

Silver–Phosphine Complexes of the Highly Methylated Carborane Monoanion [*closo*-1-H-CB₁₁Me₁₁][−]

Adam J. Clarke,[‡] Michael J. Ingleson,[†] Gabriele Kociok-Köhn,[†] Mary F. Mahon,[†]
Nathan J. Patmore,[†] Jonathan P. Rourke,[‡] Giuseppe D. Ruggiero,[†] and
Andrew S. Weller^{*†}

Contribution from the Department of Chemistry, University of Bath, Bath BA2 7AY, UK, and
Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK

Received August 28, 2003; E-mail: a.s.weller@bath.ac.uk

Abstract: The synthesis of the silver(I) salt of the highly methylated carborane anion [*closo*-1-H-CB₁₁Me₁₁][−] is described, Ag[*closo*-1-H-CB₁₁Me₁₁] **1**, which in the solid state shows close intermolecular Ag⋯H₃C contacts. Addition of various monodentate phosphines to **1** results in the formation of the complexes (R₃P)–Ag[*closo*-1-H-CB₁₁Me₁₁] [R = Ph, **2**; cyclohexyl (C₆H₁₁), **3**; (3,5-Me₂-C₆H₃), **4**]. All these complexes show close intermolecular Ag⋯H₃C contacts in the solid state that are considerably shorter than the sum of the van der Waals radius of methyl (2.00 Å) and the ionic radius of silver(I) (1.29 Å). For **2** and **3** there are other close intermolecular Ag⋯H₃C contacts in the solid state, arising from proximate carborane anions in the crystal lattice. Addition of methyl groups to the periphery of the phosphine ligand (complex **4**) switches off the majority of these interactions, leaving essentially a single cage interacting with the cationic silver–phosphine fragment through three CH₃ groups. In solution (CD₂Cl₂) Ag⋯H₃C contacts remain, as evidenced by both the downfield chemical shift change and the significant line-broadening observed for the cage methyl signals. These studies also show that the metal fragment is fluxional over the surface of the cage. The Ag⋯H₃C interactions in solution may be switched off by addition of a stronger Lewis base than [*closo*-1-H-CB₁₁Me₁₁][−]. Thus, addition of [NBu₄][*closo*-1-H-CB₁₁H₅Br₆] to **2** affords (Ph₃P)Ag[*closo*-1-H-CB₁₁H₅Br₆], while adding Et₂O or PPh₃ affords the well-separated ion-pairs [(Ph₃P)(L)Ag][*closo*-1-H-CB₁₁Me₁₁] (L = OEt₂ **5**, PPh₃ **6**), both of which have been crystallographically characterized. DFT calculations on **2** (at the B3LYP/DZVP level) show small energy differences between the possible coordination isomers of this compound, with the favored geometry being one in which the {(Ph₃P)Ag}⁺ fragment interacts with three of the {BCH₃} vertices on the lower surface of the cage, similar to the experimentally observed structure of **4**.

Introduction

The peralkylated boranes based on [*closo*-CB₁₁R₁₂][−] (R = Me,^{1,2} R = Et³) and [*closo*-B₁₂Me₁₂]^{2−4} are of significant contemporary interest, being negatively charged, weakly coordinating,⁵ “alkane balls” that also have a van der Waals diameter close to C₆₀ (ca. 10 Å). The alkyl shroud surrounding these icosahedral carboranes allows the isolation of stable radical species⁶ which are also of potential synthetic use as lipophilic strong oxidants.⁷ The monoanion [*closo*-CB₁₁Me₁₂][−] has been used as a novel electrolyte,² as a partner with lithium to mediate

pericyclic rearrangements⁸ and can be used to isolate reactive cations such as [(*n*-Bu)₃Sn]⁺.⁷ These anions complement the halogenated monocarboranes⁹ exemplified by [*closo*-1-H-CB₁₁H₅Br₆][−], [*closo*-1-H-CB₁₁Me₅Br₆][−], and [*closo*-1-Et-CB₁₁F₁₁][−], which have been used to stabilize highly reactive complexes such as protonated benzene,¹⁰ naked [SiR₃]⁺,¹¹ [AlEt₂]⁺,¹² and “nonclassical” carbonyls.¹³ Given this interest, and the general research effort surrounding the use of weakly coordinating anions in transition-metal-mediated synthesis by cationic Lewis acidic complexes, especially those partnered with the fluorinated tetraphenyl borates,¹⁴ the d-block metal chemistry of [*closo*-CB₁₁Me₁₂][−] is of considerable contemporary interest. We have recently reported the synthesis, characterization, and catalytic

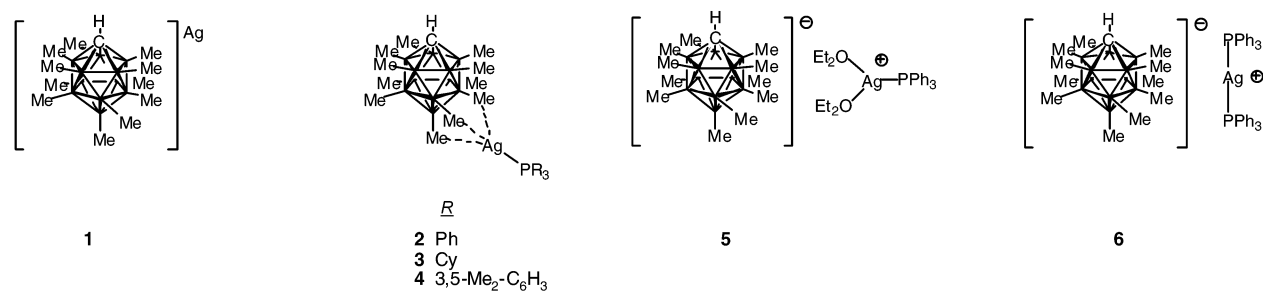
[†] University of Bath.

[‡] University of Warwick.

- King, B. T.; Janousek, Z.; Gruner, B.; Trammell, M.; Noll, B. C.; Michl, J. *J. Am. Chem. Soc.* **1996**, *118*, 3313.
- King, B. T.; Zharov, I.; Michl, J. *Chem. Innovation* **2001**, 24.
- Tsang, C. W.; Xie, Z. W. *Chem. Commun.* **2000**, 1839.
- (a) Peymann, T.; Knobler, C. B.; Khan, S. I.; Hawthorne, M. F. *Inorg. Chem.* **2001**, *40*, 1291. (b) Peymann, T.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1999**, *121*, 5601.
- Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927.
- (a) King, B. T.; Noll, B. C.; McKinley, A. J.; Michl, J. *J. Am. Chem. Soc.* **1996**, *118*, 10902. (b) Peymann, T.; Knobler, C. B.; Hawthorne, M. F. *Chem. Commun.* **1999**, 2039.
- Zharov, I.; King, B. T.; Havlas, Z.; Pardi, A.; Michl, J. *J. Am. Chem. Soc.* **2000**, *122*, 10253.

- Moss, S.; King, B. T.; Mejjere, A. d.; Kozhushko, S. I.; Eaton, P. E.; Michl, J. *Org. Lett.* **2001**, *3*, 2375.
- Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133.
- Reed, C. A.; Kim, K. C.; Stoyanov, E. S.; Stasko, D.; Tham, F. S.; Mueller, L. J.; Boyd, P. D. W. *J. Am. Chem. Soc.* **2003**, *125*, 1796.
- Kim, K. C.; Reed, C. A.; Elliott, D. W.; Mueller, L. J.; Tham, F.; Lin, L. J.; Lambert, J. B. *Science* **2002**, *297*, 825.
- Kim, K. C.; Reed, C. A.; Long, G. S.; Sen, A. *J. Am. Chem. Soc.* **2002**, *124*, 7662.
- Lupinetti, A. J.; Havighurst, M. D.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1999**, *121*, 11920.

Chart 1



competency in hetero Diels–Alder reactions, of $[(\text{PPh}_3)_n\text{Ag}]^+$ ($n = 1, 2$) complexes of $[\textit{closo}\text{-}1\text{-H-CB}_{11}\text{H}_5\text{Br}_6]^-$ and $[\textit{closo}\text{-}1\text{-H-CB}_{11}\text{H}_{11}]^-$ ^{15,16} which have structures in the solid and solution states that are contact ion pairs. Extending structural studies to the silver–phosphine complexes of $[\textit{closo}\text{-CB}_{11}\text{Me}_{12}]^-$, or its derivatives, is interesting for a number of reasons. In terms of coordinating ability the alkylated carborane would be expected to sit at the far end of the nucleophilicity scale for carborane monoanions, i.e., $[\textit{closo}\text{-}1\text{-H-CB}_{11}\text{H}_{11}]^- > [\textit{closo}\text{-}1\text{-H-CB}_{11}\text{H}_5\text{Br}_6]^- > [\textit{closo}\text{-CB}_{11}\text{Me}_{12}]^-$, making the comparative solid-state and solution structures of $[(\text{PR}_3)_n\text{Ag}]^+$ salts of $[\textit{closo}\text{-CB}_{11}\text{Me}_{12}]^-$ of interest, especially with regard to the degree of interaction between the metal fragment and the carborane methyl groups. For example, in a weakly coordinating solvent, such as CH_2Cl_2 , a negligible interaction between the cation and anion would result in silver–solvent complexes,¹⁷ while a stronger one would possibly engender *intermolecular* $\text{Ag}\cdots\text{methyl}$ interactions, which have significant contemporary relevance with regard to metal–alkane complexes.^{18–20} As far as we are aware, there are no reported examples of intra- or intermolecular (e.g., agostic or σ -complex, respectively) $\text{Ag}\cdots\text{HC}$ interactions reported in the literature, unlike the large number of group 1 and transition-metal complexes that show close intramolecular $\text{M}\cdots\text{HC}$ contacts.^{21,22} In a more general sense, the d-block chemistry of $[\textit{closo}\text{-CB}_{11}\text{Me}_{12}]^-$ or its derivatives is unknown; thus, any structural and spectroscopic markers that could be uncovered would be of benefit to future developments of the chemistry surrounding these fascinating anions.

We report here a range of silver–phosphine complexes with the simple $\text{C}_{\text{cage}}\text{-H}$ derivative of $[\textit{closo}\text{-CB}_{11}\text{Me}_{12}]^-$, namely $[\textit{closo}\text{-}1\text{-H-CB}_{11}\text{Me}_{11}]^-$, by the synthesis of $(\text{PR}_3)_n\text{Ag}(\textit{closo}\text{-}1\text{-H-CB}_{11}\text{Me}_{11})$, their resulting solid-state and solution structures, as well as DFT studies on $(\text{PPh}_3)\text{Ag}(\textit{closo}\text{-}1\text{-H-CB}_{11}\text{Me}_{11})$ (see

Chart 1). Aspects of this work have been communicated previously.²³

Results

The synthesis of $\text{NMe}_4[\textit{closo}\text{-CB}_{11}\text{Me}_{12}]$ by exhaustive methylation of $\text{NMe}_4[\textit{closo}\text{-}1\text{-Me-CB}_{11}\text{H}_{11}]$, using methyl triflate and a hindered base, was first reported by Michl and co-workers.¹ Various salts of this anion (Ag^+ , Li^+ , Cs^+) were also prepared.²⁴ As part of our study it was important to identify the specific vertices that may interact with the silver fragment in the solid state. As the spherical $[\textit{closo}\text{-CB}_{11}\text{Me}_{12}]^-$ anion can potentially suffer from positional disorder in the solid state, structural studies could be frustrated. It was thus necessary to label one of the vertices in the $[\textit{closo}\text{-CB}_{11}\text{Me}_{12}]^-$ anion to act as an unambiguous marker in structural determinations. The easiest way to do this is to leave the unique cage-carbon vertex unsubstituted (i.e. C–H). Using a slightly modified synthetic procedure which avoids the use of hindered base,^{2,25} the derivative salt $\text{Cs}[\textit{closo}\text{-}1\text{-H-CB}_{11}\text{Me}_{11}]$ can be routinely isolated as a compositionally pure solid in 60–70% isolated yield from readily available $\text{Cs}[\textit{closo}\text{-}1\text{-H-CB}_{11}\text{H}_{11}]$. The cesium cation is readily replaced by other simple cations such as $[\text{R}_4\text{N}]^+$ or Ag^+ using a two-phase $\text{H}_2\text{O}/\text{Et}_2\text{O}$ extraction. In this manner the starting material for this study, $\text{Ag}[\textit{closo}\text{-}1\text{-H-CB}_{11}\text{Me}_{11}]$ **1**, can be prepared in good yield from the Cs^+ salt. Addition of one equivalent of phosphine R_3P ($\text{R} = \text{Ph}$, C_6H_{11}), 3,5-Me₂-C₆H₃) to **1** in CH_2Cl_2 solution affords complexes of the formula $(\text{R}_3\text{P})\text{Ag}[\textit{closo}\text{-}1\text{-H-CB}_{11}\text{Me}_{11}]$. The solid-state structures of these complexes are discussed first, followed by solution and DFT studies.

[Ag]⁺ and {(R₃P)Ag}⁺ Complexes of [closo-1-H-CB₁₁Me₁₁]⁻: Solid-State Structures. **Ag[closo-1-H-CB₁₁Me₁₁]**, **1**. Crystallization of **1** from $\text{CH}_2\text{Cl}_2/\text{hexanes}$ affords colorless blocks suitable for a single-crystal X-ray diffraction study. Complex **1** is stable in the solid and solution state under an inert atmosphere, although solutions (CD_2Cl_2) are prone to decomposition on exposure to light. The solid-state structure of **1** is shown in Figure 1, and associated metrical data given in Table 2.

