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Stable Silver Complexes with $C_2B_9H_{12}^-$ Derivatives

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The reaction of 7,8-dithio-7,8-dicarba-*nido*-undecaborate(1–) (L_{s2c}^- and L_{s2n}^-) and 7-thio-8-methyl-7,8-dicarba-*nido*-undecaborate(1–) (L_{s1}^-) derivatives with Ag^+ and Lewis base, PPh_3 or bipy, yields white stable solids with the stoichiometries **[Ag(L_{s2n})(Lewis)]**, **[Ag(L_{s2c})(Lewis)]**, and **[Ag(L_{s1})(Lewis)]**, respectively. The stoichiometry is independent of the length of the S,S′-connected strings in L_{s2c}^- complexes. When the S,S′ connected string contains a possible coordinating element such as oxygen, the extra coordinating ligand, a Lewis base, is not required. Crystal structure data for **[Ag(L_{s2c15})]**: mol wt 463.6; space group $Pna2_1$; $Z = 4$; a = 14.0211(7) Å, b = 16.658(8) Å, c = 8.196(3) Å, β = 90.0°; $R_w(F_o)$ = 0.038. Crystal structure data for **[Ag(L_{s2c6})(PPh_3)]·0,5CH_2Cl_2**: mol wt 636.2; space group $P2_1/n$; $Z = 4$; a = 13.069(3) Å, b = 17.414(5) Å, c = 13.545(4) Å, β = 110.32(2)°; $R_w(F_o)$ = 0.034. In most of the crystal structures the sulfur atoms bridge two silver ions. However, the two S–Ag interactions are not equivalent, with a longer and a shorter S–Ag bond. The usual distances are Ag(1)–S(1) = 2.558(3) Å and Ag(1)–S(2) = 2.711(3) Å (L_{s2c6}^-, {7,8-μ-(SCH_2CH_2S)-7,8-$C_2B_9H_{10}$}$^-$; L_{s2c15}^-; {7,8-μ-($SCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2S$)-7,8-$C_2B_9H_{10}$}$^-$).

The incorporation of S,S′-connected strings to the moiety 7,8-dithio-7,8-dicarba-*nido*-undecaborate(1-) is being thoroughly studied in our group.[1] These macrocyclic ligands (Figure 1) have several coordinating sites: the C_2B_3 open face,[2] the thio groups[3] and the B–H units to form *exo-nido* complexes.[4] In general, however, S→M coordination has been preferred. In some of the resulting metal complexes, the agostic B(3)–H→M interaction has been proven.[5] Metal to open face coordination, M–C_2B_3, has been encountered with Hg(II), and there are certain indications that it is also found for Ag(I) with the strained 5-membered cycle (L_{s2c5}^-).[6]

Even though some examples of silver coordination to boranes are known, such as $[(PPh_3)AgC_2B_8H_{11}]_2$,[7] $AgCB_{11}H_{12}{\cdot}2C_6H_6$,[8] $(PPh_3)_2AgBH_4$, and $(PPh_3)_3AgHBH_2CO_2Et$,[9] or the Ag interaction[10] with $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$,[11] until our first report on silver,[6] little was known about silver complexes which are derivatives of $C_2B_9H_{12}^-$. In 1968,[12] it was reported that upon reaction of $C_2B_9H_{12}^-$ with $AgNO_3$, the black complex $[(C_2B_9H_{11})_2Ag]^{2-}$ was obtained, but the nature of this solid was later doubted.[13]

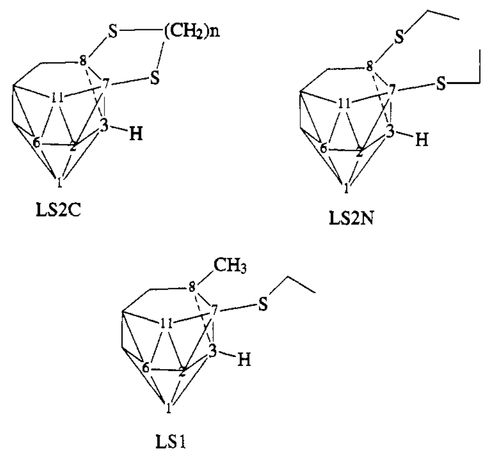

Figure 1. Schematic drawing of the ligands derivatives of 7,8-dicarba-*nido*-undecaborate (1–).

Here we report the syntheses of stable silver complexes of derivatives of monothio or dithio-7,8-dicarba-*nido*-undecaborate and examples of the different structures they provide. In the aim of having the broadest information on the stability of these silver complexes, ligands containing two sulfur atoms (L_{s2c}^- and L_{s2n}^-) and one sulfur atom (L_{s1}^-) have been studied. The ligands are named in the text as follows: L stands for the moiety 7,8-dicarba-*nido*-undecaborate, the subindexes for the carborane external fragment, e.g. **s1** and **s2**, indicate one or two exocluster sulfur

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(1) (a) Teixidor, F.; Rudolph, R. W. *J. Organomet. Chem.* **1983**, *241,* 301. (b) Viñas, C.; Butler, W. M.; Teixidor, F.; Rudolph, R. W. *Organometallics* **1984**, *3,* 503. (c) Viñas, C.; Butler, W. M.; Teixidor, F.; Rudolph, R. W. *Inorg. Chem.* **1986**, *25,* 4369. (d) Teixidor, F.; Romerosa, A. M.; Rius, J.; Miravitlles, C.; Casabó, J.; Viñas, C.; Sánchez, E. *J. Chem. Soc., Dalton Trans.* **1990**, 525. (e) Teixidor, F.; Viñas, C.; Rius, J.; Miravitlles, C.; Casabó, J. *Inorg. Chem.* **1990**, *29,* 149.

(2) Teixidor, F.; Ayllon, J. A.; Viñas, C.; Kivekäs, R.; Sillanpää, R.; Casabó, J. *J. Organomet. Chem.*, in press.

(3) Teixidor, F.; Casabó, J.; Viñas, C.; Sanchez, E.; Escriche, Ll.; Kivekäs, R. *Inorg. Chem.* **1991**, *30,* 3053.

