Inorg. Chem. **2002**, *41*, 4567–4573

Inorganic Chemistry

Article

Solution and Solid-State Structure of the Anion $[Ag_2\{closo\text{-}CB_{11}H_{12}\}_4]^{2-}$

Mark A. Fox,[†] Mary F. Mahon,*[,‡] Nathan J. Patmore,[‡] and Andrew S. Weller*[,‡]

Department of Chemistry, University of Bath, Bath BA2 7AY, U.K., and Department of Chemistry,
University Science Laboratories, South Road, Durham DH1 3LE, U.K.

Received May 20, 2002

Addition of the carbene 1,3-dimesitylimidazol-2-ylidene (IMes) to a toluene solution of Ag[*closo*-$CB_{11}H_{12}$] results in the formation of the complex $[(IMes)_2Ag]_2[Ag_2\{closo\text{-}CB_{11}H_{12}\}_4]$, the anionic component of which contains two silver(I) centers bridged by two carboranes in addition to one terminally bound carborane on each metal, in the solid-state. Comparison of the observed $^{11}B\{^1H\}$ NMR chemical shifts of $[(IMes)_2Ag]_2[Ag_2\{closo\text{-}CB_{11}H_{12}\}_4]$ or Ag[*closo*-$CB_{11}H_{12}$] with $[NBu_4]$[*closo*-$CB_{11}H_{12}$] in CD_2Cl_2 demonstrates that the silver ion interacts significantly with the cage in solution. Theoretical investigations using the ab initio/GIAO/NMR method of $[closo\text{-}CB_{11}H_{12}]^-$ and Na[*closo*-$CB_{11}H_{12}$] as model geometries for the silver salts support experimental evidence for these Ag···{BH} interactions in solution.

Introduction

Structurally characterized examples of the simple silver(I)-salts of the carborane mono anion $[closo\text{-}CB_{11}H_{12}]^-$ and its derivatives are well documented, as these complexes frequently provide crystalline materials suitable for X-ray diffraction studies of this important class of least coordinating anion.[1] In the solid-state, there are three general structural types observed: (i) coordination polymers, often with the carborane being complemented by a bound arene molecule at the silver center;[2−6] (ii) discrete molecules in which both arene and carborane interactions occur;[4,7] (iii) discrete molecules in which only silver and carborane interactions are present, although only two examples have been reported, namely $[Fe(tpp)][Ag(closo\text{-}CB_{11}H_6Br_6)_2]$[8] [tpp = tetraphenylporphyrinatoiron(III)] and the recently reported tetrameric complex $[ReAg\{\mu\text{-}5,6,10\text{-}(H)_3\text{-}\eta^5\text{-}7,8\text{-}C_2B_9H_8\}(CO)_3]_4$.[9] Although many of these structures show close Ag···{HB} interactions in the solid-state, these interactions are rarely observed in solution.[5,6,10] This is no doubt a result of the fact that the NMR spectra of these complexes are routinely recorded in coordinating solvents, such as acetone, that encourage well separated ion-pairs.

We have recently reported the coordination chemistry of silver phosphine fragments partnered with $[closo\text{-}CB_{11}H_{12}]^-$ and its derivatives, such as $(PPh_3)Ag(closo\text{-}CB_{11}H_{12})$, and have shown that these complexes are highly active catalysts for hetero Diels−Alder reactions.[10,11] As part of this ongoing research, we were interested in substituting the phosphine ligand by a alternative, neutral, 2-electron donor. *N*-Heterocyclic carbenes such as 1,3-dimesitylimidazol-2-ylidene (IMes) have been successfully used to substitute phosphine ligands in a number of catalytically relevant systems, perhaps the best example being their use in Grubbs'-type catalysts to afford significantly more active complexes.[12] We describe here that attempts to substitute PPh_3 by IMes did not afford

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* To whom correspondence should be addressed. E-mail: a.s.weller@bath.ac.uk (A.S.W.). Fax: +44 (0)1225 386231 (A.S.W.).

[†] University Science Laboratories.

[‡] University of Bath.

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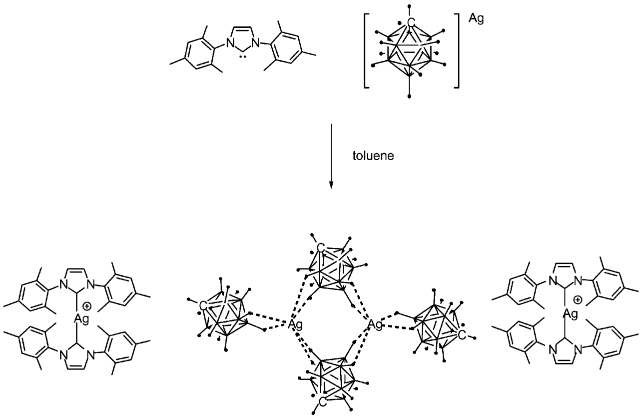
10.1021/ic025730h CCC: $22.00

the initially anticipated complex, (IMes)Ag(*closo*-$CB_{11}H_{12}$), but instead, the bis-carbene cation $[(IMes)_2Ag]^+$ results with the concomitant formation of the novel silver−carborane dianion $[Ag_2\{closo\text{-}CB_{11}H_{12}\}_4]^{2-}$: a novel coordination motif for the discrete silver salts of the carborane anions. Aided by ab initio/GIAO/NMR calculations, we also report on the solution-state structures of the simple salts of [*closo*-$CB_{11}H_{12}]^-$ and show that in a noncoordinating solvent (CH_2Cl_2) there are significant interactions between metal ion and carborane anion, analogous to those observed in the solid-state.