Complex **1** crystallizes in the $P2_1/a$ space group, with no positional disorder of the cage. In the asymmetric unit, the silver cation is not well separated from the anion, but is in relatively close contact with one of the methyl groups on the lower

- (14) (a) Chen, E. Y. X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391. (b) Kundig, E. P.; Saudan, C. M.; Bernardinelli, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1220. (c) Kundig, E. P.; Saudan, C. M.; Viton, F. *Adv. Synth. Catal.* **2001**, *343*, 51. (d) Lightfoot, A.; Schneider, P.; Pfaltz, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2897. (e) Pfaltz, A.; Blankenstein, J.; Hilgraf, R.; Hormann, E.; McIntyre, S.; Menges, F.; Schonleber, M.; Smidt, S. P.; Wstenberg, B.; Zimmermann, N. *Adv. Synth. Catal.* **2003**, *345*, 33.
- (15) Patmore, N. J.; Hague, C.; Cotgreave, J. H.; Mahon, M. F.; Frost, C. G.; Weller, A. S. *Chem. Eur. J.* **2002**, *8*, 2088.
- (16) Hague, C.; Patmore, N. J.; Frost, C. G.; Mahon, M. F.; Weller, A. S. *Chem. Commun.* **2001**, 2286.
- (17) van Seggen, D. M.; Hurlburt, P. K.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1995**, *34*, 3453.
- (18) (a) Crabtree, R. H. *Dalton Trans.* **2001**, 2437. Hall, C.; Perutz, R. N. *Chem. Rev.* **1996**, *96*, 3125. (b) Geftakis, S.; Ball, G. E. *J. Am. Chem. Soc.* **1998**, *120*, 9953.
- (19) Kubas, G. J. *Metal Dihydrogen and σ -Bond Complexes*; Kluwer: New York, 2001.
- (20) Shilov, A. E.; Shul'pin, G. B. *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*; Kluwer: Boston, 2000.
- (21) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

- (22) Braga, D.; Grepioni, F.; Biradha, K.; Desiraju, G. R. *Dalton Trans.* **1996**, 3925.
- (23) Ingleson, M. J.; Mahon, M. F.; Patmore, N. J.; Ruggiero, G. D.; Weller, A. S. *Angew. Chem., Int. Ed.* **2002**, *41*, 3694.
- (24) King, B. T.; Noll, B.; Michl, J. *Collect. Czech. Chem. Commun.* **1999**, *64*, 1001.
- (25) Michl, J. Prepared by an adaptation of the method given in ref 1; J. Michl, personal communication, 2002.

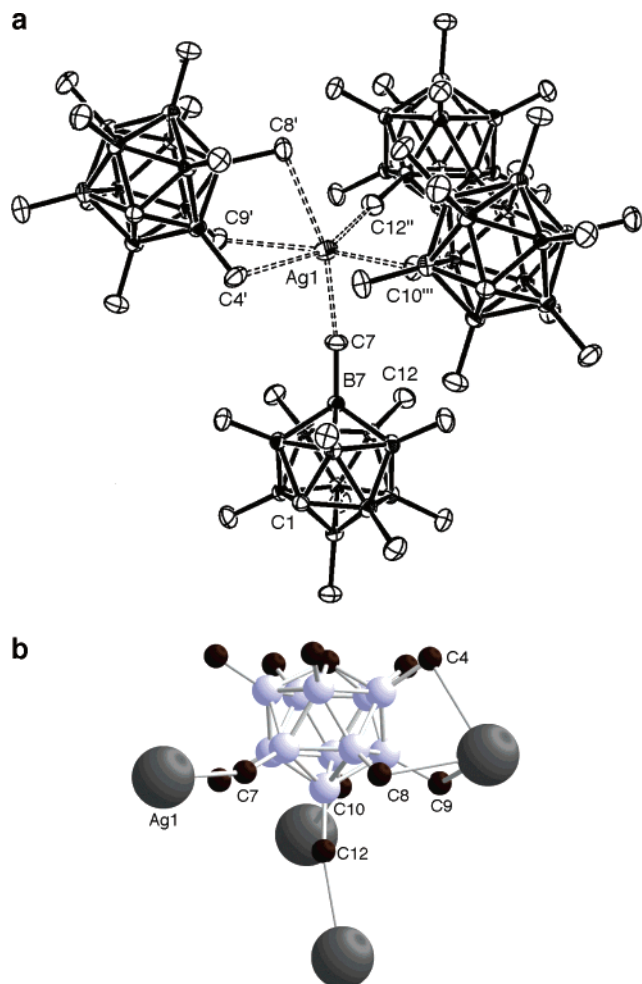


Figure 1. (a) Solid-state structure of compound **1** showing the Ag \cdots C contacts in the unit cell. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. (b) Coordination environment around a single carborane anion.

pentagonal belt of the carborane, Ag1–C7 2.653(2) Å. This distance is well within the sum (3.29 Å) of the van der Waals radius of methyl (2.00 Å) and the ionic radius of Ag(I) (1.29 Å).²⁶ Hydrogen atom positions were not located in the difference map and are thus not discussed. The close M \cdots H₃C contact in **1** is similar to that observed in $[(\eta^6-C_6H_6)_2Na][closo-CB_{11}Me_{12}]$, where the Na⁺ cation is in a van der Waals contact with a single methyl group on two separate carborane anions, forming a coordination polymer.²⁴ In **1** the Ag⁺ cation is in close contact with three further anions in the lattice, two showing a monodentate Ag \cdots C contact (C10''' and C12''), while the other is tridentate with three Ag \cdots C contacts (C4', C8', and C9'), this being a motif similar to that seen in $[(\eta^6-C_6H_6)Li][closo-CB_{11}Me_{12}]$,²⁴ in which the Li⁺ cation is closely associated with three methyl groups of one cage as well as a benzene molecule. The monodentate contacts in **1** are not linear, with the B–C–Ag angles ranging from 156° to 168° (Table 2). This coordination motif has structural similarities with LiBMe₄, which also shows two different types of close Li \cdots CB contacts, linear monodentate and bidentate, forming an extended planar sheet in the solid state.²⁷ The arrangement of the four carborane

anions around the silver in **1** affords a distorted octahedral coordination environment around the metal center. Viewed alternatively, each carborane anion is closely associated with four Ag⁺ cations (Figure 1b)—the closest Ag–Ag distance being 6.567 Å. Overall, this results in a three-dimensional coordination polymer in the crystal lattice (see Supporting Information). The six Ag \cdots C distances span the range 2.652(2)–3.089(2) Å, all comfortably within the sum of the van der Waals radius of methyl and the ionic radius of silver(I). The longest three contacts are all associated with the tridentate anion. These interactions result in C8–C9 being pushed slightly apart on the polyhedral surface (C8–C9 3.532 Å) compared to other equivalent distances in the cage (average 3.471 Å). There are no other significant differences in C–B or B–B bond lengths in the cage other than the expected differences associated with each pentagonal belt. Overall, the data presented here suggests that **1** is a closely associated ionic salt, given that the observed structure is one that maximizes the Coulombic attraction between four negatively charged carborane anions and Ag⁺. This view is further strengthened by noting that the Ag⁺ cations sit in a distorted tetrahedral hole formed from the four globular anions, reminiscent of the structure of hexagonal zinc sulfide (Wurtzite).

Simple silver salts of carborane monoanions all form coordination polymers in the solid state,^{15,28,29} as observed for **1**. In contrast, Ag(I) salts of pentafluorooxotellurate $[(OTeF_5)_6M]^-$ (M = Nb, Sb) anions¹⁷ form solvent (i.e., CH₂Cl₂) complexes rather than a close contact with Ag⁺ in the solid state. Even given that $[closo-1-H-CB_{11}Me_{11}]^-$ would be expected to be near the low end of the scale in terms of the relative coordinating ability of the carborane monoanions, in the solid state close anion–cation contacts are favored over coordination of CH₂Cl₂. This places the $[closo-1-H-CB_{11}Me_{11}]^-$ anion as being more coordinating than $[(OTeF_5)_6M]^-$. In CD₂Cl₂ solution Ag \cdots H₃C contacts are also observed, as discussed later.

(Ph₃PAg)[closo-1-H-CB₁₁Me₁₁]. Compound **1** is an excellent starting point for the investigation of the silver–phosphine complexes of $[closo-1-H-CB_{11}Me_{11}]^-$. Addition of one equivalent of PPh₃ to **1** in CH₂Cl₂ solution affords (Ph₃PAg)[*closo*-1-H-CB₁₁Me₁₁] **2** in good yield after recrystallization from CH₂Cl₂/hexanes. Details of the solid-state structure are presented in Figure 2 and Table 3.

Compound **2** crystallizes in the space group *P*-1, with the cage carbon vertex unambiguously located, and no positional disorder apparent in the cage. In the asymmetric unit there is one {Ag(PPh₃)}⁺ cation and one $[closo-1-H-CB_{11}Me_{11}]^-$ anion. These are in close contact through an intermolecular BCh₃ \cdots Ag(PPh₃) interaction from a lower pentagonal belt {BCh₃} vertex [Ag1–C7 2.544(2) Å]. Judged by the criterion of being well inside the sum of the van der Waals radius of methyl and the ionic radius of Ag⁺ (3.29 Å), this interaction can be considered as being significant. It is, however, longer than that found in the small number of crystallographically characterized Ag–C single bonds [e.g., (PPh₃)AgCH₂C₆F₅ 2.144(5) Å³⁰] but is of a similar distance to Ag–C contacts observed in silver–

(26) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*; Harper Collins: New York, 1993.

(27) Rhine, W. E.; Stucky, G.; Peterson, S. W. *J. Am. Chem. Soc.* **1975**, *97*, 6401.

(28) Shelly, K.; Finster, D. C.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 5955.

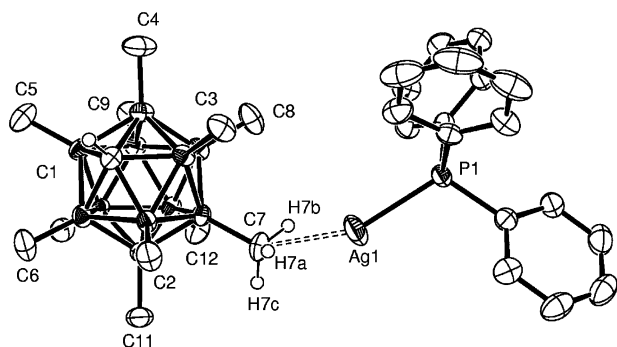
(29) (a) Tsang, C.-W.; Yang, Q.; Sze, E. T.-P.; Mak, T. C. W.; Chan, D. T. W.; Xie, Z. *Inorg. Chem.* **2000**, *39*, 5851. (b) Xie, Z. W.; Jelinek, T.; Bau, R.; Reed, C. A. *J. Am. Chem. Soc.* **1994**, *116*, 1907. (c) Xie, Z.; Wu, B.-M.; Mak, T. C. W.; Manning, J.; Reed, C. A. *Dalton Trans.* **1997**, 1213. (d) Ivanov, S. V.; Ivanova, S. M.; Miller, S. M.; Anderson, O. P.; Solntev, K. A.; Strauss, S. H. *Inorg. Chem.* **1996**, *35*, 6914.

Table 1. Crystal Data and Structure Refinement for Compounds 1, 2, 3, and 4

compound	1	2	3	4
empirical formula	C ₁₂ H ₃₄ AgB ₁₁	C ₃₀ H ₄₉ AgB ₁₁ P	C ₃₀ H ₆₇ AgB ₁₁ P	C ₃₆ H ₆₁ AgB ₁₁ P
formula weight	405.17	667.44	685.59	751.60
temperature	150(2)	173(2)	150(2)	150(2)
wavelength/Å	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	triclinic	monoclinic	monoclinic
space group	P2 ₁ /a	P-1	P2 ₁ /n	C2/c
a/Å	15.7000(1)	9.1840(1)	15.1270(2)	22.8460(6)
b/Å	8.9930(1)	13.6170(2)	15.5380(3)	12.7970(7)
c/Å	15.7050(2)	15.1520(3)	17.9050(2)	31.273(3)
α/°	90	111.637(1)	90	90
β/°	112.50	95.005(1)	113.011(1)	106.366(3)
γ/°	90	100.336(1)	90	90
volume/Å ³	2048.57(4)	1708.23(5)	3873.58(10)	8772.5(9)
Z	4	2	4	8
density (calculated)/mg/m ³	1.314	1.298	1.176	1.138
absorption coefficient/mm ⁻¹	0.975	0.658	0.581	0.519
F(000)	832	692	1456	3152
crystal size/mm	0.25 × 0.38 × 0.50	0.30 × 0.20 × 0.08	0.40 × 0.20 × 0.10	0.50 × 0.40 × 0.20
θ range for data collection/°	3.61–32.04	3.57–30.06	3.00–30.03	3.58–24.00
reflections collected	47563	38763	42682	31770
independent reflections	7100 [R(int) = 0.0345]	9965 [R(int) = 0.0417]	11139 [R(int) = 0.0472]	6200 [R(int) = 0.2107]
reflections observed (>2σ)	6230	7255	8769	2430
absorption correction	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents
data completeness	0.995	0.995	0.983	0.902
refinement method	full-matrix least-squares on F ²	full-matrix least-squares on F ²	full-matrix least-squares on F ²	full-matrix least-squares on F ²
data/restraints/parameters	7100/0/238	9965/0/433	11139/0/409	6200/0/430
goodness-of-fit on f ²	1.077	1.017	1.012	1.007
final R indices [I > 2σ(I)]	R ₁ = 0.0337 wR ₂ = 0.0853	R ₁ = 0.0378 wR ₂ = 0.0941	R ₁ = 0.0384 wR ₂ = 0.0879	R ₁ = 0.1008 wR ₂ = 0.2290
R indices (all data)	R ₁ = 0.0402 wR ₂ = 0.0895	R ₁ = 0.0627 wR ₂ = 0.1043	R ₁ = 0.0559 wR ₂ = 0.0966	R ₁ = 0.2633 wR ₂ = 0.3037
largest diff. peak and hole/e·Å ⁻³	1.611 and and -1.771	0.503 and and -0.859	0.607 and -0.897	1.118 and -0.472