(4) Teixidor, F.; Ayllon, J. A.; Viñas, C.; Rius, J.; Miravitlles, C.; Casabó, J. *J. Chem. Soc., Chem. Commun.* **1992**, 1281.

(5) Teixidor, F.; Ayllon, J. A.; Viñas, C.; Kivekas, R.; Sillanpää, R.; Casabó, J. *Organometallics*, in press.

(6) Teixidor, F.; Ayllon, J. A.; Viñas, C.; Rius, J.; Miravitlles, C.; Casabó, J. *J. Chem. Soc., Chem. Commun.* **1992**, 1279.

(7) Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1980**, 192.

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

(9) (a) Bommer, J. C.; Morse, K. W. *J. Am. Chem. Soc.* **1974**, *96,* 6222. (b) Bommer, J. C.; Morse, K. W. *Inorg. Chem.* **1979**, *18,* 531. (c) Bommer, J. C.; Morse, K. W. *Inorg. Chem.* **1980**, *19,* 587.

(10) (a) Muetterties, E. L.; Balthis, J. H.; Chia, Y. T.; Knoth, W. H.; Miller, H. C. *Inorg. Chem.* **1964**, *3,* 444. (b) Knoth, W. H.; Miller, H. C.; Saver, J. C.; Bathis, J. H.; Chia, Y. T.; Muetterties, E. L. *Inorg. Chem.* **1964**, *3,* 159.

(11) (a) Dobrott, R. D.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *37,* 1779. (b) Gill, J. T.; Lippard, S. J. *Inorg. Chem.* **1975**, *14,* 751.

(12) Battsev, V. A.; Stanko, V. I. *Zh. Obshch. Khim,* **1968**, *38* (12), 2820.

(13) Grimes, R. N., Ed. *Carboranes*; Academic Press: New York, 1970.

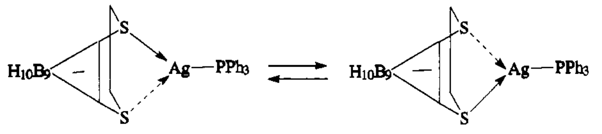
0020-1669/94/1333-1756$04.50/0

Table 1. *nido*-Carbaborane Ligands with Their Abbreviations and the Complexes Obtained

$\mathbf{L_{s2c5}}^-$	$\{7,8\text{-}\mu\text{-}(SCH_2S)\text{-}7,8\text{-}C_2B_9H_{10}\}^-$
$\mathbf{L_{s2c6}}^-$	$\{7,8\text{-}\mu\text{-}(SCH_2CH_2S)\text{-}7,8\text{-}C_2B_9H_{10}\}^-$
$\mathbf{L_{s2c12}}^-$	$\{7,8\text{-}\mu\text{-}(SCH_2CH_2OCH_2CH_2OCH_2CH_2S)\text{-}7,8\text{-}C_2B_9H_{10}\}^-$
$\mathbf{L_{s2c15}}^-$	$\{7,8\text{-}\mu\text{-}(SCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2S)\text{-}7,8\text{-}C_2B_9H_{10}\}^-$
$\mathbf{L_{s2n}}^-$	$\{7,8\text{-}(SCH_2CH_3)_2\text{-}7,8\text{-}C_2B_9H_{10}\}^-$
$\mathbf{L_{s1}}^-$	$\{7\text{-}(SCH_2CH_3)\text{-}8\text{-}(CH_3)\text{-}7,8\text{-}C_2B_9H_{10}\}^-$

$\mathbf{[Ag(L_{s2c5})(PPh_3)]}$
$\mathbf{[Ag(L_{s2c6})(PPh_3)]\cdot 0.5CH_2Cl_2}$
$\mathbf{[Ag(L_{s2c6})(bipy)]}$
$\mathbf{[Ag(L_{s2c12})]}$
$\mathbf{[Ag(L_{s2c15})]}$
$\mathbf{[Ag(L_{s2n})(PPh_3)]}$
$\mathbf{[Ag(L_{s2n})(bipy)]}$
$\mathbf{[Ag(L_{s1})(PPh_3)]}$
$\mathbf{[Ag(L_{s1})(bipy)]}$

Scheme 1



atoms respectively, and **c** or **n** stands for the **c**yclic or **n**oncyclic nature of the exocluster unit. In the case of $\mathbf{L_{s2c}}^-$ ligands, the macrocyclic size is indicated by a number, e.g. $\mathbf{L_{s2c6}}^-$ stands for a 7,8-$C_2B_9H_{10}$ moiety with two sulfur atoms connected to the cage at the 7,8 positions and externally joined by a chain producing a cycle of total size 6. Figure 1 shows a schematic drawing of these ligands. Furthermore, the influence of the additional non-carborane ligands, "Lewis base", has been investigated by introducing PPh_3 and bipy. Finally, 7,8-dithio-7,8-dicarba-*nido*-undecaborate macrocyclic ligands providing additional coordinating elements within the chain, $\mathbf{L_{s2c12}}^-$ and $\mathbf{L_{s2c15}}^-$, have also been examined. Table 1 indicates the ligands examined and the complexes produced.

Results and Discussion

To get information on the behavior of these thio-7,8-dicarba-*nido*-undecaborate ligands toward Ag(I), 7-monothio-7,8-dicarba-*nido*-undecaborate(1–) ($\mathbf{L_{s1}}^-$) and 7,8-dithio-7,8-dicarba-*nido*-undecaborate(1-) derivatives ($\mathbf{L_{s2c}}^-$ and $\mathbf{L_{s2n}}^-$) have been used as ligands.