Results and Discussion

Addition of a toluene solution of the free carbene IMes (IMes = 1,3-dimesitylimidazol-2-ylidene) to a stirred solution of Ag[*closo*-$CB_{11}H_{12}$] results in a colorless solution that affords colorless crystals of a compound of empirical formula $[Ag(IMes)_2][Ag\{closo\text{-}CB_{11}H_{12}\}_2]$ (**1**) on cooling. Compound **1** has been characterized by elemental analyses, single-crystal X-ray diffraction (Table 1), and multinuclear NMR spectroscopy.



X-ray Crystallography. The asymmetric unit in **1** consists of one cationic $[(IMes)_2Ag]^+$ moiety and one anionic fragment based on a silver atom and two [*closo*-$CB_{11}H_{12}]^-$ cages. The silver−carbene fragment (Figure 1) is compositionally identical to that previously reported for $[(IMes)_2Ag]$-$[O_3SCF_3]$ (**A**).[13] The metal−$C_{(carbene)}$ distances of the cationic fragment in **1** are indistinguishable [Ag(1)−C(22) 2.069(6) Å, Ag(1)−C(1A) 2.070(5) Å] and are also identical to those found in **A** [2.067(4) and 2.078(4) Å]. The C(22)−Ag(1)−C(1A) angle at the metal center is nonlinear [C(22)−Ag(1)−C(1A) 174.3(2)°], similar to that found in **A** [176.3(2)°]. The only significant structural difference between the cation in **1** and **A** is the angle between the least-squares planes of the five-membered imidazole rings, which is 59.1° in **1** and 39.7° in **A**. This is no doubt due to differences in the crystal packing imposed by the anions in the two complexes.

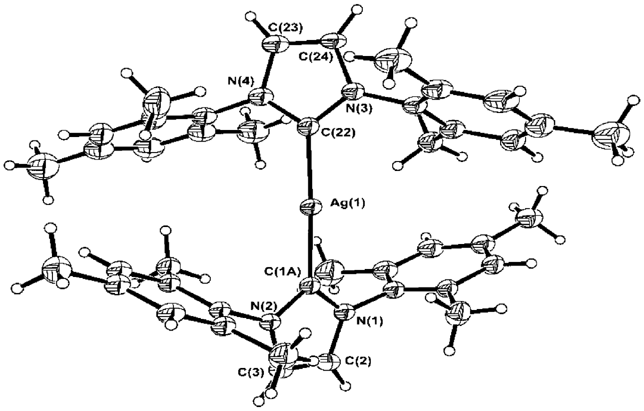


Figure 1. Cationic component of the asymmetric unit in complex **1**. Thermal ellipsoids are given at the 30% probability level.

Table 1. Crystal Data and Structure Refinement for **1**, $[(IMes)_2Ag][Ag\{Closo\text{-}CB_{11}H_{12}\}_2]$

empirical formula	$C_{22}H_{36}AgB_{11}N_2$
fw	555.31
T	150(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	$P2_1/n$
unit cell dimensions	$a = 15.4570(2)$ Å $b = 20.1150(3)$ Å; $\beta = 108.558(1)°$ $c = 19.2130(3)$ Å
V	5663.04(14) $Å^3$
Z	8
D_{calcd}	1.303 Mg/m^3
abs coeff	0.727 mm^{-1}
$F(000)$	2272
cryst size	0.13 × 0.13 × 0.15 mm^3
θ range for data collection	3.66 to 24.71°
reflns collected	85847
independent reflns	9621 [R(int) = 0.1469]
reflns obsd ($>2\sigma$)	5969
data completeness	0.996
abs correction	semiempirical from equivalents
max and min transmission	0.97 and 0.87
refinement method	full-matrix least-squares on F^2
data/restraints/params	9621/0/749
GOF on F^2	1.043
final R indices [$I > 2\sigma(I)$]	R1 = 0.0543; wR2 = 0.1160
R indices (all data)	R1 = 0.1055; wR2 = 0.1419
largest diff peak and hole	0.489 and −0.623 $eÅ^{-3}$

The anionic fragment containing the second silver atom and carborane anions is proximate to a crystallographic inversion center in the asymmetric unit, which generates a [*closo*-$CB_{11}H_{12}]^-$ bridged dimer where the symmetry related silver atoms are also terminally coordinated to the second cage (Figure 2). The bridging carborane anions are disordered in a 1:1 ratio between positions B(21) to B(32) and B(41) to B(52), respectively. This disorder can be readily resolved into the dimeric motif that contains two different orientations of the bridging carborane cages. The two disorder components are chemically and structurally identical. The presence of this disorder precluded accurate assignment of the cage carbon in the bridging carborane, and hence all atoms therein were refined as boron atoms. However, assignment of the cage carbon in the terminally bound cage [C(1)−B(12)] was unambiguous. The resulting $Ag_2[closo\text{-}CB_{11}H_{12}]_4$ anion has an overall dinegative charge and is thus associated with two $[(IMes)_2Ag]^+$ cations (see Supporting Information). The coordination geometry around each silver atom is ap-