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 1

Ag1–C7	2.653(2)	Ag1–C4'	3.067(2)	Ag1–C8'	2.832(2)
Ag1–C9'	3.089(2)	Ag1–C10'''	2.773(2)	Ag1–C12''	2.762(2)
C1–B2	1.711(2)	C1–B6	1.712(2)	C1–B3	1.712(2)
C1–B5	1.714(2)	C2–B2	1.588(2)	C3–B3	1.588(2)
C4–B4	1.597(2)	C5–B5	1.590(3)	C6–B6	1.595(2)
C7–B7	1.601(2)	C8–B8	1.603(2)	C9–B9	1.606(2)
C10–B10	1.611(2)	C11–B11	1.601(2)	C12–B12	1.608(2)
B7–C7–Ag1	158.78(13)	B4'–C4'–Ag1	94.18(11)	B8'–C8'–Ag1	101.08(11)
B9'–C9'–Ag1	95.86(10)	B10'''–C10'''–Ag1	156.05(12)	B12''–C12''–Ag1	168.48(14)
C7–Ag1–C8'	161.87(5)	C4'–Ag1–C12''	158.79(5)	C10'''–Ag1–C9'	166.61(5)

**Figure 2.** Molecular structure of compound 2. All hydrogen atoms, except those on C7 and C1 have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

arene complexes (2.47 Å).³¹ The X-ray data collected for 2 were of sufficient quality to freely locate and refine hydrogen atoms on C7 (H7a–c, Table 3). Given the usual caveats regarding the location of hydrogen atoms by X-ray crystallography, the

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 2

Ag1–P1	2.3871(5)	Ag1–C7	2.544(2)
Ag1–H7a	2.19(3)	Ag1–H7b	2.20(3)
Ag1–H7c	3.033	Ag–C9'	3.154(2)
Ag1–H9a'	2.73(4)	Ag1–H9b'	2.54(4)
Ag1–C12''	3.336(2)	Ag1–H12a''	2.45(3)
C7–H7A	0.93(3)	C7–H7B	0.93(3)
C7–H7C	0.93(4)	C7–B7	1.606(3)
P1–Ag1–C7	152.21(6)	B7–C7–Ag1	138.88(15)
H7b–C7–B7	109(2)	H7a–C7–B7	108(2)
H7c–C7–H7a	116(3)	H7c–C7–B7	112(2)
H7b–C7–H7a	114(2)	H7c–C7–H7b	97(2)

following observations can be made regarding the geometry of the Ag–C7 interaction. There are two shorter Ag–H distances, which are the same within experimental error (Ag–H7a 2.19 Å and Ag–H7b 2.20 Å) and one longer one (Ag–H7c 3.03

(30) Uson, R.; Laguna, A.; Uson, A.; Jones, P. G.; Meyer-Base, K. *Dalton Trans.* **1988**, 341.

(31) Griffith, E. A. H.; Amma, E. L. *J. Am. Chem. Soc.* **1974**, 96, 743.

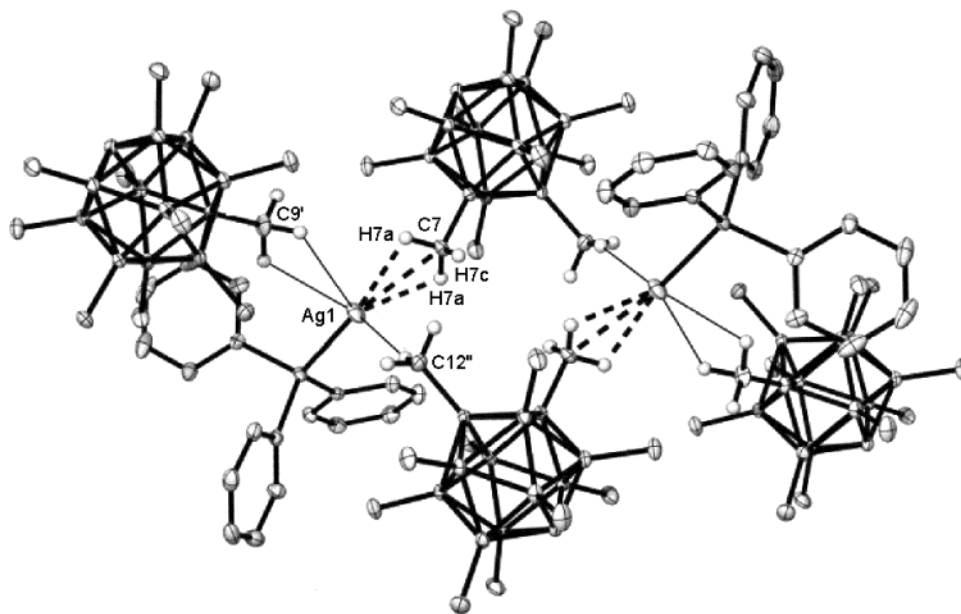


Figure 3. Extended structure of **2** in the solid state showing the close intermolecular Ag \cdots H₃C contacts from adjacent carborane methyl groups.

Å). The two closer Ag–H distances in **1** are at the longer range of previously reported bridging Ag–H–M [1.4–2.2 Å³⁶] or Ag–H–B [1.90–1.97 Å^{28,37}] interactions where the hydrogen atom has been located by X-ray crystallography. This asymmetry in the Ag–C contact is reflected in the B7–C7–Ag bond angle, which deviates significantly from 180° [138.88(15)°]. This could suggest that the {BCH₃} fragment acts as a bidentate ligand to {Ag(PPh₃)⁺} similar to that observed in LiBMe₄,²⁷ [(1,3-(SiMe₃)₂C₅H₃)₂ZrMe(μ -Me)B(C₆F₅)₃],³² and [(1,2-Me₂C₅H₃)₂-ZrMe(μ -Me)B(C₆F₅)₃].³³ [The term “bidentate” is not meant to refer to the presence of a well-defined (i.e., covalent) Ag–H or Ag–C bond but merely to the location of the hydrogen or carbon atoms relative to the metal fragment.] Isolated, symmetric, end-on, intermolecular interactions between a metal center and a {H₃C} group have been observed in (η^5 -C₅Me₅)₂-Yb(μ -Me)Be(η^5 -C₅Me₅),³⁴ and we have recently described the structure of [(η^5 -C₅H₅)₂ZrMe(12- μ -Me-1-*closo*-CB₁₁HMe₁₀)] in which a single [*closo*-1-*H*-CB₁₁Me₁₁] cage methyl group interacts end-on with the metal fragment.³⁵

These relatively close intermolecular Ag \cdots HC contacts suggest that the methyl group may be forming a σ -complex¹⁹ with the silver–phosphine fragment. A significant σ -interaction between C–H and Ag would be expected to result in a lengthening of the C–H bond and a change in the B–C–H bond angle from pseudotetrahedral for those C–H bonds involved.²¹ In **2** this is not observed; all the C–H bonds associated with C7 are the same length [0.93 Å] as are the B–C–H angles [average 110(2)°] within experimental error.

These values are close to those expected for a sp³ methyl group. Overall, this suggests that the Ag \cdots H₃C interaction in complex **2** is best described as being predominately ionic as may be expected for a closed-shell d¹⁰ metal center. This is also similar to the bonding in closed-shell alkyllithium species³⁸ and group 4 metallocene/[H₃CB(C₆F₅)₃][−] contact ion-pairs³⁹ that is best described as being essentially ionic with a small, but non-negligible, covalent contribution. The silver–phosphine bond distance [2.3871(5) Å] is at the shorter end of those reported,^{15,40} suggesting a relatively strong Ag–P bond,⁴¹ and by implication a relatively weak Ag \cdots anion interaction. This is also reflected in the large value for *J*(AgP) observed in solution for **2** (vide infra).

As solid-state packing effects could have a significant influence on the coordination environment around the d¹⁰ silver center, the asymmetric unit should not be considered in isolation. In fact, the CH₃(7)–Ag interaction observed in the asymmetric unit is not the only close CH₃ \cdots Ag contact, and consideration of the extended lattice (Figure 3) shows that there are two more, albeit substantially longer, contacts from adjacent carborane anions in the lattice. Although these are closer to the sum (3.29 Å) of the van der Waals radius of methyl and the ionic radius of silver(I) [Ag \cdots C9' 3.154(2) Å, Ag \cdots C12'' 3.336(2) Å], they can be considered as having influence on the structure, judged by the fact that they force the P1–Ag1–C7 angle away from being linear [152.21(6)°]. The hydrogen atoms on each of these methyl groups were located in the difference map, and one methyl group is bidentate [CH₃(9')] with respect to Ag \cdots H close contacts, while the other is monodentate [CH₃(12'')]. These longer-range interactions further strengthen the structural simi-

(32) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, K. M. A. *Organometallics* **1994**, *13*, 2235.

(33) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015.

(34) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 5853.

(35) Ingleson, M. J.; Clarke, A.; Mahon, M. F.; Rourke, J. P.; Weller, A. S. *Chem. Commun.* **2003**, 1930.

(36) (a) Albinati, A.; Demartin, F.; Venanzi, L. M.; Wolfer, M. K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 563 and refs. therein. (b) Albinati, A.; Anklin, C.; Janser, P.; Lehner, H.; Matt, D.; Pregosin, P. S.; Venanzi, L. M. *Inorg. Chem.* **1989**, *28*, 1105. (c) Brunner, H.; Muschiol, M.; Neuhierl, T.; Nuber, B. *Chem. Eur. J.* **1998**, *4*, 168.

(37) Liston, D. J.; Reed, C. A.; Eigenbrot, C. W.; Scheidt, W. R. *Inorg. Chem.* **1987**, *26*, 2739.

(38) (a) Kaufmann, E.; Raghavachari, K.; Reed, A. E.; Schleyer, P. v. R. *Organometallics* **1988**, *7*, 1597. Nova, J. J.; Whangbo, M. H.; Stucky, G. D. *J. Org. Chem.* **1991**, *56*, 3181. (b) Scherer, W.; Sirsch, P.; Shorokhov, D.; McGrady, G. S.; Mason, S. A.; Gardiner, M. G. *Chem. Eur. J.* **2002**, *8*, 2324.

(39) Lanza, G.; I., F.; Marks, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 12764.

(40) Bachmann, R. E.; Andretta, D. F. *Inorg. Chem.* **1998**, *37*, 5657 and references therein.

(41) Bowmaker, G. A.; Hanna, J. V.; Rickard, C. E. F.; Lipton, A. S. *Dalton Trans.* **2001**, 20.

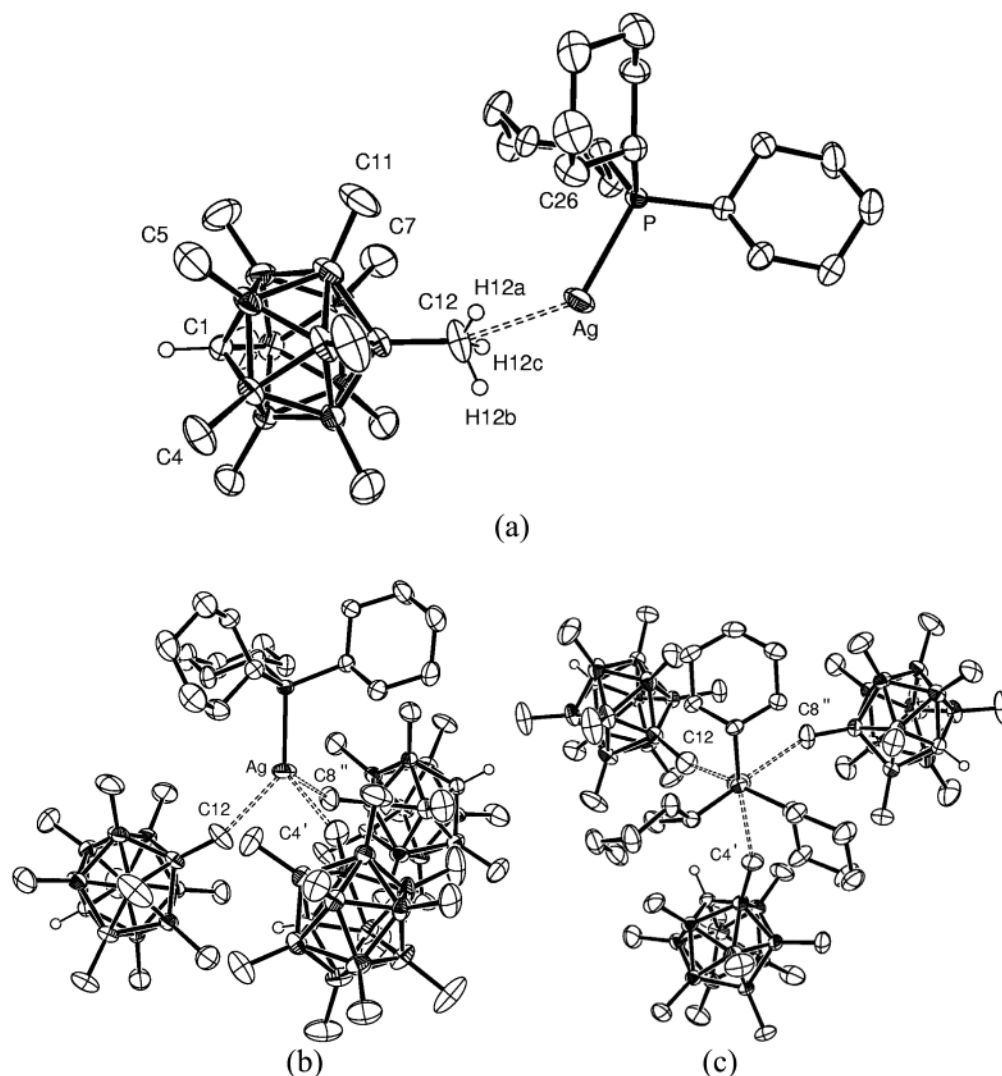


Figure 4. Molecular structure of compound **3**. (a) Asymmetric unit; (b) environment around Ag in the extended lattice [Ag–C12 2.608(2) Å, Ag–C4' 2.888(2) Å, Ag–C8'' 2.898(2) Å]; (c) viewed down the Ag–P axis. Thermal ellipsoids are shown at the 50% probability level.

larities between **2** and LiBMe₄, as both have multiple intermolecular M···H₃CB contacts in the solid state. Although these extended structures are not likely to be present in solution, some Ag···H₃CB interactions are retained, as demonstrated by ¹H, ¹¹B, and ¹H-¹¹B NMR experiments (vide infra).