The reaction of $\mathbf{L_{s2n}}^-$ or $\mathbf{L_{s2c}}^-$ with $AgNO_3$ and PPh_3 in solvents such as MeOH yields white molecular compounds with stoichiometries $\mathbf{[Ag(L_{s2n})(PPh_3)]}$ and $\mathbf{[Ag(L_{s2c})(PPh_3)]}$. See eq 1 for $\mathbf{L_{s2c6}}^-$.

$$L_{s2c6}^- + AgNO_3 + PPh_3 \underset{N_2}{\overset{\text{methanol}}{\rightarrow}} \mathbf{[Ag(L_{s2c6})(PPh_3)]} \quad (1)$$

The hydrogen bridge absorption in the ^{1}H-NMR spectrum at approx $\delta = -2.5$ ppm and the pattern and distribution of the ^{11}B-NMR spectrum (2:1:2:2:1:1) preclude any metal disposition on the open face. The resonance at $\delta \approx -2.5$ ppm is very informative in $[C_2B_9H_{10}RR']^-$ chemistry, because it provides information on the cluster's charge and indeed on the presence or absence of the open face hydrogen bridge. The lack of any absorption at higher field values than –2.5 ppm in the ^{1}H-NMR spectrum does not support any B(3)–H→M interaction.[4] The ^{11}B-NMR pattern indicates that the ligand's original symmetry is preserved upon coordination, which implies that in solution both sulfur atoms equivalently coordinate the Ag ion. This, in solution, can be interpreted either by a equivalent chelating behavior of both thio groups or by a fast exchange such as this indicated in Scheme 1. As a result we hypothesize that the metal atom is coordinated to the two sulfur and the triphenylphosphine phosphorous atoms, the positive charge being compensated by the cluster anion. To influence the coordinating capacity of the two sulfur elements, similar reactions were carried out by using bipy instead of PPh_3; bipy being a bidentate chelating ligand could compete against one of the sulfur atoms. Here, too, the ligand's behavior was comparable to that already found with PPh_3, and white stable solids were also obtained in good yields. As above, ^{1}H- and ^{11}B-NMR spectra chemical shifts are analogous to those in the free ligand, indicating no boron cage to metal interaction, and as before the ligand's original symmetry was preserved suggesting that both thio groups, in solution, did participate equivalently in the coordination. Consequently, a four-coordinate Ag(I) is postulated, with two of the positions occupied by the sulfur atoms and the other two by the nitrogen atoms of the bipy ligand.

To study the influence of the additional ligands, PPh_3 and bipy, more relaxed macrocyclic ligands incorporating one or two oxygen atoms in the cyclic moiety, $\mathbf{L_{s2c12}}^-$ and $\mathbf{L_{s2c15}}^-$, were studied. It was expected that the very ligand would provide the additional coordinating sites by means of their oxygen atoms. The reaction of either $\mathbf{L_{s2c12}}^-$ or $\mathbf{L_{s2c15}}^-$ with $AgNO_3$ in methanol yielded stable white solids with the stoichiometry $\mathbf{[Ag(L_{s2c12})]}$ or $\mathbf{[Ag(L_{s2c15})]}$. From the NMR spectra evidence the proposed structures should be quite common to the others described here, however the low solubility in common organic solvents suggested an overall polymeric character of these compounds.

These results show that it is possible to get stable Ag(I) complex derivatives of $C_2B_9H_{12}^-$, that the Ag(I) chemistry can be considered normal (tri and tetracoordination is usually observed), and that the ligands $\mathbf{L_{s2c}}^-$ and $\mathbf{L_{s2n}}^-$ operate for Ag(I) as chelating anionic ligands.

To diminish the influence of the two chelating sulfur atoms in the stability of these compounds, the monothioether derivatives, $\mathbf{L_{s1}}^-$, have also been studied (Figure 1). These provide only one sulfur atom and a negative charge to the new compound. The reaction of $\mathbf{L_{s1}}^-$ with $AgNO_3$ in the presence of monodentate or bidentate extra ligands, PPh_3 or bipy, produces white compounds of general formula $\mathbf{[Ag(L_{s1})(PPh_3)]}$ or $\mathbf{[Ag(L_{s1})(bipy)]}$ which are the same as those found for the $\mathbf{L_{s2c}}^-$ and $\mathbf{L_{s2n}}^-$ ligands. See eq 2 for the case of $\mathbf{L_{s1}}^-$.

$$L_{s1}^- + AgNO_3 + PPh_3 \underset{N_2}{\overset{\text{methanol}}{\rightarrow}} \mathbf{[Ag(L_{s1})(PPh_3)]} \quad (2)$$

Again the ^{1}H- and ^{11}B-NMR spectra do not imply any metal to cage interaction, so the metal coordination sites are provided by the PPh_3 (one) or bipy (two). In the case of $\mathbf{[Ag(L_{s1})(PPh_3)]}$, a polymer is expected with bridging thioethers and a molecular or polymer nature is hypothesized for $\mathbf{[Ag(L_{s1})(bipy)]}$.

The common and extremely simple $\mathbf{[Ag(L_s)(Lewis)]}$ stoichiometry does not take in account the great variety of $\mathbf{L_s}$ ligands used: two thio groups, cyclic ($\mathbf{L_{s2c}}^-$) and noncyclic ($\mathbf{L_{s2n}}^-$), with or without extra coordinating elements within the cycle, ($\mathbf{L_{s2c12}}^-$ and $\mathbf{L_{s2c15}}^-$), or one thio group, ($\mathbf{L_{s1}}^-$). As a result, several coordinating motifs were foreseen.