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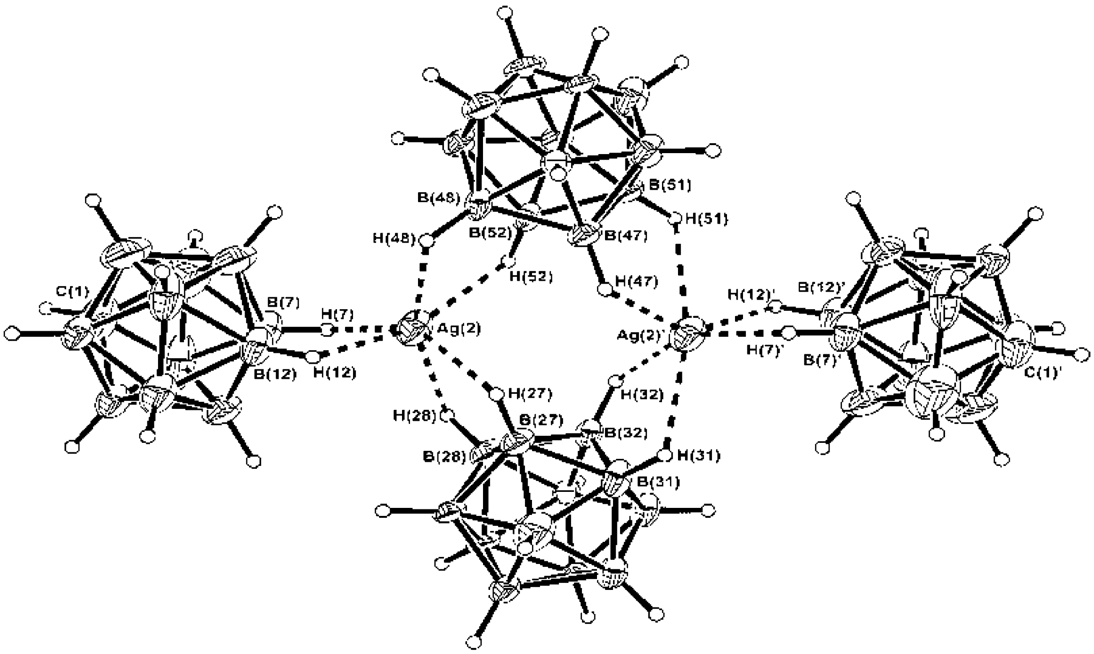

Figure 2. Anionic portion of complex **1** showing one of the disordered components. Atoms with primed labels are related to those in the asymmetric unit by the operation $-x + 1$, $-y$, $-z$. Disorder in the bridging carborane anions is omitted for clarity. Thermal ellipsoids are given at the 30% probability level.

Table 2. Bond Lengths (Å) and Angles (deg) Associated with Ag(1), Ag(2) and Ag(2)′ in Complex **1** for One of the Disordered Components in the Lattice

Ag(1)−C(22)	2.069(6)	Ag(1)−C(1A)	2.070(5)
C(22)−Ag1−C(1A)	174.3(2)		
Ag(2)−H(7)	2.05	Ag(2)−B(7)	2.586(8)
Ag(2)−H(12)	2.23	Ag(2)−B(12)	2.673(8)
Ag(2)−H(27)	2.09	Ag(2)−B(27)	2.73(2)
Ag(2)−H(28)	2.45	Ag(2)−B(28)	2.92(2)
Ag(2)−H(48)	2.35	Ag(2)−B(48)	2.84(2)
Ag(2)−H(52)	2.19	Ag(2)−B(52)	2.79(2)
Ag(2)′−H(31)	2.52	Ag(2)−B(31)′	2.94(2)
Ag(2)′−H(32)	1.96	Ag(2)−B(32)′	2.67(2)
Ag(2)′−H(47)	2.05	Ag(2)′−B(47)	2.70(2)
Ag(2)′−H(51)	2.40	Ag(2)′−B(51)	2.88(2)

proximately trigonal prismatic, with each metal center surrounded by four shorter and two longer {BH} interactions. Salient metrical data for Ag(2) and Ag(2)′ are given in Table 2. The shorter Ag···{HB} interactions vary in distance ranging from 1.96 to 2.23 Å (Ag−H) and 2.586(7) to 2.79(2) Å (Ag−B). The longer interactions are in the range 2.84(2)−2.94(2) Å (Ag−B). These Ag−B distances can be compared with those found in the silver(I)−phosphine complexes (PPh_3)Ag(*closo*-$CB_{11}H_{12}$) [2.504(3)−2.619(3) Å] and (PPh_3)$_2$Ag(*closo*-$CB_{11}H_{12}$) [2.892(2)−3.494(2) Å], where significant Ag−B interactions are suggested to exist in solution in the former but not the latter complex, on the basis of observed ^{11}B chemical shifts.[10] The shorter Ag···{HB} distances are also comparable with those found in the benzene solvate of Ag[*closo*-$CB_{11}H_{12}$] [2.581(6) and 2.681(5) Å][2] but are shorter than those found in the tetrameric complex [ReAg{μ-5,6,10-(H)$_3$-η^5-7,8-$C_2B_9H_8$}(CO)$_3$]$_4$ [2.978(7), 2.905(6) Å] in which the Ag−{HB} interactions are suggested to lie between regular covalent agostic and longer range electrostatic.[9] Overall, these comparisons suggest that the Ag···{HB} interactions in **1** are significant, with this interpretation strengthened by the solution ^{11}B NMR data and ab initio/GIAO/NMR calculations.