Given the significant contemporary interest in isolating structurally characterized examples of intermolecular M···H₃C interactions with regard to putative intermediates in alkane activation,^{18–20} we were interested in the possibility of shutting off the extended interactions observed in the solid-state structure of **2**, thereby isolating any Ag···H₃CB contacts to those involving a single cage. Our reasons for doing this were twofold. First, isolating interactions to a single cage would be expected to more closely reflect the coordination environment of the {Ag(PPh₃)₃}⁺ fragment in solution. Second, a single cage interaction significantly reduces the complexity of the system when looking at Ag–methyl contacts. This would have the added benefit of allowing theoretical techniques that do not include solid-state or solution effects (gas-phase DFT) to more closely reflect the experimentally observed structure. The simplest way to approach this is to increase the steric bulk of the phosphine in the anticipation that the silver(I) center becomes

less accessible to multiple intermolecular interactions from bulky methylated carborane anions adjacent in the lattice. Efforts toward this are discussed next.

(P(C₆H₁₁)₃Ag)[*closo*-1-H-CB₁₁Me₁₁]. Addition of one equivalent of P(C₆H₁₁)₃ to **1** and recrystallization from CH₂Cl₂/pentane afforded crystalline (P(C₆H₁₁)₃Ag)[*closo*-1-H-CB₁₁Me₁₁] **3** in moderate isolated yield. The solid-state structure of **3** is shown in Figure 4. Compound **3** crystallizes in the space group *P2*₁/*n*, with no positional disorder observed, and the cage carbon vertex [C1] was unambiguously located. As found for **2**, in the asymmetric unit of **3** there is a single close BCH₃···Ag contact lying well within the sum of the van der Waals radius of CH₃ and the ionic radius of Ag⁺ [C12–Ag 2.608(2) Å], this time from the antipodal BCH₃(12) vertex. The hydrogen atoms on C12 were located in the difference map and refined freely. In contrast to **2**, this shows that there is only one relatively close Ag–H distance in **3** [Ag–H12c 2.21(5) Å] (although this is at the upper limit of reported Ag–H distances³⁶), while the other two are further away [Ag–H12a 2.38 Å, Ag–H12b 2.74 Å]. The silver–phosphine fragment is not located end-on to CH₃(12), but tilted significantly away from linear [B12–C12–Ag 157.04(18)°], similar to **2**. As for **2** the C–H

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex 3

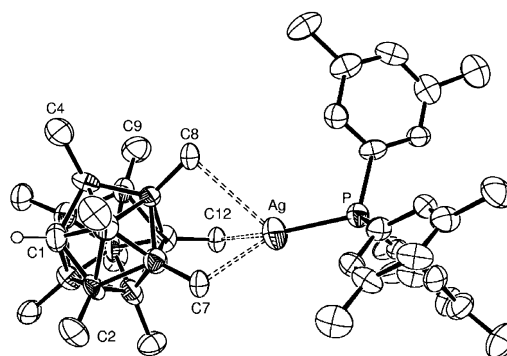
Ag–P	2.360(3)	Ag–C12	2.608(2)
Ag–C4'	2.888(2)	Ag–C8'''	2.898(2)
Ag–P	2.3881(4)	C12–Ag–C8''	92.92(8)
C4'–Ag–C12	88.50(8)	C4'–Ag–C8''	97.73(7)

angles and bond lengths around CH₃(12) do not deviate significantly from those expected for a methyl group [average C–H 0.95 Å and average B–C–H 114.6°].

In the extended lattice there are two other relatively close Ag–C distances from neighboring carborane methyl groups [Ag–C4' 2.888(2) and Ag–C8''' 2.898(2) Å] (Figure 4b). As in **2**, the C12–Ag1–P angle is forced away from linear [136.81(7)°] to accommodate these. These close contacts result in an approximate C_{3v} motif (Figure 4c) around the central silver atom [C4'–Ag–C12 88.50(8)°, C4'–Ag–C8''' 97.73(7)°, C12–Ag–C8'' 92.92(8)°]. The Ag–P bond length [2.3881(4)Å] is longer than that found in three-coordinate [P(C₆H₁₁)₃AgL] complexes (e.g., [P(C₆H₁₁)₃Ag(μ-Cl)]₂ 2.354(2) Å⁴³ and [P(C₆H₁₁)₃Ag{(pz)₂B(pz)₂}] 2.351 Å⁴⁴) but shorter than that found for four-coordinate complexes [e.g., [P(C₆H₁₁)₃AgI]₄ average Ag–P distance 2.43(1) Å⁴³ or (P(C₆H₁₁)₃)₂Ag(η²-NO₂) 2.460(1) Å⁴⁵].

Although P(C₆H₁₁)₃ is sterically more demanding than PPh₃ [cone angles 170° and 145°, respectively⁴²], the increase in cone angle is not enough to switch off the extended interactions in the lattice. Attempts to use bulkier phosphines than P(C₆H₁₁)₃ only led to mixtures. For example, addition of P(2-Me-C₆H₄)₃ (cone angle 198°) to **1** resulted in intractable mixtures of products. The implication is that too much steric shielding around the silver prevents close approach of even one bulky carborane anion, resulting in decomposition of the coordinatively unsaturated silver(I) center. Equivalent complexes using the same phosphine but with sterically less demanding anions are perfectly stable.⁴⁵ As for **2**, the coordination motif observed for **3** strongly suggests predominantly ionic bonding between Ag and carborane.

(P(3,5-Me₂-C₆H₃)₃Ag)[closo-1-H-CB₁₁Me₁₁]. As increasing the cone angle of the phosphine did not result in the switching-off of the extended interactions in the lattice, we attempted to remove, or at least substantially reduce, these by a slightly different but complementary approach. Taking cues from the extended solid-state structure of **2** (Figure 3), we reasoned that suitable placement of bulky groups in the 3,5-position on the phenyl rings might discourage the close approach of more than one large carborane anion with the silver(I) center, thus restricting the Ag···carborane interactions to a single cage. Addition of one equivalent of P(C₆H₃-3,5-Me₂)₃ to **1** and recrystallization from CH₂Cl₂/pentane afforded very air-sensitive crystals of relatively poor quality. Repeated attempts to obtain better-quality material were not successful. A single-crystal X-ray diffraction study on the best available sample (see Experimental Section for more detail) resulted in a structure refinement that was unambiguous in defining the gross structural

**Figure 5.** Molecular structure of compound **4**. Hydrogen atoms are omitted for clarity apart from that on C1. Ellipsoids are shown at the 50% probability level.**Table 5.** Selected Bond Lengths (Å) and Angles (deg) for Complex 4

Ag–P	2.360(3)	Ag–C12	2.554(10)
Ag–C7	2.785(10)	Ag–C8	3.166(10)
C12Ag–C7	83.5(3)	C12–Ag–C8	75.5(3)
C7–Ag–C8	71.7(3)		

features [R1 = 0.1008] but not adequate for the location of the hydrogen atoms. This showed that the complex formed was (P(3,5-Me₂-C₆H₃)₃Ag)(closo-1-H-CB₁₁Me₁₁), **4**, the molecular structure of which is shown in Figure 5, with selected bond lengths and angles given in Table 5.

Complex **4** crystallizes in the space group C_{2/c}, and there is no crystallographically imposed symmetry in the asymmetric unit, and no positional disorder of the cage is observed. The distal (in relation to the silver(I) center) steric bulk of the 3,5-methyl groups has switched off any significant extra interactions from carborane anions adjacent in the lattice, there being only three close intermolecular Ag···H₃C contacts from a single carborane anion. These come from three methyl groups all on the lower surface of the cage, consistent with the distribution of charge on the {BCH₃} vertices.⁴⁶ Two of these contacts are relatively short [Ag–C7 2.785(10) Å, Ag–C12 2.554(10) Å], while the other is longer [Ag–C8 3.166(10) Å]. However, all are well within the sum of the van der Waals radius of CH₃ and the ionic radius of silver(I) (3.29 Å) and can thus be considered as significant. There is an approach from an adjacent carborane anion in the lattice that distorts the silver–phosphine bond vector away from lying over the middle of the C7–C8–C12 face (as is predicted by DFT studies—see later). This also has the effect of compressing the C8–Ag–P angle compared with C7–Ag–P and C12–Ag–P [119, 131, and 143°, respectively]. The Ag–C contact from this adjacent carborane (Ag–C2' 3.726 Å) is long, lying just outside the combined van der Waals radii of methyl and silver (3.70 Å)²⁶ and we interpret this as efficient crystal packing of the globular carborane anion rather than a CH₃···Ag interaction per se. The Ag–P distance [2.360(3) Å] in **4** is slightly shorter than that found in **2**. However, the poor quality of the structure refinement means that any comparisons of the structural metrics for **4** must be interpreted with care and are not discussed further.

In terms of the coordination environment around silver, the tridentate motif observed in **4** is similar to the three close Ag···C contacts also seen **2** and **3**, where each silver center is

(42) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.(43) Bowmaker, G. A.; Effendy, Harvey, P. J.; Healy, P. C.; Skelton, B. W.; White, A. H. *Dalton Trans.* **1996**, 2459.(44) Effendy; Lobb, G. G.; Pettinari, C.; Santini, C.; Skelton, B. W.; White, A. H. *Dalton Trans.* **1998**, 2739.(45) Cingolani, A.; Effendy; Pelli, M.; Pettinari, C.; Santini, C.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **2002**, *41*, 6633.(46) McKee, M. I. *J. Am. Chem. Soc.* **1997**, *119*, 4220.

surrounded by three carborane methyl groups in the lattice. Unlike the previous two structures, in **4** it is three methyl groups from the *same* cage that interact with the silver(I) center. This switching-off of the extended interactions in the solid state can be traced back to the additional methyl groups on the phosphine phenyl rings, which effectively block the close approach of other carborane anions in the lattice. This results in a structure in which the $\{\text{Ag}(\text{PPh}_3)\}^+$ fragment gets as close as possible to a single cage, presumably to maximize ionic attractions between the anion and cation. This tridentate coordination is very similar to that observed for $[(\eta^6\text{-C}_6\text{H}_6)\text{Li}][\text{closo-CB}_{11}\text{Me}_{12}]$,²⁴ as well as the bidentate coordination mode observed in LiBMe_4 .²⁷ As **4** is the only example of the compounds studied here that shows close contacts between silver and only one carborane anion, it is perhaps the best model for the structure of these complexes in solution. In fact for **4**, as well as the other complexes reported here, there is evidence for $\text{Ag}\cdots\text{H}_3\text{CB}$ contacts still being present in solution, as is discussed next.

