coordinating than those in the upper belt (positions 2–6), since the CB_{11} cage is polarized.[14] The polarity of the cage is expected to be changed after deprotonation of the cage C–H proton, which would lead to a brand new coordination motif. Here, we report the synthesis of the first argentate salt of a carborane anion and single-crystal structures of $(C_5H_5N)_2Ag(1\text{-H–}2,3,4,5,6\text{-}Br_5\text{-}7,8,9,10,11,12\text{-}I_6\text{–}CB_{11})(C_5H_5N)$ and $[\{(CH_3CN)_4Ag_3\}\{Ag(2,3,4,5,6\text{-}I_5\text{-}7,8,9,10,11,12\text{-}Br_6\text{–}CB_{11})_2\}]_n$. The coordination features of the $1\text{-}H\text{–}CB_{11}Br_5I_6^{-}$ monoanion and $CB_{11}I_5Br_6^{2-}$ dianion are also described.

RESULTS AND DISCUSSION

Synthesis and spectroscopic characterization

Recrystallization of $Ag(1\text{-H–}CB_{11}Br_5I_6)$ from a mixed solvent of pyridine–acetonitrile gave X-ray-quality crystals of $(C_5H_5N)_2Ag(1\text{-H–}CB_{11}Br_5I_6)(C_5H_5N)$ (**1**). Treatment of $[Me_3NH][1\text{-H–}CB_{11}I_5Br_6]$ with two equivalents of KOH in hot water, presumably giving $K_2[CB_{11}I_5Br_6]$, followed by reaction with two equivalents of $AgNO_3$ afforded, after recrystallization from CH_3CN, $[\{(CH_3CN)_4Ag_3\}\{Ag(CB_{11}I_5Br_6)_2\}\cdot(CH_3CN)]_n$ (**2**·CH_3CN). Both complexes are only soluble in donor solvents such as pyridine, acetonitrile, and acetone. They are air- and moisture-stable, but are light sensitive.

These two complexes were characterized by ^1H and ^{11}B NMR spectroscopic data, as well as by elemental analyses. The disappearance of δ(cage CH) 2.95 ppm[14] in the ^1H NMR of **2** suggested the formation of the $CB_{11}I_5Br_6^{2-}$ dianion. Its ^{11}B NMR spectrum exhibits a 1 : 5 : 5 splitting pattern, and the range of ^{11}B chemical shifts (−4.0 to −23.5 ppm) is smaller

---

*Correspondence to: Zuowei Xie, Department of Chemistry, The Chinese University of Hong Kong, Shatin NT, Hong Kong, People's Republic of China.
E-mail: zxie@cuhk.edu.hk

†Dedicated to Professor Thomas P. Fehlner on the occasion of his 65th birthday, in recognition of his outstanding contributions to organometallic and inorganic chemistry.

Contract/grant sponsor: Research Grants Council of the Hong Kong Special Administration Region; Contract/grant number: CUHK4026/02P.

than that found in 1-H–$CB_{11}I_5Br_6^-$,[14] indicating that the polarity of $CB_{11}I_5Br_6^{2-}$ is smaller than that of 1-H–$CB_{11}I_5Br_6^-$.

Crystal structures

The molecular structures of both **1** and **2** have been confirmed by single-crystal X-ray analyses. Selected bond distances are listed in Table 1.

Figure 1 shows the coordination around silver in the solid-state structure of **1**. It is a monomeric structure with no obvious intermolecular interactions. The four-coordinate silver atom is in a distorted-tetrahedral arrangement of two iodine atoms from the monoanion 1-H–$CB_{11}Br_5I_6^-$ and two pyridine molecules. There are no interactions between silver and any one of the five bromine atoms from the upper belt (Br2 to Br6) of the cage; this is understandable, since I^- is a softer base than Br^- and the lower-belt atoms bear more negative charge than the upper-belt ones.[14] It is interesting to note that the third pyridine molecule points toward the cage C–H proton with an N(3)–C(1) distance of 3.061(15) Å and a C(1)–H(1)–N(3) angle of 172(1)°, indicating there is a hydrogen bonding between N(3) and the acidic cage C–H proton.