In order to ascertain their geometry, the crystal structures of some representative examples were determined. A part of the polymeric structure of the complex $\mathbf{[Ag(L_{s2c15})]}$ is shown in Figure 2. Table 2 lists positional parameters, and Table 3lists selected bond lengths and angles. In this structure each ligand is asymmetrically bonded to one Ag through the two sulfur atoms with bond lengths of 2.558(3) and 2.711(3) Å, respectively. The sulfur atom that provides the longest bond is nonequivalently bridging another silver ion with a short distance of 2.502(3) Å, and thus an infinite Ag–S–Ag–S– chain is formed, as shown in Figure 3. The S,S′ organic chain provides the fourth coordination site through one of the three oxygen atoms with a distance of 2.501(8) Å. Consequently the Ag(I) can also be considered trigonally coordinated with a fourth weaker interaction through

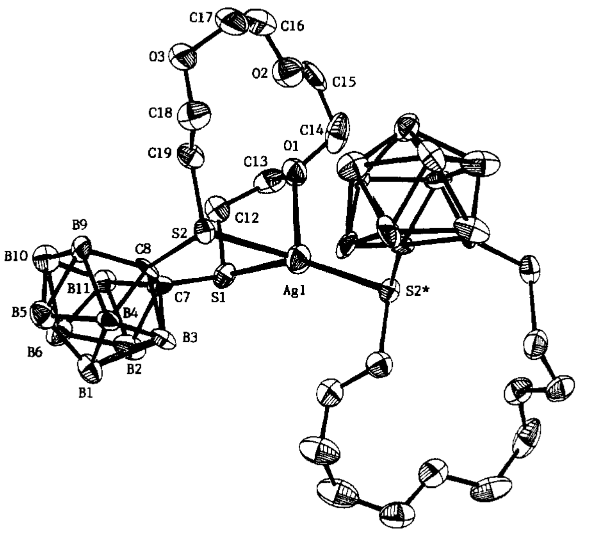


Figure 2. View of the mononuclear fragment of polymeric **[Ag(L_{s2c15})]**.

Table 2. Final Positional Parameters and Isotropic Thermal Parameters with Esd's in Parentheses for **[Ag(L_{s2c15})]**

atom	x	y	z	U_{eq},[a] Å^2
Ag(1)	0.02711 (6)	0.06400 (5)	0.0000[b]	0.0476 (5)
S(1)	0.0295 (3)	0.2118 (2)	0.0845 (4)	0.034 (2)
S(2)	0.0422 (2)	0.0455 (2)	0.3276 (4)	0.029 (2)
O(1)	0.1980 (6)	0.1041 (5)	−0.032 (1)	0.046 (6)
O(2)	0.3260 (7)	−0.0040 (6)	0.117 (1)	0.056 (7)
O(3)	0.3041 (6)	−0.0224 (5)	0.476 (2)	0.059 (7)
C(12)	0.1557 (9)	0.2279 (7)	0.096 (2)	0.039 (8)
C(13)	0.2097 (8)	0.1900 (8)	−0.045 (2)	0.05 (1)
C(14)	0.264 (1)	0.059 (1)	−0.126 (2)	0.06 (1)
C(15)	0.3519 (9)	0.0402 (8)	−0.022 (3)	0.06 (1)
C(16)	0.400 (1)	−0.0146 (8)	0.227 (2)	0.05 (1)
C(17)	0.363 (1)	−0.0621 (9)	0.367 (2)	0.07 (1)
C(18)	0.206 (1)	−0.0251 (8)	0.439 (2)	0.05 (1)
C(19)	0.1693 (8)	0.0503 (7)	0.370 (2)	0.037 (8)
B(1)	−0.1619 (9)	0.2244 (7)	0.505 (3)	0.041 (8)
B(2)	−0.103 (1)	0.2732 (9)	0.335 (2)	0.05 (1)
B(3)	−0.111 (1)	0.1688 (9)	0.326 (2)	0.033 (9)
B(4)	−0.1040 (9)	0.1319 (9)	0.535 (2)	0.030 (9)
B(5)	−0.084 (1)	0.2154 (9)	0.664 (2)	0.04 (1)
B(6)	−0.085 (1)	0.3048 (9)	0.537 (2)	0.04 (1)
C(7)	−0.0044 (8)	0.2157 (7)	0.296 (1)	0.028 (7)
C(8)	−0.003 (1)	0.1392 (8)	0.410 (2)	0.026 (7)
B(9)	0.018 (1)	0.154 (1)	0.607 (2)	0.03 (1)
B(10)	0.030 (1)	0.2661 (8)	0.619 (2)	0.04 (1)
B(11)	0.015 (1)	0.2965 (9)	0.402 (2)	0.04 (1)

[a] U has been defined as $U = {}^1/_3\Sigma_i\Sigma_jU_{ij}a_i{}^*a_j{}^*a_i{\cdot}a_j$. [b] The z-coordinate of Ag(1) has been fixed to the origin.

a S atom as a result of the asymmetric behavior of the carborane ligand. The Ag is anti with regard to the C_2B_3 open face, which is common with other complexes of this type of ligands. The dihedral **w** angle, see Figure 4, between the planes S(1)–Ag(1)–S(2) and S(1)–C(7)–C(8)–S(2), has a value of 156° which is in agreement with others found[3] for this type of relaxed ligands. The molecular structure of the complex **[Ag(L_{s2c6})(PPh$_3$)]·0.5CH$_2$Cl$_2$** is shown in Figure 5. Table 4 lists positional parameters and Table 5 selected bond lengths and angles. The complex **[Ag(L_{s2c6})(PPh$_3$)]·0,5CH$_2$Cl$_2$** presents a molecular structure where the Ag atom is in a distorted trigonal environment with vertexes occupied by two sulfur atoms of the nonsymmetrically acting carborane ligand (Ag–S distances 2.665(2), 2.584(2) Å). The third vertex is occupied by the phosphorous of the PPh$_3$ group (Ag–P distance 2.390(2) Å). The silver atom deviates 0.305(1) Å from the plane through the three coordinated atoms. The **w** angle found has a value of 120.4(1)° which is considerably smaller than that found in **[Ag(L_{s2c15})]**. Even though the silver anti disposition with regard to the C_2B_3 open face is the most abundant (72%) the syn structure is also observed in the crystal (28%).

Table 3. Selected Bond Lengths (Å) and Angles (deg) with Esd's in Parentheses for **[Ag(L_{s2c15})]**.