Solution Studies. All the complexes discussed thus far have close $\text{Ag}\cdots\text{H}_3\text{CB}$ contacts in the solid state. Of interest is whether these interactions remain in solution and if they can be observed. For the simple salt, **1**, comparison between NMR spectra in a coordinating solvent (acetone) and a solvent that does not generally favor the formation of solvent complexes (CH_2Cl_2) is informative. In d_6 -acetone complex **1** shows sharp, well-resolved signals for the cage methyl groups in the $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum [fwhm = ca. 1 Hz]. These are observed in a relative intensity of 15 H: 15 H: 3H demonstrating that the cage anion has C_{5v} symmetry in solution. This is confirmed by ^{11}B NMR spectroscopy, which shows the expected three singlets in a 1:5:5 ratio. In CD_2Cl_2 the cage methyl region in **1** changes significantly. The peaks are now broadened significantly [fwhm = ca. 30 Hz], suggesting that the cage methyl groups and the silver(I) center are interacting in solution. The ^{11}B NMR spectrum still shows C_{5v} symmetry, demonstrating that the silver(I) cation is fluxional over the surface of the cage. As far as chemical shift comparisons are concerned, making these when the solvent has been changed as significantly as from acetone to dichloromethane is difficult, as differences observed may be due to simple solvent effects rather than an indication of interactions per se. A more useful comparison can be made between **1** and $[\text{NBu}_4][\text{closo-1-H-CB}_{11}\text{Me}_{11}]$ in CD_2Cl_2 , as the tetrabutylammonium cation is expected to be innocent with regard to the cage anion. Changing the cation from $[\text{NBu}_4]^+$ to Ag^+ affords the same line width change in the $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum as is observed on changing from acetone to CD_2Cl_2 solvent, but the cage methyl signals now become bunched together with an apparent downfield change in chemical shift. We discuss this in more detail with regard to the monophosphine complexes, but it is clear that in acetone solution **1** forms a solvent separated ion pair, i.e., $[(\text{acetone})_n\text{Ag}]^+[\text{closo-1-H-CB}_{11}\text{Me}_{11}]^-$, while in CD_2Cl_2 a more closely associated ion pair results that has significant $\text{Ag}\cdots\text{H}_3\text{C}$ interactions, as judged by both the observed line-broadening and chemical shift change of the cage methyl groups. The polymeric structure of **1** observed in the solid state is unlikely to persist in solution. Possible solution structures could be oligomeric, perhaps related to those observed for $[(\text{IMes})_2\text{Ag}][\text{Ag}(\text{closo-1-H-CB}_{11}\text{H}_{11})_2]$ (IMes = 1,3-dimesitylimidazol-2-ylidene) that forms a $[\text{Ag}_2(\text{closo-1-H-CB}_{11}\text{H}_{11})_4]^{2-}$ dianion in the solid state⁴⁷ or

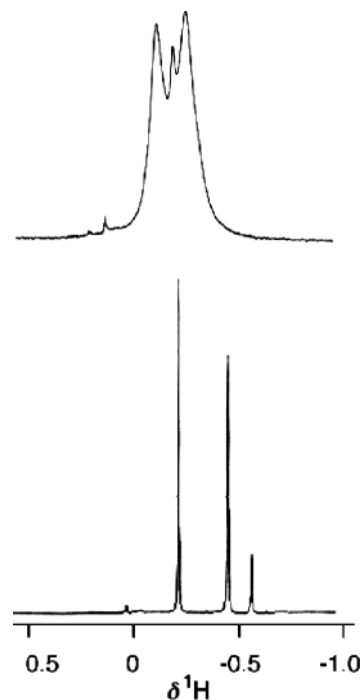


Figure 6. $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum (CD_2Cl_2) of the methyl region of complex **2** (top) and $[\text{NBu}_4][\text{closo-1-H-CB}_{11}\text{Me}_{11}]$ (bottom).

$[\text{Ag}(\text{closo-1-H-CB}_{11}\text{H}_5\text{Br}_6)_2]^-$ in which silver(I) is sandwiched between two cage anions.⁴⁸

Similar chemical shift changes and line broadenings are observed in the $^1\text{H}\{^{11}\text{B}\}$ NMR spectra of the monophosphine salts **2** to **4** when compared with $[\text{NBu}_4][\text{closo-1-H-CB}_{11}\text{Me}_{11}]$ in CD_2Cl_2 solution. Figure 6 shows this for **2**, but very similar spectra are observed for all the complexes **2**–**4**. Notable from Figure 6 is the significant line broadening [fwhm = ca. 30 Hz] and downfield chemical shift observed in these complexes compared with those in $[\text{NBu}_4][\text{closo-1-H-CB}_{11}\text{Me}_{11}]$ and that the 15 H: 3H: 15H relative intensity pattern is retained, corresponding to a 5:1:5 ratio of methyl groups and C_{5v} symmetry of the cage. As expected, the ^1H NMR spectra without broadband ^{11}B decoupling show these signals as being significantly broader due to quadrupolar relaxation from ^{11}B .

We have used a combination of $^1\text{H}\{^{11}\text{B}\}$ -selective, ^{11}B , ^1H – ^{11}B HMQC and ^{11}B – ^{11}B COSY NMR experiments to assign these methyl resonances to specific BCH_3 vertices on the anion. Given the C_{5v} symmetry observed in solution there are three different methyl group environments that the $\{\text{Ag}(\text{PR}_3)\}^+$ cation can interact with: upper pentagonal [$\text{BCH}_3(2-6)$], lower pentagonal [$\text{BCH}_3(7-11)$], and antipodal [$\text{BCH}_3(12)$]. By using the criteria that, on comparison with $[\text{NBu}_4][\text{closo-1-H-CB}_{11}\text{Me}_{11}]$, a chemical shift change of CH_3 groups in the $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum (alongside the observed changes in line-width) is an indication of a significant interaction, identification of the individual resonances should give information about which cage methyl groups interact with the metal fragment.

In the ^{11}B NMR spectra of complexes **2**–**4**, C_{5v} symmetry for the cage (1:5:5 ratio of resonances) is observed in all cases, and there is not a significant change in chemical shift compared

(47) Fox, M. A.; Mahon, M. F.; Patmore, N. J.; Weller, A. S. *Inorg. Chem.* **2002**, *41*, 4567.

(48) Xie, Z.; Bau, R.; Reed, C. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2433.

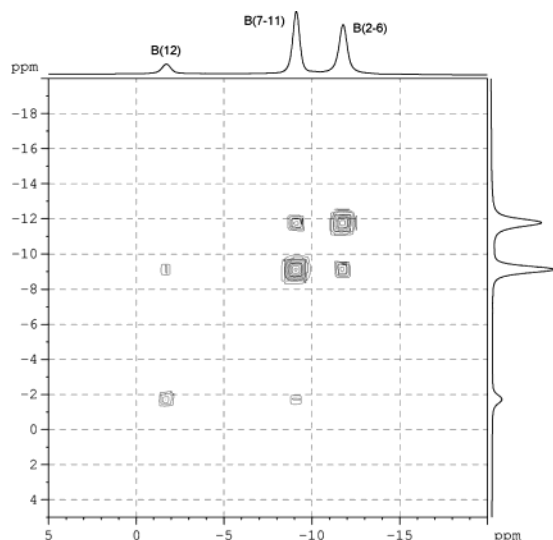


Figure 7. ^{11}B - ^{11}B COSY NMR spectrum of complex **4**.

with that of $[NBu_4][closo-1-H-CB_{11}Me_{11}]$, apart from B(12) moving ca. 1 ppm upfield on formation of the silver complexes. This contrasts to situations where a metal fragment interacts with the surface of $[closo-1-H-CB_{11}H_{11}]^-$ and significant upfield chemical shifts are observed for those vertices that interact through direct 3-center 2-electron M-H-B bonds.^{15,49} The lack of chemical shift position in **2-4** is not unexpected, given the relatively remote position of the boron vertex compared with the metal fragment. ^{11}B - ^{11}B COSY experiments were used to identify the three resonances observed in the ^{11}B NMR spectra and follow the order (low field to high field) $BCH_3(12)$, $BCH_3(7-11)$, $BCH_3(2-6)$. Figure 7 shows this for complex **4**, and very similar spectra are observed for all the monophosphine complexes.

Having assigned the boron resonances from the COSY spectrum, $^1H\{^{11}B\text{-selective}\}$ or 1H - ^{11}B HMQC experiments were used to identify the methyl signals in the 1H NMR spectrum. We found the latter 2-D experiment the most reliable, with Figure 8 showing the resulting spectrum and peak assignment for complex **4**. The equivalent spectrum for $[NBu_4][closo-1-H-CB_{11}Me_{11}]$ is given in the Supporting Information. Individual assignments of the resonances comes from the following: B(12) uniquely identifies $CH_3(12)$ in addition to its being the only integral 3 H signal. B(2-6) only shows one correlation to the lowest-field methyl signal, identifying this as arising from $CH_3(2-6)$. By elimination, $CH_3(7-11)$ can thus be identified. Interestingly, B(7-11) also shows longer-range correlations with both the cage C-H proton and $CH_3(12)$. However, these are not indicative of metal interaction, as they are also observed in the 1H - ^{11}B HMQC spectrum of $[NBu_4][closo-1-H-CB_{11}Me_{11}]$.

With the identity of the methyl resonances in hand, comparison with $[NBu_4][closo-1-H-CB_{11}Me_{11}]$ in the same solvent shows that coordination of the silver(I)-phosphine fragment in **4** results in a downfield shift of all the cage methyl resonances in the 1H NMR spectrum. $CH_3(2-6)$ are shifted the least (0.10 ppm), followed by $CH_3(7-11)$ (0.20 ppm) and $CH_3(12)$ (0.34 ppm) in complex **4**. Similar downfield shifts are also observed

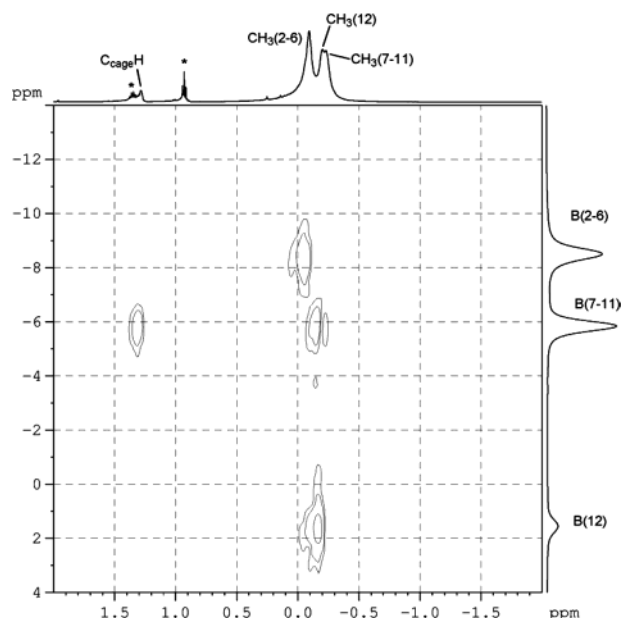


Figure 8. 1H - ^{11}B HMQC spectrum of complex **4**. Peaks marked with an asterisk are due to residual pentane from recrystallization.

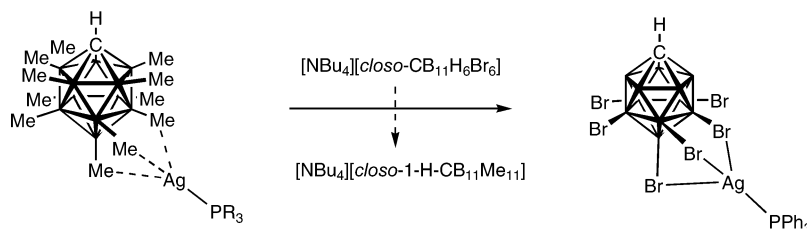
in **2**²³ and **3**. The greater chemical shift change of the methyl groups associated with the lower hemisphere of the cage suggests that the silver fragment interacts predominately with these methyl groups in solution. However, that all the resonances are broadened suggests that the metal fragment visits all of the methyl groups on the NMR time scale, being fluxional over the $\{BCH_3\}$ surface of the cage. The broadening observed could result from unresolved $^{109/107}Ag$ -H coupling or an undetermined relaxation mechanism induced by the proximity of the silver fragment that is fluxional over the surface of the cage.⁵⁰ Broadening caused by slow molecular tumbling of the ion pair in solution can be discounted as resonances due to the phosphine ligands in all the complexes **2-4** are observed to be sharp at room temperature. Although one-bond Ag -H couplings have been observed in bi- and trimetallic complexes with bridging hydrides, and are in the approximate range 70–20 Hz,⁵¹ given that the silver fragment is fluxional over 11 methyl groups, thus reducing the magnitude of any coupling, any fine structure could easily not be observed in the complexes reported here. Unfortunately, we did not observe a signal in the ^{109}Ag NMR spectra for these complexes, thwarting attempts to obtain $^1H\{^{109}Ag\}$ NMR spectra, which would have further confirmed the presence of $Ag\cdots H_3C$ coupling in solution. Nevertheless, there is no doubt that these interactions are present in solution, and they do result in the chemical shift and line width changes. Added confirmation of the presence is given by the fact that they can be turned off (vide infra) on addition of suitable Lewis bases. We have not found ^{13}C NMR spectroscopy useful in determining the structure of these complexes. All the cage methyl groups are observed as a quadrupolar broadened, ill-defined, resonance just below zero ppm, yielding no structural information (e.g., C-H coupling constants). Cooling samples to -80 °C (400 MHz,

(50) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*, 3rd ed.; Wiley-VCH: Weinheim, 1998.

(51) (a) Hutton, A. T.; Pringle, P. G.; Shaw, B. L. *Organometallics* **1983**, *2*, 1889. (b) Brunner, H.; Mijolovic, D.; Wrackmeyer, B.; Nuber, B. *J. Organomet. Chem.* **1999**, *579*, 298. (c) Brown, S. D. D.; McCarthy, P. J.; Salter, I. D.; Bates, P. A.; Hursthouse, M. B.; Colquhoun, I. J.; McFarlane, W.; Murray, J. *Dalton Trans.* **1988**, 2787.

(49) (a) Rifat, A.; Laing, V. E.; Kociok-Köhn, G.; Mahon, M. F.; Ruggiero, G. D.; Weller, A. S. *J. Organomet. Chem.* **2003**. (b) Patmore, N. J.; Mahon, M. F.; Steed, J. W.; Weller, A. S. *J. Chem. Soc., Dalton Trans.* **2001**, 277.

Scheme 1



CD₂Cl₂ solution) resulted in a slight sharpening (in part due to thermal decoupling of boron) and a general upfield shift of the methyl signals, so that their chemical shifts now lie between complex **2** and [NBu₄][*closo*-1-H-CB₁₁Me₁₁]. C_{5v} symmetry is still observed for the cage at this temperature. These data suggest a low-temperature structure in which there are less intimate Ag–cage interactions—possibly a solvent complex of the type (PPh₃)Ag(Cl₂CH₂)(*closo*-1-H-CB₁₁Me₁₁). Gradual heating to +70 °C resulted in decomposition to unidentified products.