Table 1. Selected bond distances (Å)

Complex $(C_5H_5N)_2Ag(1\text{-H–}CB_{11}Br_5I_6)(C_5H_5N)$ (**1**)	
Ag(1)–N(1)	2.258(11)
Ag(1)–N(2)	2.267(10)
Ag(1)–I(8)	2.894(1)
Ag(1)–I(12)	2.835(1)
Complex $[\{(CH_3CN)_4Ag_3\}\{Ag(CB_{11}I_5Br_6)_2\}\cdot(CH_3CN)]_n$ (**2**·CH_3CN)	
Ag(1)–C(1)	2.142(7)
Ag(2)–N(1)	2.396(18)
Ag(2)–N(2)	2.283(12)
Ag(2)–Br(8)	3.030(2)
Ag(2)–I(4)	2.953(2)
Ag(3)–I(2)	3.008(1)
Ag(3)–I(6)	2.986(1)
Ag(3)–Br(11)	2.954(1)

The Ag–I distances of 2.894(1) and 2.835(1) Å, with an average value of 2.865(1) Å, are comparable to the corresponding values observed in Ag(1-CH_3–$CB_{11}H_5I_6$).[11] The Ag–N distances of 2.258(11) and 2.267(10) Å, with an average value of 2.263(11) Å, are similar to those normally observed in $Ag(CH_3CN)_n^+$ complexes.[13]

Deprotonation of the cage C–H proton resulted in the formation of the $CB_{11}I_5Br_6^{2-}$ dianion, in which the cage carbon bears one pair of electrons. This carbon can form a σ bond with silver, leading to the structural characterization of the first argentate salt of a carborane anion, as shown in Fig. 2. The Ag(1)–C(1) distance of 2.142(7) Å and the linearity of Ag(1) are best compared with the average Ag–C distances of 2.097(9) Å in $[Li(THF)_4][Ag(C_6H_2\text{-}2,4,6\text{-}Ph_3)_2]$ and 2.110(19) Å in $[Li(THF)_4][Ag(C_6H_3\text{-}2,4\text{-}Mes_2)_2]$ (Mes = C_6H_2-2,4,6-Me_3).[17] This measured value is *ca* 0.23 Å longer than the Cu–C distance in $[ClCu(CB_{11}F_{11})]^{2-}$,[18] which is close to the difference (0.21 Å) in the effective ionic radius of two-coordinate Ag^+ and Cu^+.[19]

Another structural feature of **2** is the strong bonding interactions between the second silver and the upper belt iodine atoms. This is a brand new coordination motif that has not been observed before in the silver salts of any carborane monoanions.[4–16] The reason is probably due to the increased electron density of the upper-belt cage atoms caused by the deprotonation of the cage C–H proton. Each six-coordinate silver Ag(3) links two cages together, leading to the formation of a zig-zag coordination polymeric chain, as shown in Fig. 3. The Ag–I distances vary from 2.953(2) to 3.008(1) Å, which are longer than those found in **1**, but fall in the range 2.777(4)–3.306(5) Å for Ag(1-H–$CB_{11}H_5I_6$)[15]

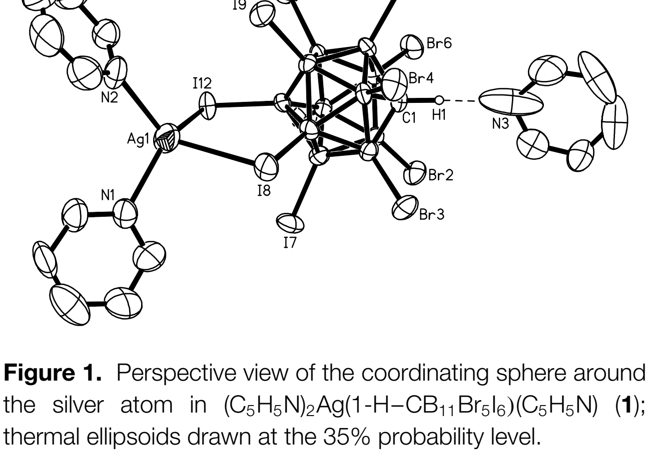

Figure 1. Perspective view of the coordinating sphere around the silver atom in $(C_5H_5N)_2Ag(1\text{-H–}CB_{11}Br_5I_6)(C_5H_5N)$ (**1**); thermal ellipsoids drawn at the 35% probability level.