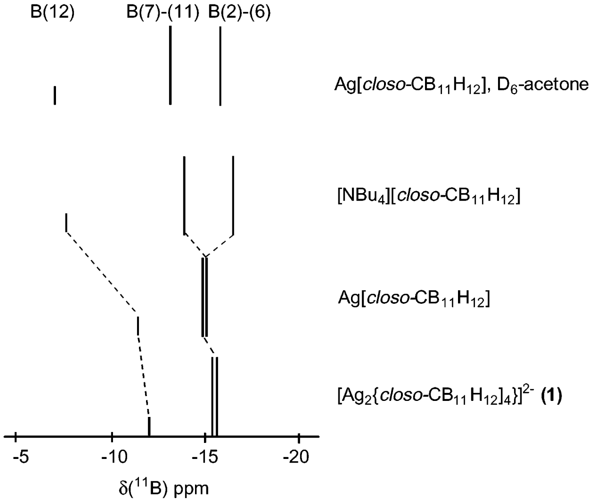

Figure 3. Diagrammatic stick diagram of ^{11}B chemical shifts observed for **1**, [NBu_4][*closo*-$CB_{11}H_{12}$], and Ag[*closo*-$CB_{11}H_{12}$], all measured as CD_2Cl_2 solutions, and Ag[*closo*-$CB_{11}H_{12}$] measured in d_6-acetone.

^{11}B NMR Spectroscopy. Although NMR spectroscopy alone does not allow us to determine whether the {Ag_2(*closo*-$CB_{11}H_{12}$)$_4$} motif remains wholly intact in solution, the presence of significant Ag···{HB} interactions is indicated by the solution ^{11}B{^{1}H} NMR spectrum of **1** in CD_2Cl_2. This shows resonances due to one {*closo*-$CB_{11}H_{12}$} cage species with C_5v symmetry that displays a marked upfield shift for the cage boron atoms B(7)−B(11) and B(12) when compared with that found for [*closo*-$CB_{11}H_{12}$]$^-$ partnered with the non-Lewis-acidic counterion [NBu_4]$^+$ (Figure 3). Thus, in the ^{11}B{^{1}H} NMR spectrum of **1**, signals are observed at δ −12.4 (1B) and −15.7 (5B + 5B coincidence), compared with δ −8.0 (1B), −14.1 (5B), −16.9 (5B) found for [NBu_4][*closo*-$CB_{11}H_{12}$]. Values found for Ag[*closo*-$CB_{11}H_{12}$] and **1** in acetone, a solvent in which any ion-pairs would be expected to be well separated, are similar to those found for [Cs]$^+$ or

[NBu_4][*closo*-$CB_{11}H_{12}$],[14,15] cations with which the carborane periphery is not expected to interact significantly in solution.

The $^{11}B\{^1H\}$ NMR spectrum of Ag[*closo*-$CB_{11}H_{12}$] in CD_2Cl_2 (in which it is poorly soluble and hence not usually used as a solvent) is very similar to that of **1**, with signals observed at δ −11.9 (1B) and −15.0 (5 + 5 coincidence) (Figure 3). Although in **1** the ratio Ag/[*closo*-$CB_{11}H_{12}$] is 1:2, while for Ag[*closo*-$CB_{11}H_{12}$] it is 1:1, this similarity suggests that comparable Ag···{HB} interactions are present in solution in these two species, and perhaps that Ag[*closo*-$CB_{11}H_{12}$] exists in CD_2Cl_2 solution as weakly associated oligomeric units, similar to **1**. The very low solubility of Ag[*closo*-$CB_{11}H_{12}$] in CD_2Cl_2 is perhaps indicative of this extended structure. Reed and co-workers have observed similar chemical shift changes for Ag[*closo*-CB_9H_{10}] when measured in toluene and acetone or acetonitrile.[6] Similar interactions (and relative ^{11}B NMR chemical shift differences) have been previously proposed by us as being present in solution for the silver-salt metathesis intermediate complex [$CpMo(CO)_3I\cdot Ag\{$*closo*-$CB_{11}H_{12}\}$]$_2$ (Cp = η^5-C_5H_5).[5] We have also previously shown that significant upfield shifts occur in the ^{11}B NMR spectra of [*closo*-$CB_{11}H_{12}$]$^-$ when coordinated to [(η^5-C_5R_5)$Mo(CO)_3$]$^+$ (R = H, Me),[5] [(cod)-Rh]$^+$ (cod = 1,5-cyclooctadiene),[16] and [$Ag(PPh_3)$]$^+$ [10] fragments. The data in hand here suggest that the Ag cation in **1** interacts significantly with the carborane periphery in CD_2Cl_2 solution and, in particular, with the boron atoms B(12) and B(7)−B(11). This is confirmed by the results of ab initio calculations on model complexes for **1**, Ag[*closo*-$CB_{11}H_{12}$], and "free" [*closo*-$CB_{11}H_{12}$]$^-$, which follow.