Ag(1)–S(1)	2.558 (3)	C(7)–B(3)	1.71 (2)
Ag(1)–S(2)	2.711 (3)	C(7)–C(8)	1.58 (2)
Ag(1)–O(1)	2.501 (8)	C(7)–B(11)	1.63 (2)
Ag(1)–S(2)[a]	2.503 (3)	C(8)–B(3)	1.74 (2)
S(1)–C(7)	1.80 (1)	C(8)–B(9)	1.65 (2)
S(1)–C(12)	1.79 (1)	B(9)–B(10)	1.88 (2)
S(2)–C(8)	1.81 (1)	B(10)–B(11)	1.86 (2)
S(2)–C(19)	1.82 (1)		

S(1)–Ag(1)–S(2)	80.83 (9)	C(8)–S(2)–Ag(1)[b]	106.3 (5)
Ag(1)–S(2)–C(8)	104.2 (5)	O(1)–Ag(1)–S(2)[a]	120.5 (2)
S(1)–Ag(1)–O(1)	76.0 (2)	C(19)–S(2)–Ag(1)[b]	107.7 (4)
Ag(1)–S(2)–C(19)	105.1 (4)	Ag(1)–S(1)–C(7)	106.9 (4)
S(1)–Ag(1)–S(2)[a]	149.2 (1)	Ag(1)–O(1)–C(13)	112.4 (6)
Ag(1)–S(2)–Ag(1)[b]	127.7 (1)	Ag(1)–S(1)–C(12)	99.9 (4)
S(2)–Ag(1)–O(1)	93.4 (3)	Ag(1)–O(1)–C(14)	122.7 (8)
C(8)–S(2)–C(19)	103.3 (6)	C(7)–S(1)–C(12)	101.7 (6)
S(2)–Ag(1)–S(2)[a]	120.42 (9)	C(13)–O(1)–C(14)	114 (1)

[a] Equivalent position: $-x, -y, z - {}^1/_2$. [b] Equivalent position: $-x, -y, z + {}^1/_2$.

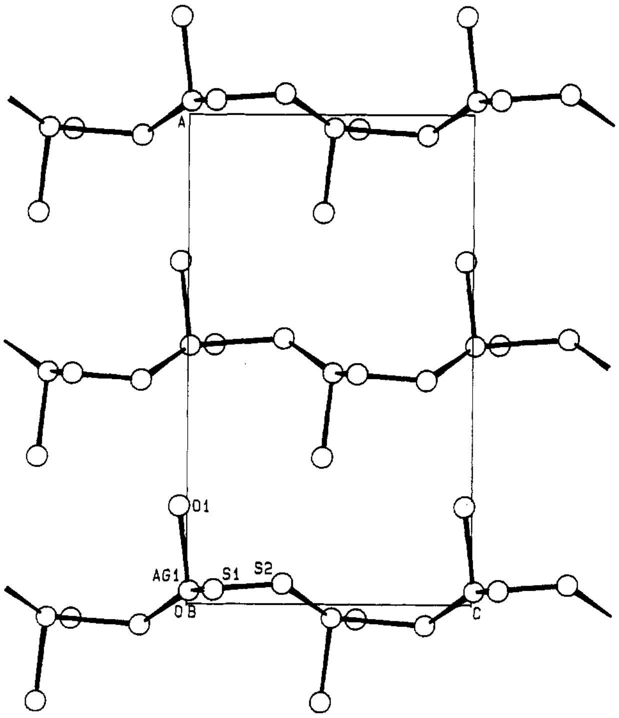


Figure 3. Simplified drawing of infinite Ag–S–Ag–S chain.

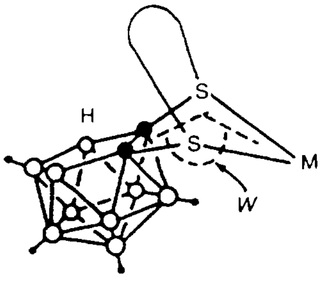


Figure 4. The **w** angle concept.

Considering these crystal structures and the previous report on **[NMe$_4$][AgL$_{s2c6}$]**, it can be stated that these ligands, mono- and dithio-7,8-dicarba-*nido*-undecaborate(1−) derivatives, do not present a unique way of coordination toward Ag$^+$. On the contrary, up to four coordination motifs have been found: three of those are represented in Figure 6 as motifs A, B, and C. The fourth motif would correspond to a C_2B_3–Ag open face coordination, presumably found with the highly strained **L_{s2c5}^-** ligand.

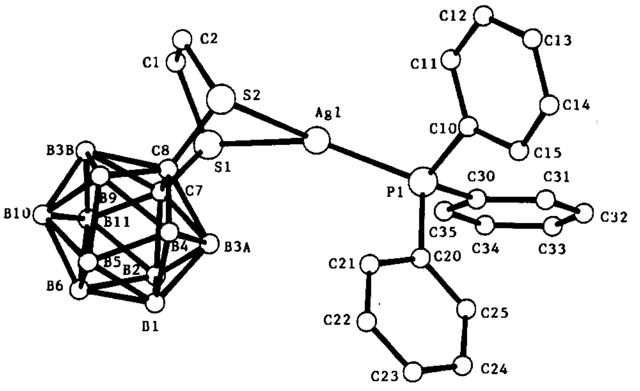


Figure 5. Molecular structure of $[Ag(L_{s2c6})(PPh_3)]\cdot 0.5CH_2Cl_2$.

Table 4. Final Positional Parameters and Isotropic Thermal Parameters with Esd's in Parentheses for $[Ag(L_{s2c6})(PPh_3)]\cdot 0.5CH_2Cl_2$.