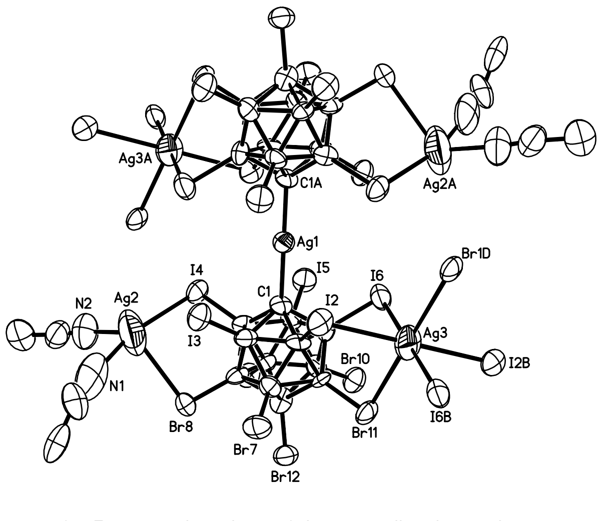

Figure 2. Perspective view of the coordinating sphere around the silver atom in $[\{(CH_3CN)_4Ag_3\}\{Ag(CB_{11}I_5Br_6)_2\}\cdot(CH_3CN)]_n$ (**2**); the solvated acetonitrile molecule is not shown; thermal ellipsoids drawn at the 35% probability level.

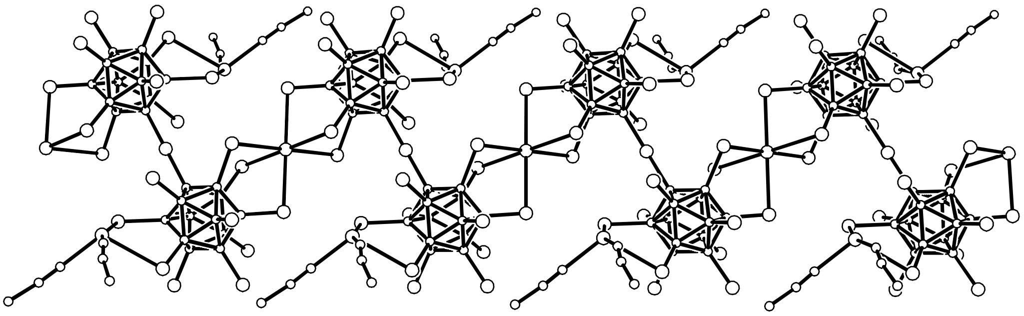

Figure 3. Projection view of one layer of **2**.

and diiodoalkane complexes of silver(I).[20,21] The Ag–Br distances of 2.954(1) and 3.030(2) Å are longer than those (2.84–2.90 Å) found in the silver salts of polybromocarborane anions,[10–15] but they lie in the range found in dibromoalkane complexes of silver(I): 2.81–3.08 Å.[22] The Ag–N distances of 2.283(12) and 2.396(18) Å are comparable to those in **1**.

In summary, the first argentate salt of a carborane anion was prepared and structurally characterized. This work demonstrates that: (1) the polarity of the CB_{11} cage can be changed via deprotonation of the cage C–H proton; (2) the $CB_{11}I_5Br_6{}^{2-}$ dianion shows a significantly different coordination motif than that of the $CB_{11}Br_5I_6{}^{-}$ monoanion. It is anticipated that carborane dianions would have a rich coordination chemistry.