Calculations. In the past decade, the reliable "ab initio/GIAO/NMR" method has been used to determine the molecular structures of carboranes in solution.[17−20] However, there are only two reports of the method being used to determine the likely geometries of metal salts of carborane anions in solution.[21] Given the marked differences observed between the ^{11}B NMR spectra of Ag[*closo*-$CB_{11}H_{12}$] when measured in CD_2Cl_2 versus acetone, we sought to use the ab initio/GIAO/NMR method to elucidate the structures of the species present in these two solvents, in addition to the structure of complex **1** in solution. However, the silver cation [Ag]$^+$ is at present not computationally feasible at the MP2/6-31G* level of theory required for the accurate determination of chemical shifts.[18] Copper would be an obvious replacement, but it is computationally inhibitive at the MP2/6-31G* level for the compounds under discussion. We have thus chosen to replace [Ag]$^+$ by [Na]$^+$ in ab initio computations described here. Although [Na]$^+$ and [Ag]$^+$ are hard and soft Lewis acids, respectively, and thus may be expected to interact somewhat differently with the cage (electrostatic and covalent respectively), our approach is validated by that fact that they have similar ionic radii[22] and that calculations (MP2 level optimized geometries) on the model complexes $Na(BH_4)$ and $Ag(BH_4)$ show that both complexes adopt very similar structures (tridentate, C_{3v}).[23] Moreover, the chemical shifts calculated for Na[*closo*-$CB_{11}H_{12}$] (vide infra) are very close to those experimentally observed for Ag[*closo*-$CB_{11}H_{12}$], further supporting this approach.

Initially, we focused on modeling the structure of Ag[*closo*-$CB_{11}H_{12}$] in a noncoordinating solvent, such as CD_2Cl_2, where ^{11}B NMR spectroscopy shows that tight ion pairs are likely to be present. A geometry optimization of Na[*closo*-$CB_{11}H_{12}$] at the MP2/6-31G* level of theory gave the lowest energy minimum **I** with the sodium metal capping the triangular face defined by B(7), B(8), and B(12) (Figure 4). This structure is similar to that which we have observed for (PPh_3)Ag(*closo*-$CB_{11}H_{12}$)[10] and also that calculated for protonated [*closo*-$CB_{11}H_{12}$]$^-$,[24] in agreement with [Na]$^+$ and

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(15) During the course of this work, we found that the ^{11}B chemical shift literature values for Ag[*closo*-$CB_{11}H_{12}$] in acetone differed from those one of us (A.S.W.) had previously reported by δ −3.3. Examination of authentic carborane samples recorded at Bath and Durham with literature values confirmed this discrepancy. Although in this paper, and all subsequent contributions from Bath, ^{11}B chemical shifts are correctly referenced to $BF_3\cdot OEt_2$, previous papers from us do not take this into account. However, in all discussions, as it is the relative positions of the resonances which are important, this small change in chemical shift does not alter any conclusions made on the basis of ^{11}B NMR spectroscopy.

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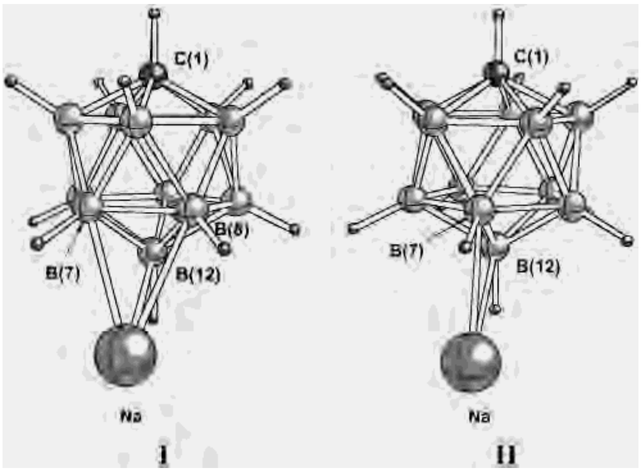

Figure 4. Ball and stick representation of the MP2/6-31G* calculated structures for Na[*closo*-CB$_{11}$H$_{12}$] showing the μ^3 (**I**) and μ^2 (**II**) bridging modes of the Na ion, respectively.

Table 3. Comparison of Experimental and Theoretical ^{11}B NMR Shifts (δ) for Various Salts of [*closo*-CB$_{11}$H$_{12}$]$^-$

	experiment[a]			calculated[b]			
	[NBu$_4$]$^+$	[Ag]$^+$	**1**	none	**I**	**III**[c]	**IV**
B(12)	−8.0	−11.9	−12.4	−6.9	−12.5	−10.1	−10.8
B(7)−B(11)	−14.1	−15.0	−15.7	−13.8	−15.3	−14.4	−14.9
B(2)−B(6)	−16.9	−15.0	−15.7	−17.8	−15.4	−16.7	−16.3

[a] Measured in CD$_2$Cl$_2$. [b] Averaged values at the GIAO-B3LYP/6-311G*//MP2/6-31G* level. [c] Averaged values at the GIAO-B3LYP/6-311G*//HF/6-31G* level.