There is literature precedent for the chemical shift changes in the ¹H NMR spectrum on the interaction of a CH₃ group with a metal center. *Intramolecular* agostic M–H–C interactions generally show upfield shifts for dⁿ metal centers where n > 0, while for d⁰ systems chemical shifts downfield from 0 ppm generally occur.²¹ More relevant to this study, complexes that have *intermolecular* M···{H₃CB} close contacts in solution such as [(1,3-(SiMe₃)₂C₅H₃)₂ZrMe(μ-Me)B(C₆F₅)₃],³² [(1,2-Me₃)₂C₅H₃)₂ZrMe(μ-Me)B(C₆F₅)₃],³³ and [(i-Pr-ATI)InMe(μ-Me)B(C₆F₅)₃] (ATI = N,N'-diisopropylaminotroponiminate)⁵² demonstrate upfield shifts of the methyl group on coordination with the metal compared with free [MeB(C₆F₅)₃][−].⁵³ We have observed similar upfield chemical shift changes in [(η⁵-C₅H₅)₂ZrMe(12-μ-Me-1-H-*closo*-CB₁₁Me₁₀)] in which a single [*closo*-1-H-CB₁₁Me₁₁][−] cage methyl group interacts end-on with the metal fragment at low temperature in solution and in the solid state.³⁵ In contrast, (η⁵-C₅Me₅)₂Yb(μ-Me)Be(η⁵-C₅Me₅) shows a small downfield shift for the bridging methyl group, as observed for **2–4**.³⁴

The room-temperature ³¹P{¹H} NMR spectra for complexes **2** and **3** show the expected concentric doublets of doublets, due to a single phosphorus environment coupling to both ¹⁰⁹-Ag and ¹⁰⁷-Ag (I = 1/2, natural abundance 51.8 and 48.2%, respectively). In complex **4** the separate doublets are not resolved, and only a broad doublet corresponding to J(^{107/109}AgP) is observed. The magnitude of the one bond Ag–P coupling constant is indicative of both the strength of the Ag–P bond⁴¹ and also the coordinative unsaturation, and resulting s-orbital character, of the Ag center.⁵⁴ Low-coordinate silver complexes such as monomeric P(*o*-tolyl)₃Ag(NO₂)⁴⁵ show large values [ca. J(AgP_{average}) 695 Hz], while higher coordinate [AgP₃]⁺ or [AgP₄]⁺ complexes show lower values [ca. J(AgP_{average}) 230 Hz] and are often fluxional at room temperature via phosphine dissociation.⁵⁴ The values for J(AgP) for the complexes **2–4** are among the highest reported for silver(I) monophosphine complexes, ranging from 731 to 824 Hz, consistent with low-coordinate silver(I) centers having a single strong Ag–P bond.

Further evidence for Ag···H₃C interactions being present in solution for complexes **2–4** comes from the ability to switch

them off on addition of a Lewis base that coordinates more strongly than [*closo*-1-H-CB₁₁Me₁₁][−]. Addition of one equivalent of [NBu₄][*closo*-1-H-CB₁₁H₅Br₆] (which is considered to be one of the least coordinating anions known to date) to a CD₂-Cl₂ solution of **2** results in the immediate formation of (PPh₃)Ag(*closo*-1-H-CB₁₁H₅Br₆)¹⁵ and [NBu₄][*closo*-1-H-CB₁₁Me₁₁] (Scheme 1). This anion exchange is clearly demonstrated in the ¹H{¹¹B} NMR spectrum of the resulting mixture which shows the cage methyl region to be sharp, upfield shifted, and essentially identical to pure [NBu₄][*closo*-1-H-CB₁₁Me₁₁], as well as the ³¹P{¹H} NMR spectrum that shows the formation of (PPh₃)Ag(*closo*-1-H-CB₁₁H₅Br₆). This observation strengthens the view that the observed broadening of the methyl groups in **2** is due to interactions with {Ag(PPh₃)⁺. In contrast, addition of [NBu₄][B(C₆F₅)₄][B(Ar_F)₄][−] does not switch off these interactions, with broad unshifted resonances due to **2** still observed in the methyl region of the ¹H{¹¹B} NMR spectrum. Thus, [*closo*-1-H-CB₁₁Me₁₁][−] can be considered to be more weakly coordinating than [*closo*-1-H-CB₁₁H₅Br₆][−] but less weakly coordinating than [B(Ar_F)₄][−] in terms of coordinating ability with the {Ag(PPh₃)⁺ fragment. We have recently reported a similar ranking based on the catalytic competency of [(η⁵-C₅H₅)Mo(CO)₃]⁺ cations partnered with these (or closely related) anions in the transfer hydrogenation of ketones.⁵⁵ Addition of other weak ligands such as Et₂O (5 equiv) or 2,3-dimethylbutene (10 equiv) to **2** resulted in the sharpening and upfield shift of the cage methyl groups, indicating the loss of Ag···H₃C interactions and the formation of well-separated [PPh₃AgL_n]⁺[*closo*-1-H-CB₁₁Me₁₁][−] salts in solution. The diethyl ether adduct [PPh₃Ag(OEt₂)₂]⁺[*closo*-1-H-CB₁₁Me₁₁][−] **5**, has been crystallographically characterized (see Supporting Information). Likewise, addition of one equivalent of the potent Lewis base PPh₃ to **2** immediately forms [(PPh₃)₂Ag][*closo*-1-H-CB₁₁Me₁₁] **6**, which has also been crystallographically characterized (see Supporting Information). Compound **6** also results after the addition of two equivalents of PPh₃ to **1**.

In solution there are no Ag···H₃C interactions present in **5** and **6**, as judged by both the chemical shift and line-width of the cage methyl groups in the ¹H{¹¹B} spectrum being similar to those observed for [NBu₄][*closo*-1-H-CB₁₁Me₁₁]. The ¹¹B NMR spectra of **5** and **6** show C_{5v} symmetry for the cage anion, as expected. For **6** the ³¹P{¹H} NMR spectrum displays a single species by a well-defined concentric set of doublets, due to ¹⁰⁷AgP and ¹⁰⁹AgP coupling to one phosphorus environment. The size of this coupling constant [J(Ag_{average}P) 561 Hz] agrees well with that observed for other two-coordinate species, such as [(PPh₃)₂Ag][BF₄] [J(Ag_{average}P) 550 Hz],⁴⁰ suggesting similar structures in solution. For **5**, the weakly bound diethyl ether

(52) Delpech, F.; Guzei, I. A.; Jordan, R. F. *Organometallics* **2002**, *21*, 1167.

(53) Beswick, C. L.; Marks, T. J. *Organometallics* **1999**, *18*, 2410.

(54) Muetterties, E. L.; Alegrianti, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 6386.

(55) (a) Ingleson, M. J.; Patmore, N. J.; Mahon, M. F.; Weller, A. S. *Dalton Trans.* **2003**. (b) Bullock, R. M.; Voges, M. H. *J. Am. Chem. Soc.* **2000**, *122*, 12594.

Table 6. Comparison of the Charges (from NBO analysis) on the Anion [closo-1-H-CB₁₁Me₁₁]⁻, and the Relative Energies of the Isomers of (closo-1-H-CB₁₁Me₁₁)Ag(PPh₃) **2**, All Calculated at the B3LYP/DZVP Level

vertex/ isomer	charge (NBO) [closo-1-H-CB ₁₁ Me ₁₁] ⁻		relative energy (closo-1-H-CB ₁₁ Me ₁₁)Ag(PPh ₃) energy/kcal mol ⁻¹
	CH ₃	BCH ₃	
(μ-7,8,12)	–	–	0
(12)	–0.28	–0.09	+ 1.9
(7)–(11)	–0.28	–0.13	+ 3.8
(2)–(6)	–0.29	+0.07	+ 8.1

ligands result in a larger Ag–P coupling constant [$J(\text{Ag}_{\text{average}}\text{P})$ 801 Hz] than for **6**.

Addition of one equivalent of [NBu₄][closo-1-H-CB₁₁Me₁₁] to **2** in CD₂Cl₂ results in the observation of only one cage C–H resonance at δ 1.20 ppm in the ¹H NMR spectrum and a single set of cage methyl resonances. The chemical shift of the C–H group is exactly midpoint between **2** and [NBu₄][closo-1-H-CB₁₁Me₁₁] (δ 1.26 and 1.14 ppm, respectively). The signals for the cage methyl groups remain broadened in the ¹H{¹¹B} NMR spectrum of this mixture, but they are shifted slightly upfield and their line-width has decreased slightly [fwhm = 18 Hz]. These observations are consistent with rapid exchange of free and bound cage anions on the NMR time scale.

DFT Calculations. DFT calculations on the permethylated [closo-CB₁₁Me₁₂]⁻ anion have been independently reported by McKee (B3LYP/6-31* level)⁴⁶ and Michl and co-workers (B3LYP/SDD level).⁷ The latter report also describes the optimized model structure for the closely associated ion-pair [n-Bu₃Sn][closo-CB₁₁Me₁₂]. Both of these studies show a good agreement regarding the distribution of charge on the three different {BCH₃} vertices on the cage. The five equivalent upper pentagonal belt vertices [BCH₃(2–6)] carry a small calculated positive charge [+0.05 (B3LYP/6–31*)/+0.11 (B3LYP/SDD)], while the lower pentagonal belt vertices [BCH₃(7–11)] carry the most negative charge [–0.14/–0.15] with the antipodal BCH₃(12) vertex being slightly less negative [–0.09/–0.10]. We have used the B3LYP/DZVP basis set in our studies here due to its ability to parametrize silver reliably, and this gives essentially the same result as previous studies in terms of the calculated charge for [closo-1-H-CB₁₁Me₁₁]⁻ (Table 6). From a purely electrostatic model a {Ag(PR₃)⁺} fragment would thus be expected to favor interaction with BCH₃(7–11), followed by BCH₃(12), as these carry the most negative charge. However, this simple model does not take into account any (albeit small) covalent contributions to the interactions. Indeed, calculations on [Me₃Sn][closo-CB₁₁Me₁₂] show that the 12-isomer is the most favored, followed closely by the 7-isomer (2.8 kcal mol⁻¹ higher), even though the BCH₃(7–11) vertices carry the most negative charge.⁷ Likewise, the parent unmethylated carborane, [closo-1-H-CB₁₁H₁₁]⁻ shows virtually the same charge distribution,⁴⁶ but electrophilic substitution by halogens occurs preferentially at the 12-vertex, followed closely by the 7–11 vertices.⁵⁶ For **2** the three possible monodentate isomers of {Ag(PPh₃)⁺} interacting with the [closo-1-H-CB₁₁Me₁₁]⁻ anion have been calculated [Figure 9], and we find that the 12-isomer is marginally favored over the 7-isomer by 1.9 kcal mol⁻¹ (see

Experimental Section for full details). The 2-isomer is slightly higher again in energy compared with the 12-isomer [6.2 kcal mol⁻¹]. All of these optimized structures have an essentially linear B–C–Ag–P motif. This linear, end-on coordination, is not observed in the solid state as extended interactions in the lattice distort the local coordination environment in complexes **2** and **3**. Complex **4**, however, shows interactions with only one cage anion, and the silver–phosphine fragment is in close contact with three vertices on the lower hemisphere of the cage: B7, B8, and B12. The lack of interactions with other cage anions makes this a good model for solution structure. Using this experimentally determined structure as a guide, optimization of a model in which the silver–phosphine is placed over the triangular face defined by BCH₃(7,8,12) results in an energetically more favored structure [Figure 9d], although the gain in energy is modest, being 1.9 kcal mol⁻¹ more stable than the 12-isomer. Specific comparisons of bond lengths and angles between experimentally and theoretically determined structure is not appropriate, however, as the structure of **4** is influenced to a small extent by crystal packing.

Given the size of this system, we have not carried out a search for transition states on the potential energy surface moving from each of these isomers, or a more rigorous study of all the potential coordination isomers. Nevertheless, calculations suggest that a plausible mechanism for the experimentally observed facile movement of the {Ag(PPh₃)⁺} over the surface of the cage is one that invokes a tridentate ⇌ monodentate ⇌ tridentate coordination mode (Scheme 2). A fluxional process that involves a bidentate coordination mode is also possible, although we have not investigated this latter coordination motif. The small energy difference between all the isomers studied [8.1 kcal mol⁻¹] suggests that they are all potentially accessible in solution. Experimental observations are consistent with this, the broadening indicative of interaction with the silver fragment being observed for *all* the BCH₃ resonances in the ¹H{¹¹B} NMR spectrum. That the 2-isomer is calculated to be the energetically least favored, is also consistent with solution-state experimental observations, as the resonance due to the BCH₃(2–6) methyl groups undergoes the *smallest* chemical shift change, suggesting that the silver fragment spends less time on average interacting with these methyl groups. As the silver fragment is still in rapid motion around the cage periphery at –80 °C in **2**, the energetic barriers in this fluxional process must also be small.

Turning to the local coordination environment of the Ag⋯H₃C interactions, the most stable calculated structure [Figure 9d] shows no significant lengthening of the C–H bonds on interaction with silver (see Supporting Information for bond lengths and angles). Likewise, the B–C–H angles do not deviate significantly from tetrahedral, and the B–C bonds do not lengthen. However, the slightly higher in energy monodentate structures (Figure 9, a–c) all show a small lengthening of the B–C bond of the methyl group that interacts with the metal fragment (ca. 0.03 Å) and a slight flattening of the B–C–H angles from tetrahedral to ca. 106–107°, when compared with the calculated structure of [closo-1-H-CB₁₁Me₁₁]⁻ (see Supporting Information). This is possibly indicative of a *small* contribution from a dative CH₃ → {AgPPh₃} interaction, although overall the calculated structural markers suggest predominately ionic bonding in **2** between metal fragment and

(56) Jelinek, T.; Baldwin, P.; Scheidt, W. R.; Reed, C. A. *Inorg. Chem.* **1993**, *32*, 1982.