EXPERIMENTAL

General

Ag(1-H–$CB_{11}Br_5I_6$) and [Me_3NH][1-H–$CB_{11}I_5Br_6$] were prepared according to the literature methods.[14] All other chemicals were purchased from Aldrich Chemical Company and used as received unless otherwise noted. ^{1}H NMR spectra were recorded on a Bruker 300 MHz DPX spectrometer at 300.13 MHz. ^{11}B NMR spectra were recorded on a Varian Inova spectrometer at 128.32 MHz. All chemical shifts are reported in δ units with reference to the residual protons of deuterated solvent for proton and to external $BF_3{\cdot}OEt_2$ (0.00 ppm) for ^{11}B chemical shifts.

Preparation of $(C_5H_5N)_2Ag(1\text{-}H\text{–}CB_{11}Br_5I_6)(C_5H_5N)$ (1)

Recrystallization of Ag(1-H–$CB_{11}Br_5I_6$) (100 mg, 0.07 mmol) from a mixed solvent of pyridine–acetonitrile (5 ml, 1 : 3) at room temperature gave **1** as pale yellow crystals (83 mg, 71%). ^{1}H NMR (acetone-d_6): δ 8.75 (s, 6H), 7.75 (s, 3H), 7.44 (s, 6H) (pyridine), 3.20 (s, 1H) (cage C*H*); ^{11}B NMR (acetone-d_6): δ −3.0 (s, 1B), −5.4 (s, 5B), −11.2 (s, 5B). Anal. Found: C, 11.43; H, 1.15; N, 2.31. $C_{16}H_{16}AgB_{11}Br_5I_6N_3$ requires: C, 11.73; H, 0.98; N, 2.57%.

Preparation of $[\{(CH_3CN)_4Ag_3\}\{Ag(CB_{11}I_5Br_6)_2\}{\cdot}(CH_3CN)]_n$ ($2{\cdot}CH_3CN$)

To a suspension of [Me_3NH][1-H–$CB_{11}I_5Br_6$] (100 mg, 0.076 mmol) in water (10 ml) was added KOH (9.0 mg, 0.16 mmol), and the mixture was heated at 90 °C for 2 h. Removal of the trimethylamine under vacuum and addition of 1 ml of acetone gave a clear solution. An aqueous solution of $AgNO_3$ (27 mg, 0.16 mmol) was then added at 0 °C,

Table 2. Crystal data and summary of data collection and refinement for **1** and **2**$\cdot CH_3CN$

	1	**2**$\cdot CH_3CN$
Formula	$C_{16}H_{16}AgB_{11}Br_5I_6N_3$	$C_6H_{7.5}Ag_2B_{11}Br_6I_5N_{2.5}$
Crystal size (mm^3)	0.60 × 0.50 × 0.40	0.40 × 0.40 × 0.62
Fw	1638.05	1563.26
Crystal system	monoclinic	triclinic
Space group	*Cc*	$P\bar{1}$
a (Å)	10.353(1)	10.689(3)
b (Å)	23.959(1)	11.002(3)
c (Å)	15.535(1)	13.971(2)
α (°)	90.00	87.53(2)
β (°)	91.72(1)	79.02(1)
γ (°)	90.00	74.46(1)
V (Å^3)	3851.6(4)	1553.9(6)
Z	4	2
D_{calcd} (Mg m^{-3})	2.825	3.341
2θ range (°)	3.4–56.0	3.0–50.0
μ (mm^{-1})	10.538	13.948
$F(000)$	2912	1370
No. of observed reflections	6567	3769
No. of parameters refined	380	289
Goodness of fit	1.04	1.08
R_1	0.037	0.069
wR_2	0.091	0.172

affording a suspension. Removal of acetone led to a white precipitate that was collected by filtration. Recrystallization from a CH_3CN solution gave **2**·CH_3CN as pale yellow crystals (89 mg, 75%). ^1H NMR (acetone-d_6): δ 1.88 (s) (CH_3CN); ^{11}B NMR (acetone-d_6): δ −4.0 (s, 1B), −6.9 (s, 5B), −23.5 (s, 5B). Anal. Found: C, 4.30; H, 0.62; N, 2.11. $C_{12}H_{15}Ag_4B_{22}Br_{12}I_{10}N_5$ requires: C, 4.61; H, 0.48; N, 2.24%.