{(PPh$_3$)Ag}$^+$ being nominally isolobal with a proton.[25] Because observed NMR data for Ag[*closo*-CB$_{11}$H$_{12}$] show 5-fold symmetry with the greatest perturbation from [NBu$_4$][*closo*-CB$_{11}$H$_{12}$] observed for B(7)−B(12) (Figure 3), the metal ion must be fluxional over all triangular faces involving the B(12) vertex. In agreement with this, the symmetry-constrained minimum **II** with the sodium atom bridging between B(7) and B(12) is only ca. 3.0 kcal mol^{-1} higher in energy than **I**. This small energy difference supports the metal ion being fluxional over the five triangular faces of the cage in solution, moving from face to face via bridging a B−B vertex. This low calculated energy barrier is also reflected experimentally by the fact that {Ag(PPh$_3$)},[10] {Rh(cod)},[16] and {Rh(PPh$_3$)$_2$}[26] fragments are highly fluxional over the lower surfaces of [*closo*-CB$_{11}$H$_{12}$]. Values obtained by averaging the calculated ^{11}B NMR shifts (at B3LYP/6-311G*) generated from the optimized geometry of Na[*closo*-CB$_{11}$H$_{12}$] **I** are in very good agreement with observed ^{11}B chemical shifts for Ag[*closo*-CB$_{11}$H$_{12}$] and **1** in CD$_2$Cl$_2$ (Table 3). Importantly, the computed ^{11}B shifts generated from the MP2/6-31G* geometry[27] for "free" [*closo*-CB$_{11}$H$_{12}$]$^-$ are also in good agreement with observed shifts for Ag[CB$_{11}$H$_{12}$] in acetone and [NBu$_4$][CB$_{11}$H$_{12}$] in CD$_2$Cl$_2$ (Table 3).

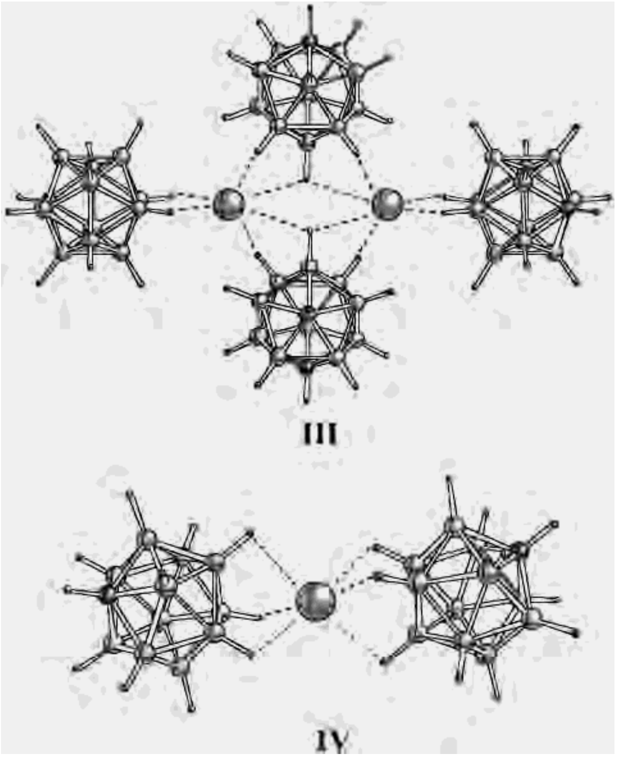

Figure 5. Ball and stick representations of the calculated structures for {Na$_2$[*closo*-CB$_{11}$H$_{12}$]$_4$}$^{2-}$ **(III)** (HF/6-31G*) and {Na[*closo*-CB$_{11}$H$_{12}$]$_2$}$^-$ (**IV**) (MP2/6-31G*).

These changes in the calculated boron chemical shifts on going from optimized geometries of Na[*closo*-CB$_{11}$H$_{12}$] to "free" [*closo*-CB$_{11}$H$_{12}$]$^-$ mirror those observed experimentally in solution for Ag[*closo*-CB$_{11}$H$_{12}$] on going from a noncoordinating solvent (e.g., CD$_2$Cl$_2$) to a coordinating solvent (e.g., acetone). Particularly noteworthy is that all the chemical shift changes observed experimentally are accurately reflected in the calculations, with both the upfield shifts for B(12) and B(7)−B(11) along with the more subtle downfield shift of B(2)−B(6) being reproduced. It is clear from these computations that metal−carborane interactions exist in noncoordinating solvents for Ag[*closo*-CB$_{11}$H$_{12}$] and thus, by implication, also for **1**, confirming our experimental observations. The geometry optimization of the dianion {Na$_2$(*closo*-CB$_{11}$H$_{12}$)$_4$}$^{2-}$ (**III**), as a model geometry for the dianion in **1**, further demonstrates that replacement of [Na]$^+$ for [Ag]$^+$ is valid, showing a similar structural motif at the HF/6-31G* level of theory as that found in the X-ray structure of **1** (Figure 5), with only the small twist of the bridging carborane cages not being reproduced. However, these calculations do not determine the molecular structures of either **1** or Ag[*closo*-CB$_{11}$H$_{12}$] in a noncoordinating solvent, that is, whether the structural motif of the dianion in **1** is retained in solution and whether Ag[CB$_{11}$H$_{12}$] is a discrete monomer, dimer, or oligomer in solution. In an attempt to address this, we have performed the same ab initio/GIAO/NMR calculations on {Na[*closo*-CB$_{11}$H$_{12}$]$_2$}$^-$, **IV**, and for {Na$_2$(*closo*-CB$_{11}$H$_{12}$)$_4$}$^{2-}$, **III**, although for this latter compound the computationally less intensive HF/6-31G* basis set was used because of the relatively large number of atoms in the molecule. The calculated geometries of **III** and **IV** are presented in Figure 5, which shows that for **IV** the sodium ion is η^3-sandwiched between two carborane anions.