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Ag(1)	0.04594 (5)	0.23292 (4)	0.17305 (5)	0.0628 (4)
S(1)	0.2345 (2)	0.3044 (1)	0.2706 (2)	0.054 (1)
S(2)	0.1877 (2)	0.1779 (1)	0.0984 (1)	0.054 (1)
P(1)	–0.1108 (1)	0.2183 (1)	0.2238 (1)	0.041 (1)
C(1)	0.2693 (8)	0.3289 (6)	0.1571 (8)	0.071 (6)
C(2)	0.2440 (8)	0.2663 (6)	0.0711 (7)	0.070 (6)
C(10)	–0.1593 (6)	0.3095 (4)	0.2548 (5)	0.043 (4)
C(11)	–0.1359 (7)	0.3760 (6)	0.2136 (7)	0.055 (6)
C(12)	–0.1676 (8)	0.4470 (5)	0.2355 (7)	0.068 (6)
C(13)	–0.2243 (9)	0.4515 (6)	0.3004 (8)	0.087 (7)
C(14)	–0.2496 (9)	0.3877 (6)	0.3449 (7)	0.090 (7)
C(15)	–0.2185 (8)	0.3168 (5)	0.3214 (6)	0.071 (6)
C(20)	–0.0814 (6)	0.1652 (4)	0.3461 (5)	0.044 (4)
C(21)	0.0183 (8)	0.1747 (5)	0.4240 (7)	0.067 (6)
C(22)	0.044 (1)	0.1381 (7)	0.5200 (8)	0.084 (8)
C(23)	–0.030 (1)	0.0905 (6)	0.5368 (8)	0.078 (8)
C(24)	–0.1296 (9)	0.0788 (5)	0.4622 (7)	0.064 (6)
C(25)	–0.1539 (8)	0.1154 (5)	0.3679 (7)	0.054 (5)
C(30)	–0.2275 (6)	0.1710 (4)	0.1296 (5)	0.044 (4)
C(31)	–0.3331 (8)	0.1793 (5)	0.1251 (8)	0.066 (6)
C(32)	–0.418 (1)	0.1410 (8)	0.050 (1)	0.095 (9)
C(33)	–0.396 (1)	0.0930 (8)	–0.018 (1)	0.094 (9)
C(34)	–0.293 (1)	0.0831 (6)	–0.0166 (8)	0.090 (8)
C(35	–0.2084 (9)	0.1222 (5)	0.0566 (7)	0.069 (6)
B(1)	0.3402 (9)	0.0824 (6)	0.4079 (8)	0.068 (7)
B(2)	0.3420 (8)	0.1814 (6)	0.4271 (7)	0.059 (6)
B(3A)[b]	0.2394 (9)	0.1347 (6)	0.3242 (8)	0.038 (4)
B(3B)[c]	0.427 (2)	0.204 (1)	0.251 (2)	0.027 (9)
B(4)	0.3003 (8)	0.0660 (6)	0.2729 (8)	0.064 (6)
B(5)	0.4379 (9)	0.0619 (7)	0.3505 (8)	0.073 (7)
B(6)	0.4640 (8)	0.1359 (6)	0.4483 (8)	0.069 (7)
C(7)	0.3137 (5)	0.2182 (4)	0.3077 (5)	0.045 (4)
C(8)	0.2910 (6)	0.1548 (4)	0.2216 (5)	0.047 (4)
B(9)	0.4013 (8)	0.1081 (6)	0.2298 (8)	0.062 (6)
B(10)	0.5051 (8)	0.1470 (7)	0.3387 (9)	0.071 (7)
B(11)	0.4421 (7)	0.2219 (6)	0.3835 (7)	0.058 (6)
Cl(1)[d]	0.007 (2)	–0.0157 (9)	0.025 (1)	0.14 (1)
Cl(2)[d]	–0.0041 (5)	0.0029 (4)	–0.1897 (5)	0.153 (5)
C(3)[d]	–0.026 (3)	0.047 (2)	–0.088 (2)	0.12 (1)

[a] *U* has been defined as $U = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$. [b] Population parameters 0.72 (1). [c] Population parameter 0.28 (1). [d] Population parameter 0.5.

Notwithstanding this elevated number of possible coordinating ways, there are certain rules in the behavior of these ligands which permit an easy interpretation of the structures found. These can be summarized as follows: **(i)** All these ligands coordinate to Ag^+ via the sulfur atoms with the probable exception of the very strained L_{s2c5}^-. **(ii)** The L_{s2c}^- and L_{s2a}^- ligands tend to be nonchelating or nonsymmetrically chelating, in the solid state, so both sulfur atoms are not equivalently bonded to a common Ag^+ ion. **(iii)** It is common that each sulfur atom participates in a strong and a weak S–Ag interaction; consequently, polymeric structures are favored. These are easily built up with motifs A and C, while motif B is more convenient for monomeric complexes.

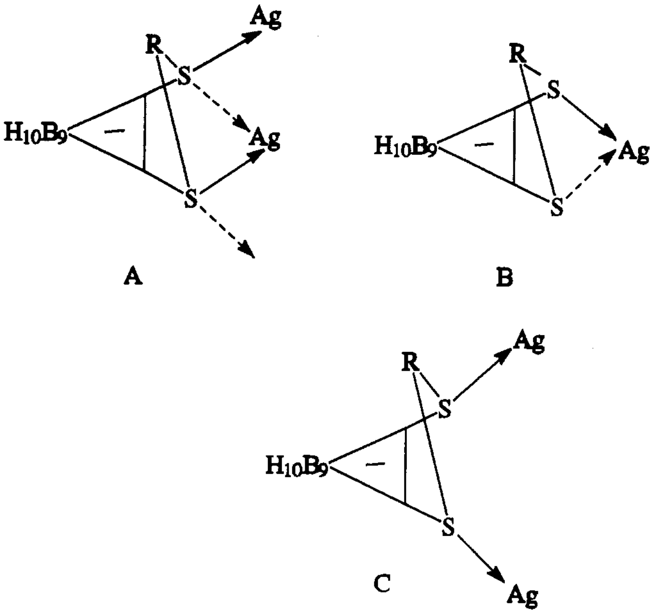


Figure 6. Observed motifs in the L_{s2}^- coordination to Ag^+.

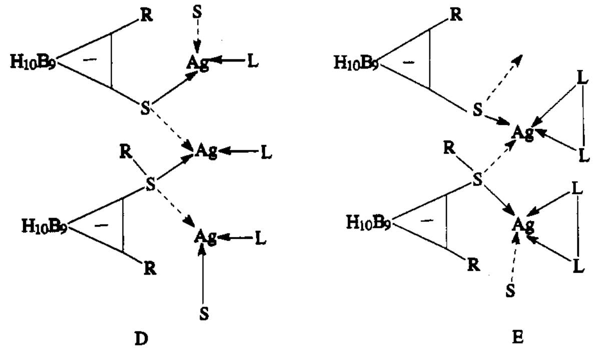


Figure 7. Predicted motifs in the L_{s1}^- coordination to Ag^+.