X-ray structure determination

Single crystals were immersed in Paraton-N oil and then sealed in thin-walled glass capillaries. Data were collected at 293 K on an MSC/Rigaku RAXIS-IIC imaging plate using Mo Kα radiation (0.710 73 Å) from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. An absorption correction was applied by correlation of symmetry-equivalent reflections using the ABSCOR program.[23] Both structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F^2 using the Siemens SHELXTL V 5.03 program package (PC version).[24] The hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinement are given in Table 2. The CCDC reference numbers are 199 360 and 199 361 for **1** and **2** respectively.

Acknowledgements

We thank the Research Grants Council of the Hong Kong Special Administration Region (project no. CUHK4026/02P) for financial support.

REFERENCES

1. Reed CA. *Acc. Chem. Res.* 1998; **31**: 133.
2. Reed CA. *Acc. Chem. Res.* 1998; **31**: 325.
3. Strauss SH. *Chem. Rev.* 1993; **93**: 927.
4. Shelly K, Finster DC, Lee YJ, Scheidt WR, Reed CA. *J. Am. Chem. Soc.* 1985; **107**: 5955.
5. Jelínek T, Baldwin P, Scheidt WR, Reed CA. *Inorg. Chem.* 1993; **32**: 1982.
6. Xie Z, Jelínek T, Bau R, Reed CA. *J. Am. Chem. Soc.* 1994; **116**: 1907.
7. Xie Z, Bau R, Reed CA. *Angew. Chem. Int. Ed. Engl.* 1994; **33**: 2433.
8. Ivanov SV, Rockwell JJ, Miller SM, Anderson OP, Solntsev KA, Strauss SH. *Inorg. Chem.* 1996; **35**: 7882.
9. Ivanov SV, Lupinetti AJ, Miller SM, Anderson OP, Solntsev KA, Strauss SH. *Inorg. Chem.* 1995; **34**: 6419.
10. Xie Z, Tsang CW, Sze ETP, Yang Q, Chan DTW, Mak TCW. *Inorg. Chem.* 1998; **37**: 6444.
11. Xie Z, Tsang CW, Xue F, Mak TCW. *J. Organometal. Chem.* 1999; **577**: 197.
12. Tsang CW, Yang Q, Sze ETP, Mak TCW, Chan DTW, Xie Z. *Inorg. Chem.* 2000; **39**: 3582.
13. Tsang CW, Sun J, Xie Z. *J. Organometal. Chem.* 2000; **613**: 99.
14. Tsang CW, Yang Q, Sze ETP, Mak TCW, Chan DTW, Xie Z. *Inorg. Chem.* 2000; **39**: 5851.
15. Xie Z, Wu BM, Mak TCW, Manning J, Reed CA. *J. Chem. Soc. Dalton Trans.* 1997; 1213.
16. Ingleson MJ, Mahon MF, Patmore NJ, Ruggiero GD, Weller AS. *Angew. Chem. Int. Ed. Engl.* 2002; **41**: 3694.
17. Hwang CS, Power PP. *J. Organometal. Chem.* 1999; **589**: 234.
18. Ivanov SV, Rockwell JJ, Polyakov OG, Gaudinski CM, Anderson OP, Solntsev KA, Strauss SH. *J. Am. Chem. Soc.* 1998; **120**: 4224.
19. Shannon RD. *Acta Crystallogr. Sect. A* 1976; **32**: 751.
20. Powell J, Horvath MJ, Lough A. *J. Chem. Soc. Dalton Trans.* 1996; 1669.
21. Powell J, Horvath MJ, Lough A. *Chem Commun.* 1993; 773.
22. Seggen DMV, Hurlburt PK, Anderson OP, Strauss SH. *Inorg. Chem.* 1995; **34**: 3453.
23. Higashi T. *ABSCOR—an empirical absorption correction based on Fourier coefficient fitting*. Rigaku Corp., Tokyo, 1995.
24. *SHELXTL V 5.03 program package*. Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1995.