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The averages of the calculated ^{11}B NMR shifts (at B3LYP/6-311G*) generated from these optimized geometries are given in Table 3 and show a close similarity to both those calculated for **I** and observed for **1** and Ag[*closo*-$CB_{11}H_{12}$] in CD_2Cl_2, even though model compound **III** was geometry optimized at a lower level of theory (HF/6-31G*) and silver has been substituted for sodium. The match is nevertheless a good one, with the difference between experiment and theory when **1** and **III** are compared ranging between 2.3 and 1.0 ppm. Moreover, the calculated shifts for **III** and **IV** show the upfield shift of the B(12) vertex and a compression of the two integral 5-B signals, as is observed experimentally for **1**. The close similarity of all these data (compound **1**, model compounds **I**, **III**, and **IV)** suggests that the actual solution structure, as determined by ^{11}B NMR spectroscopy, is ambiguous with regard to the degree of aggregation, although it is clear that significant Ag···{HB} interactions do occur in noncoordinating solvent. However, it is more than likely that a species such as [Ag(IMes)$_2$][Ag(*closo*-$CB_{11}H_{12})_2$] (model compound **IV**) exists as the predominant species in solution, similar to that observed for [Ag(*closo*-$CB_{11}H_6Br_6)_2]^-$.[8]

Conclusions

Addition of IMes to Ag[*closo*-$CB_{11}H_{12}$] results in the formation of the novel complex [(IMes)$_2$Ag]$_2$[Ag$_2${*closo*-$CB_{11}H_{12}\}_4$] in the solid-state, an anion in which each silver is surrounded by three carborane units. In CD_2Cl_2 solution, the Ag−carborane interactions are still present, as evidenced by significant downfield shifts being observed in the ^{11}B NMR spectrum. That these shifts are due to Ag···{HB} interactions is confirmed by the following: (i) The ^{11}B chemical shifts of Ag[*closo*-$CB_{11}H_{12}$] in coordinating solvent (acetone) and [NMe$_4$][*closo*-$CB_{11}H_{12}$] in CD_2Cl_2 are similar and closely match the computed ^{11}B shifts for “naked” [*closo*-$CB_{11}H_{12}]^-$. (ii) Calculated ^{11}B chemical shifts for Na[*closo*-$CB_{11}H_{12}$], {Na[*closo*-$CB_{11}H_{12}]_2\}^-$, and {Na$_2$[*closo*-$CB_{11}H_{12}]_4\}^{2-}$ which all have metal cation−anion interactions agree well with experimental ^{11}B data measured for **1** and Ag[*closo*-$CB_{11}H_{12}$] in CD_2Cl_2, suggesting that both silver complexes form significant ion-pairs in solution with similar structural features. This close match between calculated and experimentally determined chemical shifts initially surprised us given the disparity in the relative hardness of the two cations $[Na]^+$ and $[Ag]^+$. However, this perhaps suggests that the $[Ag]^+$ interactions with the cage periphery in [*closo*-$CB_{11}H_{12}$] are in fact more electrostatic than covalent (agostic) in nature than previously assumed, as we have suggested previously.[10] We have also shown that the previously proposed model for the interactions of metal fragments across the lower surface of [*closo*-$CB_{11}H_{12}]^-$ in solution may be confirmed by the calculations reported here.

Overall, these results show that metal cation−carborane anion interactions significantly affect the ^{11}B NMR shifts of the simple salts of carborane anions and that the solvent and the conjugate cation both need to be taken into account when comparing the ^{11}B chemical shifts of different salts.

Experimental

All manipulations were carried out under an argon atmosphere using standard Schlenk line or drybox techniques. Hexane and toluene were distilled from sodium. NMR spectra were measured on Brüker Advance 300 MHz and Varian Mercury 400 MHz FT-NMR spectrometers in CD_2Cl_2 solutions. Residual protio solvent was used as reference (*δ*, ppm: CD_2Cl_2 5.33) in ^{1}H NMR spectra. ^{11}B NMR spectra were referenced to $BF_3{\cdot}OEt_2$ (external). Coupling constants are given in hertz. Spectra were recorded at room temperature in CD_2Cl_2 solutions. Elemental analysis was performed in-house in the Department of Chemistry, University of Bath. The compounds Ag[*closo*-$CB_{11}H_{12}$] [2] and IMes[28] were prepared by published procedures or slight variations thereof. [NBu$_4$][*closo*-$CB_{11}H_{12}$] was prepared by metathesis of Cs[*closo*-$CB_{11}H_{12}$] with [NBu$_4$]Cl in CH_2Cl_2, filtration, and crystallization from CH_2Cl_2/hexanes.