Table 5. Selected Bond Lengths (Å) and Angles (deg) with Esd's in Parentheses for $[Ag(L_{s2c6})(PPh_3)]\cdot 0.5CH_2Cl_2$

Ag(1)–S(1)	2.665 (2)	C(1)–C(2)	1.55 (1)
Ag(1)–S(2)	2.584 (2)	C(7)–B(3A)	1.81 (1)
Ag(1)–P(1)	2.390 (2)	C(7)–B(3B)	1.90 (3)
S(1)–C(1)	1.80 (1)	C(7)–C(8)	1.558 (9)
S(1)–C(7)	1.793 (7)	C(7)–B(11)	1.64 (1)
S(2)–C(2)	1.80 (1)	C(8)–B(3A)	1.78 (2)
S(2)–C(8)	1.790 (6)	C(8)–B(3B)	1.89 (3)
P(1)–C(10)	1.814 (8)	C(8)–B(9)	1.62 (1)
P(1)–C(20)	1.819 (7)	B(9)–B(10)	1.76 (1)
P(1)–C(30)	1.811 (7)	B(10)–B(11)	1.76 (2)

S(1)–Ag(1)–S(2)	72.66 (7)	Ag(1)–S(2)–C(8)	97.5 (3)
S(1)–Ag(1)–P(1)	130.11 (7)	C(2)–S(2)–C(8)	98.9 (4)
S(2)–Ag(1)–P(1)	151.16 (7)	Ag(1)–P(1)–C(10)	112.2 (3)
Ag(1)–S(1)–C(1)	98.7 (3)	Ag(1)–P(1)–C(20)	112.7 (3)
Ag(1)–S(1)–C(7)	95.3 (2)	Ag(1)–P(1)–C(30)	116.3 (3)
C(1)–S(1)–C(7)	98.3 (4)	S(1)–C(1)–C(2)	115.2 (8)
Ag(1)–S(2)–C(2)	99.4 (4)	S(2)–C(2)–C(1)	116.4 (8)

The polymeric shapes found for these compounds are the result of the intrinsic negative charge of the $C_2B_9H_{10}^-$ moiety which compensates the Ag charge. With it, the silver ion does not require the presence of coordinating anions in its coordination sphere permitting the structures presented here.

The structures proposed for $[Ag(L_{s1})(PPh_3)]$ and $[Ag(L_{s1})(bipy)]$ may be explained by considering motifs D and E, in Figure 7, which are similar to motif A in Figure 6.

Experimental Section

Instrumentation. Elemental analyses were performed using a Perkin-Elmer 240-B microanalyzer. IR spectra were obtained with KBr pellets on a Nicolet 710-FT spectrophotometer. The ^1H-NMR and ^{11}B-NMR spectra were obtained by using a Bruker AM 400WB instrument.

Materials. Before use, *o*-carborane (Dexsil Chemical Corp.) was sublimed under high vacuum ; 7,8-(1′,3′-dithiamethane-1′,3′-diyl)-7,8-dicarba-*nido*-undecaborate ($\mathbf{L}_{s2c5}^-$), –7,8-(1′,4′-dithiaethane-1′,4′-diyl)-7,8-dicarba-*nido*-undecaborate ($\mathbf{L}_{s2c6}^-$); 7,8-bis(thiaethane)-7,8-dicarba-*nido*-undecaborate ($\mathbf{L}_{s2a}^-$), 7-(methylthio)-8-methyl-7,8-dicarba-*nido*-undecaborate ($\mathbf{L}_{s1}^-$), 7,8-(1′,10′-dithia-4′,7′-dioxadecane-1′,10′-diyl)-7,8-dicarba-*nido*-undecaborate ($\mathbf{L}_{s2c12}^-$), and 7,8-(1′,13′-dithia-4′,7′,10′-trioxatridecane-1′,13′-diyl)-7,8-dicarba-*nido*-undecaborate ($\mathbf{L}_{s2c15}^-$) were prepared from *o*-carborane according to the literature.[14] A 1.7 M solution of n-butyllithium in hexane from Fluka was used as purchased. Ethanol was reagent grade.

Synthesis of $[NMe_4]\mathbf{L}_{s2a}$. To 40 cm^3 of deoxygenated ethanol containing 350 mg (6.23 mmol) of KOH was added 1,2-dithiol-o-carborane (500 mg, 2.40 mmol). After 4 cm^3 (54 mmol) of bromoethane were added, the mixture was refluxed, under nitrogen, for 1 h. Insolubles were separated by filtering the warm mixture. After addition of potassium hydroxide (0.8 g, 14 mmol) to the ethanol solution, it was refluxed for 1 h. After evaporation of the solvent, water was added. Insolubles were separated by filtering the mixture. Excess of tetramethylammonium chloride was added to the aqueous solution, resulting in the formation of a white precipitate. This was filtered off, washed with water and ether, and dried in vacuum to yield an analytically pure solid $[NMe_4]$-$\mathbf{L}_{s2a}$. Yield: 630 mg (80%). FTIR (KBr): ν [cm^{-1}] = 2550, 2517 (B–H). ^1H-FTNMR (400 MHz, CD_3COCD_3, 25 °C, TMS): δ –2.5 (br, 1, B*H*B), 1.08–1.14 (m, 6, C*H*$_3$), 2.66 (2.75 (m, 2, –SC*H*$_2$), 3.45 (s, 12, N(C*H*$_3$)$_4$). ^{11}B-FTNMR (128 MHz, CH_3COCH_3, 25 °C, $BF_3 \cdot Et_2O$): δ = –7.3 (d, ^1J(B,H) = 138 Hz, 2B), –12.5 (d, ^1J(B,H) = 159 Hz, 1B), –16.4 (d, ^1J(B,H) = 152 Hz, 2B), –17.9 (d, ^1J(B,H) = 183 Hz, 2B), –34.1 (d, ^1J(B,H) = 115 Hz, 1B), –35.5 (d, ^1J(B,H) = 144 Hz, 1B). Anal. Calcd for $C_{10}H_{32}B_9NS_2$: C, 36.64; H, 9.84; N, 4.27; S, 19.56. Found: C, 36.08; H, 10.14; N, 4.62; S, 17.89.