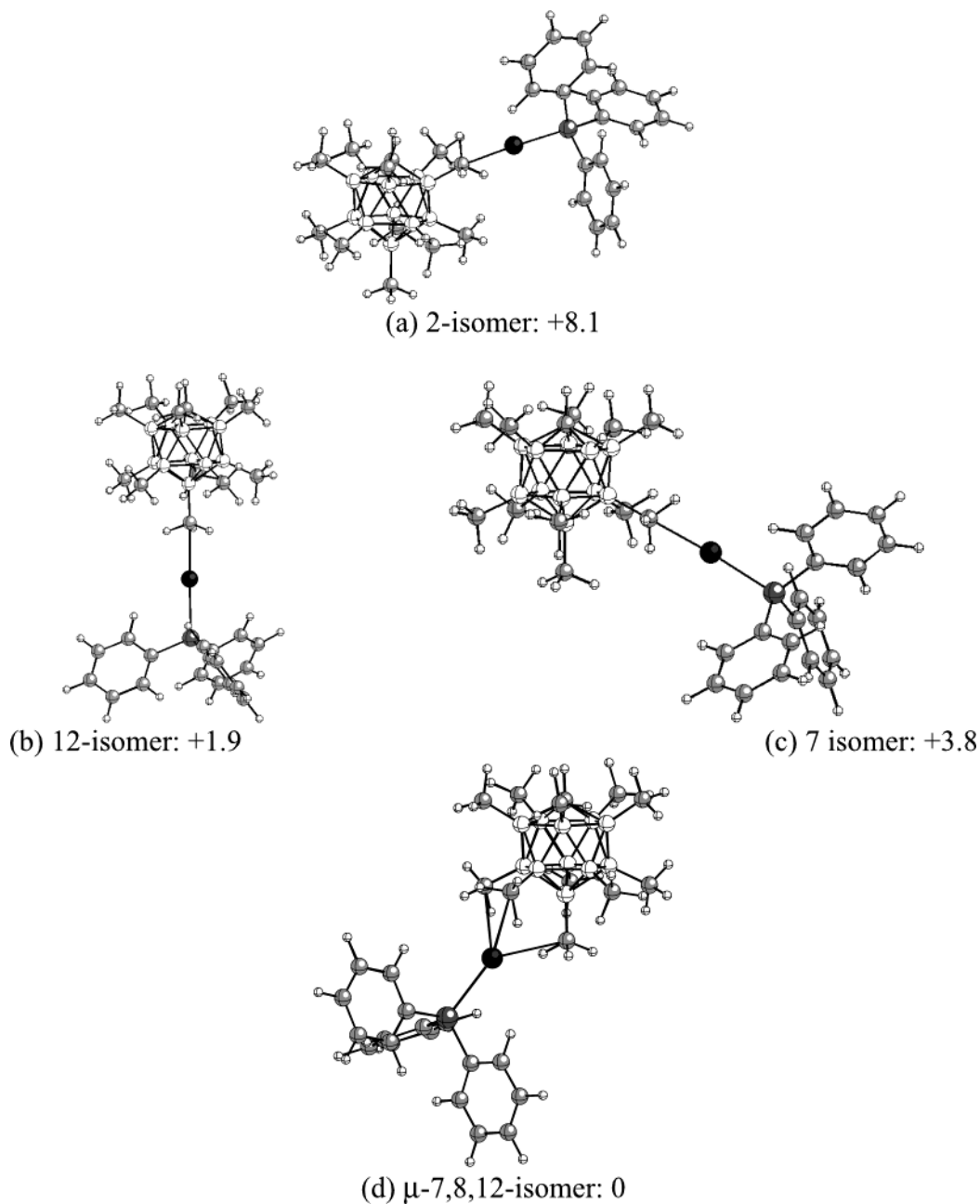
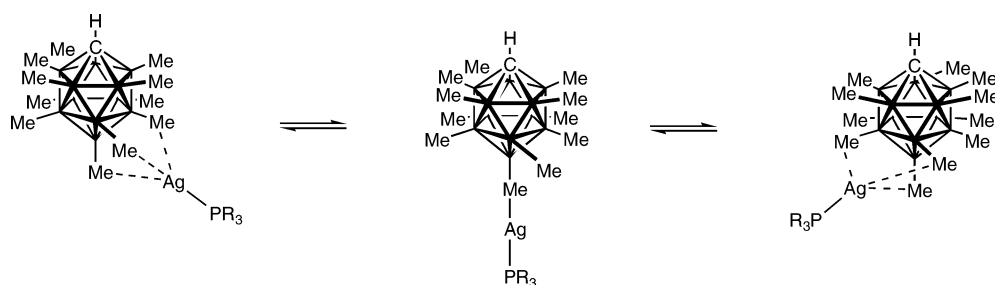


Figure 9. DFT optimized structures (BLYP/DZVP level) of the isomers of $(\text{PPh}_3)\text{Ag}(\text{closo-1-H-CB}_{11}\text{Me}_{11})$, **2**. Energies (kcalmol^{-1}) are given relative to the most stable of these optimized structures (μ -7,8,12-isomer).

Scheme 2



anion. Significantly larger increases in the B–C distance and more compressed B–C–H angles have been calculated by Michl and co-workers for the model complex $[\text{Me}_3\text{Sn}][\text{closo-CB}_{11}\text{Me}_{12}]$ (0.09 Å and 97° respectively) which is suggested to

interact through a combination of electrostatic and donor–acceptor interactions between Sn and CH_3 .⁷ Similar orbital interactions have also been suggested to be present in the related compound $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Yb}(\mu\text{-Me})\text{Be}(\eta^5\text{-C}_5\text{Me}_5)$.³⁴

Conclusions

Reported here are the synthesis of a number of compounds (PR₃)Ag(*closo*-1-*H*-CB₁₁Me₁₁) that display novel intermolecular Ag⋯H₃C interactions in both the solid state and solution. As far as we are aware these are the first reported example of such interactions for a later d-block metal. Variation of the phosphine on silver results either in extended coordination polymers or discrete ion-pairs in the solid state. Consideration of these structures in concert with DFT calculations indicates that these interactions can be thought of as being primarily electrostatic in origin, although there may also be a small orbital contribution to the bonding. This is consistent for closed-shell Ag⁺ and is similar to group I cations that also show intermolecular CH⋯M interactions. Ag⋯H₃C interactions are retained in solution (i.e. they are simply not crystal packing effects), and we have observed some key spectroscopic markers for their existence (chemical shift change and line broadening of the cage methyl groups) that unambiguously link the solid-state and solution structures. These markers may be of assistance in the future development of the coordination chemistry of these highly methylated anions. Such investigations are of significant contemporary relevance due to the interest that surrounds putative intermediates in C–H activation of alkanes, i.e., metal–alkane complexes. Although closed-shell silver(I) does not necessarily present a good model for those metal centers that are known to take part in C–H activation processes (e.g., group 9 and 10 transition-metal complexes²⁰), the observation of CH₃⋯Ag interactions in solution suggests that related complexes may be accessible with these later transition metals, potentially forming σ-complexes with [*closo*-1-*H*-CB₁₁Me₁₁]⁻.

Experimental Section

General. All manipulations were performed under an inert atmosphere of argon, using standard Schlenk-line and glovebox techniques. Glassware was dried in an oven at 130 °C overnight and flamed with a blowtorch, under vacuum, three times before use. CH₂Cl₂ and pentane were distilled from CaH₂, diethyl ether from sodium/benzophenone ketal and hexane from sodium. C₆D₆ and *d*₈-toluene were dried over a potassium mirror, CD₂Cl₂ was distilled under vacuum from CaH₂. Microanalyses were by Mr. Alan Carver (University of Bath Microanalytical Service). Cs[*closo*-1-*H*-CB₁₁Me₁₁]^{1,25} was prepared using literature procedures. All other compounds were used as found from Aldrich or Strem.

NMR Spectroscopy. ¹H, ¹¹B, ¹³C, and ³¹P NMR spectra were recorded on a Bruker Avance 300 MHz, Varian 400 MHz (Bath) or Bruker 500 MHz (Warwick) FT-NMR spectrometers. Residual protio solvent was used as reference for ¹H NMR spectra (CD₂Cl₂: δ = 5.33, C₇D₈: δ = 2.10, *d*₆-acetone: δ = 2.09) and ¹³C NMR spectra (CD₂Cl₂: δ = 53.8). ¹¹B and ³¹P NMR spectra were referenced against BF₃·OEt₂ (external) and 85% H₃PO₄ (external), respectively. Coupling constants are quoted in Hertz. Unless otherwise stated, assignments of vertices in the carborane cage are from ¹H–¹¹B HMQC and ¹¹B–¹¹B COSY experiments.

Infrared Spectroscopy. Infrared spectra were recorded on a Nicolet NEXUS FT-IR spectrometer. Solid-state samples were made up using oven-dried potassium bromide in a glovebox. Solution spectra were recorded using a 0.1 mm path length cell.

Ag(*closo*-1-*H*-CB₁₁Me₁₁) (1). Cs[*closo*-1-*H*-CB₁₁Me₁₁] (407 mg, 0.95 mmol) was dissolved in Et₂O (30 cm³) and treated with 3 × 30 cm³ portions of 10% w/v AgNO₃ aqueous solution. The combined aqueous layers were extracted with three aliquots of Et₂O (25 cm³). These were combined and evaporated to dryness in vacuo. The resultant off-white solid was redissolved in CH₂Cl₂ (20 mL) and filtered, and

the solvent was removed in vacuo to leave a white solid. This was dissolved in a minimum volume of CH₂Cl₂, layered with hexanes, and stored at –30 °C for 2 days. Colorless crystals of [Ag(*closo*-1-*H*-CB₁₁Me₁₁)] (1) (303 mg, 79% yield) were isolated.

¹H{¹¹B} (300 MHz, 22 °C, *d*₆-acetone): δ 1.09 (1H, s, C_{cage}–H), –0.16 (15H, s, B(2–6)CH₃), –0.39 (15H, s, B(7–11)CH₃), –0.51 (3H, s, B(12)CH₃). ¹¹B (96 MHz, 22 °C, *d*₆-acetone): –0.6 (1B, s, B(12)), –8.8 (5B, s, B(7)–B(11)), –12.2 (5B, s, B(2)–B(6)). ¹H{¹¹B} (300 MHz, 22 °C, CD₂Cl₂): δ 1.27 (1H, s, C_{cage}–H), –0.15 (15H, s, B(2–6)CH₃), –0.33 (18H, s, B(7–12)CH₃). ¹¹B (96 MHz, 22 °C, CD₂Cl₂): δ 1.5 (1B, s, B(12)), –5.9 (5B, s, B(7)–B(11)), –8.5 (5B, s, B(2)–B(6)). Elemental Analysis: Calcd for C₁₂H₃₄B₁₁: %C 35.6; %H 8.40. Found: %C 33.1; %H 8.31.

Ag(PPh₃)(*closo*-1-*H*-CB₁₁Me₁₁) (2). PPh₃ (60 mg, 0.23 mmol) was dissolved in CH₂Cl₂ (5 cm³) and added dropwise to a Schlenk flask charged with Ag[*closo*-1-*H*-CB₁₁Me₁₁] (92 mg, 0.23 mmol). The resulting solution was stirred in the dark for 16 h and cannula filtered, and the solvent was removed in vacuo. The white solid resulting was redissolved in the minimum volume of CH₂Cl₂, layered with hexanes, and then placed in a freezer overnight at –30 °C to afford colorless crystals of [Ag(PPh₃)(*closo*-1-*H*-CB₁₁Me₁₁)] (2) (122 mg, 81% yield).

¹H{¹¹B} (300 MHz, 22 °C, CD₂Cl₂, assignments from ¹H{¹¹B-selective} experiments): δ 7.66–7.36 (15H, m, Ph), 1.26 (1H, s, C_{cage}–H), –0.14 (15H, br s, B(7–11)CH₃), –0.22 (3H, br s B(12)CH₃), –0.28 (15H, br s, B(2–6)CH₃). ¹H{¹¹B} (300 MHz, –70 °C, CD₂Cl₂): δ 7.72–7.33 (30H, m, Ph), 1.19 (1H, s, C_{cage}–H), –0.26 (15H, s, BCH₃(2–6)), –0.44 (18H, s, BCH₃(7–12)). ¹¹B (96 MHz, 22 °C, CD₂Cl₂): δ –1.3 (1B, s B(12)), –9.0 (5B, s B(7–11)), –11.9 (5B, s, B(2–6)). ¹³C{¹H} (75 MHz, 22 °C, CD₂Cl₂): δ 133.9 (s, C_{phenyl}), 132.3 (s, C_{phenyl}), 130.0 (s, C_{phenyl}), 128.2 [d, C_{phenyl}, J(CP) = 37], 61.3 (s br, C_{cage}), –0.7 to –6.0 (v br, BCH₃). δ ³¹P{¹H} (122 MHz, 22 °C, CD₂Cl₂): δ 17.5 [dd, J(¹⁰⁹AgP) 853, J(¹⁰⁷AgP) 794]. IR (KBr): ν(CH₃) = 2921, 2895, 2829, 2736 cm⁻¹. Elemental Analysis: Calcd for C₃₀H₄₉AgB₁₁P: %C 54.0; %H 7.35. Found: %C 53.4; %H 7.30.