[(IMes)$_2$Ag]$_2$[Ag$_2${*closo*-$CB_{11}H_{12}\}_4$] (1). IMes (55 mg, 0.18 mmol) was dissolved in toluene (5 mL) and added dropwise to a Schlenk tube charged with Ag[*closo*-$CB_{11}H_{12}$] (47 mg, 0.19 mmol) dissolved in toluene, and then the mixture stirred for 16 h. This solution was cannula filtered and the toluene removed in vacuo. The resulting solid was dissolved in the minimum volume of toluene and crystals of product grown at −80 °C for 5 days. The solvent was decanted and the resulting product dried under high vacuum to yield 46 mg (46%) of white crystalline solid.

^{1}H{^{11}B}: 1.57 (s, 10H, BH), 1.65 (s, 12H, o-CH_3), 1.69 (s, 10H, BH), 2.25 (s, 2H, BH), 2.32 (s, 2H, CH_{cage}), 2.35 (s, 6H, p-CH_3), 6.85 (s, 8H, m-CH), 7.00 (s, 4H, NCH). ^{11}B: −12.4 [d, 2B, *J*(BH) 125], −15.7 [d, 10B + 10B coincidence, *J*(BH) 145]. ^{13}C{^{1}H}: 17.8 (s, CH_3), 21.7 (s, CH_3), 55.3 (s br, CH_{cage}), 123.6 (s, NCCN), 129.9 (s, C_{phenyl}), 135.3 (s, C_{phenyl}), 135.6 (s, C_{phenyl}), 140.2 (s, C_{phenyl}), 183.6 [dd, NCN, *J*(^{109}AgC) 208, *J*(^{107}AgC) 180]. Calcd: %C, 47.6; %H, 6.48; %N, 5.04. Found: 47.7%, 6.55%, 4.93%.

X-ray Crystallography. The crystal structure data for compound **1** were collected on a Nonius Kappa-CCD diffractometer at 150 K. The asymmetric unit in **1** consists of one biscarbene silver moiety and of a fragment based on a silver atom and two carborane anions. The second fragment in the asymmetric unit is proximate to a crystallographic inversion center, which serves to generate a carborane bridged dimer where each of the symmetry related silver atoms are terminally coordinated to a second carborane cage. It is noteworthy that the bridging carborane is disordered in a 1:1 ratio between positions B(21) to B(32) and B(41) to B(52), respectively. The presence of disorder precluded accurate assignment of the cage carbon in the bridging carborane, and hence, all atoms therein were refined as borons. Assignment of the cage carbon in the terminally bound cage was unambiguous. Structure solution followed by full-matrix least squares refinement was performed using the SHELX suite of programs throughout.[29] All non-hydrogen atoms were treated anisotropically, and hydrogen atoms were included at calculated positions throughout. Diagrams were produced using ORTEX.[30]

Computational. All ab initio computations were carried out with the Gaussian 98 package.[31] The geometries discussed here were first optimized at the HF/6-31G* level with no symmetry constraints for **I**, **III**, and **IV** and C_s symmetry constraints for **II**. Frequency calculations were computed on these optimized geometries at the

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HF/6-31G* level for imaginary frequencies. None were found for **I**, **III**, and **IV**, and one imaginary frequency was found for geometry **II**. Optimization of geometries **I**, **II**, and **IV** were then carried out at the computationally intensive MP2/6-31G* level. NMR shifts were calculated on these MP2-optimized geometries at the GIAO-B3LYP/6-311G* level. Theoretical ^{11}B chemical shifts at the GIAO-B3LYP/6-311G*//MP2/6-31G* level listed in the table have been referenced to B_2H_6 (16.6 ppm[32]) and converted to the usual $BF_3 \cdot OEt_2$ scale: $\delta(^{11}B) = 102.83 - \sigma(^{11}B)$. For ^{11}B shifts at the GIAO-B3LYP/6-311G*//HF/6-31G* level, the equation $\delta(^{11}B) = 102.49 - \delta(^{11}B)$ was used. Relative energies were computed at the MP2/6-31G* level with ZPE (calculated at HF/6-31G*) corrections scaled by 0.89.

Acknowledgment. EPSRC and Royal Society are acknowledged for research fellowships (M.A.F. and A.S.W., respectively). The University of Bath is also thanked (N.J.P.). EPSRC/JREI are acknowledged for funding for a Nonius Kappa-CCD diffractometer (Bath) and for a high performance computer (Durham). The referees of this paper are thanked for useful comments.

Supporting Information Available: Tables giving crystallographic data and structure refinement details, positional and thermal parameters, and bond distances and angles for complex **1**, and computational details for structures **I** to **IV**. This material is available free of charge via the Internet at http://pubs.acs.org.

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