Ag(P(C₆H₁₁)₃)(*closo*-1-*H*-CB₁₁Me₁₁) (3). The procedure given above for 2 was followed except that 60 mg (0.11 mmol) of P(C₆H₁₁)₃ and 43 mg (0.11 mmol) of Ag[*closo*-1-*H*-CB₁₁Me₁₁] were used and recrystallization was from CH₂Cl₂/pentane. This afforded 34 mg (0.05 mmol) of (3) as colorless crystals, isolated in 46% yield.

¹H{¹¹B} (300 MHz, 22 °C, CD₂Cl₂): δ 2.01–1.75 (18H, m, (C₆H₁₁)), 1.37–1.21 (16H, m, (C₆H₁₁) and C_{cage}–H), –0.13 (15H, br s, B(2–6)CH₃), –0.23 (18H, v br s B(12)CH₃ and B(7–11)CH₃). ¹¹B (96 MHz, 22 °C, CD₂Cl₂): δ –1.8 (1B, s B(12)), –9.2 (5B, s, B(7–11)), –11.8 (5B, s, B(2–6)). ³¹P{¹H} (122 MHz, 22 °C, CD₂Cl₂): δ 49.9 [dd, J(¹⁰⁹AgP) 821, J(¹⁰⁷AgP) 711]. IR (KBr): ν(CH₃) = 2932, 2893, 2856, 2827 cm⁻¹. Elemental Analysis: Calcd for C₃₀H₆₇AgB₁₁P: %C 52.6; %H 9.8. Found: %C 52.0, %H 9.8.

Ag(P{3,5-Me₂C₆H₃})₃(*closo*-1-*H*-CB₁₁Me₁₁) (4). The procedure for 2 was followed except that 39 mg (0.11 mmol) of P(3,5-Me₂C₆H₃)₃ and 50 mg (0.12 mmol) of Ag[*closo*-1-*H*-CB₁₁Me₁₁] were used. This afforded 53 mg (0.07 mmol) of [Ag(P{3,5-Me₂C₆H₃})₃(*closo*-1-*H*-CB₁₁Me₁₁)] (4) as colorless crystals, isolated in 63% yield.

¹H{¹¹B} (300 MHz, 22 °C, CD₂Cl₂): δ 7.28–7.02 (9H, m, Ph), 2.39 (18H, s, Ph-CH₃), 1.30 (1H, s, C_{cage}–H), –0.08 (15H, br s, BCH₃(2–6)), –0.21 (3H, br s, BCH₃(12)), and –0.23 (15H, br s, BCH₃(7–11)). ¹¹B (96 MHz, 22 °C, CD₂Cl₂): δ –1.7 (1B, s B(12)), –9.1 (5B, s B(7–11)), –11.8 (5B, s, B(2–6)). ³¹P{¹H} (122 MHz, 22 °C, CD₂Cl₂): δ 19.14 [br d, J(^{109/107}AgP) 731]. IR (KBr): ν(CH₃) = 2921, 2895, 2828, 2726 cm⁻¹. Elemental Analysis: Calcd for C₃₆H₆₁AgB₁₁P: %C 57.6; %H 8.13. Found: %C 58.1; %H 8.42.

[(OEt)₂Ag(PPh₃)] [*1*-*H*-CB₁₁Me₁₁] (5). Crystalline PPh₃Ag(*closo*-1-*H*-CB₁₁Me₁₁) 2 (30 mg.) was dissolved in Et₂O (5 mL) in a Young's tube and layered with pentane. Recrystallization in the dark at –30 °C resulted in colorless crystals suitable for X-ray diffraction. Crystals of 5 immediately start to lose diethyl ether on removal from the mother liquor, and thus, a satisfactory microanalysis was not obtained.

^1H (400 MHz, 22 °C, CD_2Cl_2): δ 7.65–7.37 (15H, m, Ph), 3.55 (8H, q, O–CH₂), 1.24 (12H, t, CH₃) 1.17 (1H, s, C_{cage}–H), –0.16 (15H, s, B(CH₃)₂–BCH₃(6)), –0.38 (15H, s, B(CH₃)₇–BCH₃(11)), –0.45 (3H, s, B(CH₃)₁₂). $^{31}\text{P}\{^1\text{H}\}$ (161 MHz, 22 °C, CD_2Cl_2): δ 18.95 [dd, $^1J(^{109}\text{AgP})$ 858 Hz, $^1J(^{107}\text{AgP})$ 774 Hz]. ^{11}B (96 MHz, 22 °C, CD_2Cl_2): δ 2.0 (3H, s, B(12)), –5.7 (15H, s, B(7–11)), –8.6 (15H, s, B(2–6)).

[Ag(PPh₃)₂][closo-1-H-CB₁₁Me₁₁] (**6**). PPh₃ (130 mg, 0.50 mmol) was dissolved in CH_2Cl_2 (5 cm³) and added dropwise to a Schlenk flask charged with Ag[closo-1-H-CB₁₁Me₁₁] (100 mg, 0.25 mmol). The resulting solution was stirred in the dark for 16 h and cannula filtered, and the solvent was removed in vacuo. The white solid formed was redissolved in the minimum volume of CH_2Cl_2 , layered with hexanes, and then placed in a freezer overnight at –30 °C to afford colorless crystals of [Ag(PPh₃)₂(closo-1-H-CB₁₁Me₁₁)] (**6**): 193 mg, 84%.

$^1\text{H}\{^{11}\text{B}\}$ (300 MHz, 22 °C, CD_2Cl_2): δ 7.62–7.43 (30H, m, Ph), 1.09 (1H, s, C_{cage}–H), –0.22 (15H, s, B(CH₃)₂–(6)), –0.46 (15H, s, B(CH₃)₇–(11)), –0.58 (3H, s, B(CH₃)₁₂). ^{11}B (96 MHz, 22 °C, CD_2Cl_2): δ –0.9 (1B, s, B(12)), –8.9 (5B, s, B(7–11)), –12.2 (5B, s, B(2–6)). $^{31}\text{P}\{^1\text{H}\}$ (122 MHz, 22 °C, CD_2Cl_2): δ 15.80 [dd, $^1J(^{109}\text{AgP})$ 580, $^1J(\text{Ag}^{107}\text{P})$ 541]. $^{31}\text{P}\{^1\text{H}\}$ (122 MHz, 70 °C, $\text{C}_2\text{D}_4\text{Cl}_2$): δ 17.0 (br, s). IR (KBr): $\nu(\text{CH}_3) = 2924, 2890, 2825 \text{ cm}^{-1}$. Elemental Analysis: Calcd for C₄₈H₆₄B₁₁P₂Ag: %C 62.0; %H 6.94. Found: %C 62.4; %H 6.79.

[¹¹⁵Bu₄N][closo-1-H-CB₁₁Me₁₁]. Cs(closo-1-H-CB₁₁Me₁₁) (150 mg, 0.35 mmol) was dissolved in 30 cm³ of Et₂O and washed three times with an aqueous solution of [¹¹⁵Bu₄N]Br (560 mgs, 1.75 mmol in 100 cm³ of H₂O). The aqueous layer was extracted three times with 20 cm³ portions of Et₂O. The ether washing were combined and evaporated to dryness to yield 105 mg of [¹¹⁵Bu₄N][closo-1-H-CB₁₁Me₁₁] (0.19 mmol, 57%) as a white solid.

$^1\text{H}\{^{11}\text{B}\}$ (300 MHz, 22 °C, CD_2Cl_2): δ 3.10–3.04 (8H, m, N–CH₂), 1.66–1.40 (16H, m, CH₂), 1.14 (1H, s, C_{cage}–H) 1.04 (12H, t, CH₃) –0.18 (15H, s, B(CH₃)₂–(6)), –0.43 (15H, s, B(CH₃)₇–(11)), –0.55 (3H, s, B(CH₃)₁₂). ^{11}B (96 MHz, 22 °C, CD_2Cl_2): δ –0.1 (1B, s B(12)), –7.9 (5B, s B(7–11)), –11.2 (5B, s, B(2–6)).

Crystallographic Studies. Crystallographic measurements for all structures were recorded on a Nonius KappaCCD diffractometer with Mo K α radiation (0.71073 Å). Details of data collection are summarized in Table 1. Structure solution followed by full-matrix least-squares refinement was performed by using the WINGX or XSEED suites of programs throughout.⁵⁷ Hydrogen atoms were included in calculated positions unless otherwise stated.

For complex **1** the hydrogen atoms on two methyl groups (C3 and C10) are positionally disordered in 50:50 ratio. In **2**, hydrogen atoms associated with C7, C9, and C12 were located and freely refined without any constraints/restraints. Unfortunately, for **4** the sample was poor in quality, despite many attempts to produce better-quality crystals. Early indications were that mosaicity (at approximately 2°) left something to be desired, as indeed did the spots in data frames. These combined observations were reflected in a premature fall off diffracting power, poor esds on the refined unit cell parameters, and an uninspiring R(int) value on the data set as a whole. Nonetheless, the model for the structure proposed is unambiguous. Full-matrix least-squares refinement was effected using data to a 2 θ maximum of 48°. Restraints were applied to C12, C7, and C8 which share the same anisotropic displacement parameters. Three space group possibilities were identified on the basis of absences for complex **6**: $P6_3$, $P6_3/m$, and $P6_{322}$. The latter space group did not conform to the Laue symmetry of the data set and was eliminated. Solution was readily achieved in $P6_3$, with a disordered carborane anion. However, the optimal refinement was achieved in $P6_3/m$ where the asymmetric unit consisted of one-sixth of each cation and anion. The remaining portion of the cation was generated by virtue of the –6 axis on which the silver and phosphorus atoms were located.

(57) Sheldrick, G. M. *SHELX-97*. A computer program for refinement of crystal structures. University of Göttingen, 1997.

The portion of the anion contributing to the asymmetric unit which also straddles the 6/ m axis was seen to contain four cage atoms (treated as borons) and four methyl groups, all at 0.5 occupancy. This affords one total anion, disordered over two positions, on invoking the crystallographic symmetry. This high symmetry means that the two disordered contributors cannot be separated in the usual fashion using SHELXL PART instructions. Nevertheless, the refinement proceeded without constraints, the only regrettable aspect being that the cage carbon could not be identified.

Calculation Details. Gas-phase geometry optimization for all multinuclear solutes were performed using the Gaussian 98 program⁵⁸ using DFT at the B3LYP hybrid method⁵⁹ with the DZVP basis sets.⁶⁰ Geometry optimization for minimas used the Berry routine. No symmetry constraints were imposed. The charge distributions were obtained from the DFT wave function employing a natural population analysis. The silver complex study used the double- ζ -valence-polarization (DZVP) basis set developed for DFT. Previous work on metals using this basis set has shown that DZVP produces structures and energies comparable to those obtained using the better tested basis set, 6-31+G(d).⁶¹ In our original communication,²³ we reported that the 7-isomer was slightly favored energetically over the 12-isomer by ca. 1.4 kcal mol^{–1}—the opposite to that reported here. Subsequent refinements of the model have since revealed new local minima, and the 12-isomer is in fact 1.9 kcal mol^{–1} more stable than the 7-isomer. This is now consistent with calculations previously reported for [Me₃Sn][closo-CB₁₁Me₁₂].⁷ Since the potential energy surface for the isomers of **2** is quite flat, great care must be taken with geometry optimization to ensure convergence toward stationary points with zero gradients. Even though the RMS residual force in our original calculations was well below the usual standard exit threshold for convergence, they may not be the lowest energies possible when investigating large flexible systems, such as those discussed here. By tightening the cutoffs on forces (opt = tight keyword) and the step size that are used to determine convergence, it was possible to lower the gradient and energy of the system so that modest (ca. 3 kcal mol^{–1}) improvements were made over our original calculations. Nevertheless, the conclusion is still exactly the same: interaction of the metal fragment with those {BCH₃} vertices on the lower hemisphere of the cage is energetically favored over those on the upper part, fully consistent with the observed chemical shift changes of the methyl groups in the ^1H NMR spectra.

Acknowledgment. This work was supported by the Royal Society (A.S.W.), the EPSRC (M.J.I., Grant GR/R36824), and the University of Bath (N.J.P.). Dr. Mark Fox (University of Durham) and Professor P. R. Raithby are thanked for useful discussions. Johnson Matthey plc are thanked for the generous loan of silver salts.

Supporting Information Available: Packing Diagram for **1** (S1), ^{11}B – ^1H HMQC spectra for NBu₄[closo-1-H-CB₁₁Me₁₁]

- (58) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; J. A. Montgomery, J.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc: Pittsburgh, PA, 1998.
- (59) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3089. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
- (60) (a) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560. (b) Godbout, N. PhD Dissertation. Université de Montréal, 1996.
- (61) Shoeib, T.; Milburn, R. K.; Koyanagi, G. K.; Lavrov, V. V.; Bohme, D. K.; Siu, K. W. M.; Hopkins, A. C. *Int. J. Mass Spectrom.* **2000**, *201*, 87.

(S2), DFT calculated structures and energies for the 2-, 7-, 12-, and μ^3 -7,8,12-isomers of **2** (S3–S6), X-ray structures of [(PPh₃)Ag(OEt₂)₂][closo-1-H-CB₁₁Me₁₁] (**5**) and [Ag(PPh₃)₂][closo-1-H-CB₁₁Me₁₁] (**6**) (S7–S9), and the CIF files for all the crystal

structures reported in this paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA038173M