Synthesis of $[Ag(\mathbf{L}_{s2c5})(PPh_3)]$. To 15 cm^3 of deoxygenated methanol containing 65.5 mg (0.231 mmol) of $[NMe_4](\mathbf{L}_{s2c5})$ was added $[Ag(NO_3)(PPh_3)]$ (100 mg, 0.231 mmol) dissolved in 10 cm^3 of deoxygenated methanol. Then 4 cm^3 of hexane was added to the solution. A crystalline white solid was obtained when the solution was left for 12 h at –20 °C. This solid was separated by filtering the cold mixture. The solid was washed with methanol/hexane (5/1) to yield an analytically pure solid $[Ag(\mathbf{L}_{s2c5})(PPh_3)]$. Yield: 68 mg (51%).

FTIR (KBr): ν [cm^{-1}] = 2533 (B–H). ^1H-FTNMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ –2.53 (br, 1, B*H*B), 3.61 (d, ^1J = 11 Hz, 1, C*H*$_2$), 3.81 (d, ^1J = 11 Hz, 1, C*H*$_2$), 7.50–7.35 (m, 15, aryl–*H*). ^{11}B-FTNMR (128 MHz, CH_2Cl_2, 25 °C, $BF_3 \cdot Et_2O$): δ = –12.6 (d, ^1J(B,H) = 123 Hz, 2B), –15.7 (3B), –17.6 (2B), –30.2 (d, ^1J(B,H) = 104 Hz, 1B), –35.1 (d, ^1J(B,H) = 140 Hz, 1B). Anal. Calcd for $C_{21}H_{27}AgB_9PS_2$: C, 43.51; H, 4.69; S, 11.06. Found: C, 44.58; H, 4.83, S, 9.80.

Synthesis of $[Ag(\mathbf{L}_{s2c6})(PPh_3)]\cdot 0.5CH_2Cl_2$. To 15 cm^3 of deoxygenated methanol containing 70.1 mg (0.235 mmol) of $[NMe_4](\mathbf{L}_{s2c6})$ was added $[Ag(NO_3)(PPh_3)]$ (100 mg, 0.231 mmol) dissolved in 10 cm^3 of deoxygenated methanol. Then 4 cm^3 of hexane was added to the solution. A white precipitate was obtained when the solution was left for 48 h at –20 °C. This solid was separated by filtering the cold mixture. After recrystallization in dichloromethane/hexane (1/1), 62 mg of $[Ag(\mathbf{L}_{s2c6})(PPh_3)]\cdot 0.5CH_2Cl_2$ was obtained (42%). FTIR (KBr): ν [cm^{-1}] = 2542 (B–H). ^1H-FTNMR (400 MHz, CD_2Cl_2, 25 °C, TMS): δ –2.61 (br, 1, B*H*B), 3.13 (m, 2, C*H*$_2$), 3.26 (m, 1, C*H*$_2$), 5.32 (s, 1, C*H*$_2$Cl$_2$), 7.30–7.60 (m, 15, aryl–*H*). ^{11}B-FTNMR (128 MHz, CH_2Cl_2, 25 °C, $BF_3 \cdot Et_2O$): δ = –8.6 (d, ^1J(B,H) = 135 Hz, 2B), –9.9 (1B), –17.6 (d, ^1J(B,H) = 134 Hz, 2B), –20.3 (d, ^1J(B,H) = 156 Hz, 2B), –33.6 (d, ^1J(B,H) = 90 Hz, 1B), -37.4 (d, ^1J(B,H) = 146 Hz, 1B). Anal. Calcd for $C_{22.5}H_{30}AgB_9ClPS_2$: C, 42.48; H, 4.75; S, 10.08. Found: C, 42.50; H, 4.70, S, 10.11.

Synthesis of $[Ag(\mathbf{L}_{s2c6})(bipy)]$. To 15 cm^3 of deoxygenated methanol containing 70 mg (0.235 mmol) of $[NMe_4](\mathbf{L}_{s2c6})$ were added $AgNO_3$ (39 mg, 0.230 mmol) and 2,2′-bipyridine (39 mg, 0.250 mmol) dissolved in 15 cm^3 of deoxygenated methanol. A white solid precipitate was obtained. This solid was left at room temperature for 4 h and then was separated by filtering the mixture. The solid was washed with methanol to yield an analytically pure solid, $[Ag(\mathbf{L}_{s2c6})(bipy)]$. FTIR (KBr): ν [cm^{-1}] = 2537, 2525, 2490 (B–H). ^1H-FTNMR (400 MHz, CD_3COCD_3, 25 °C, TMS): δ –2.50 (br, 1, B*H*B), 3.30 (m, 2, S–C*H*$_2$), 3.46 (m, 2, S–C*H*$_2$), 7.74 (t, ^1J = 5.8 Hz, 2, bipy (*H*: 5,5′)), 8.21 (t, ^1J = 8.0 Hz, 2, bipy (*H*: 4,4′)), 8.53 (d, ^1J = 8.7 Hz, 2, bipy (*H*: 3,3′)), 8.84 (d, ^1J = 4.4 Hz, 2, bipy (*H*: 6,6′)). ^{11}B-FTNMR (128 MHz, CH_2Cl_2, 25 °C, $BF_3 \cdot Et_2O$): δ = –7.6 (d, ^1J(B,H) = 138 Hz, 3B), –16.5 (d, ^1J(B,H) = 139 Hz, 2B), –19.1 (d, ^1J(B,H) = 156 Hz, 2B), –32.8 (d, ^1J(B,H) = 106 Hz, 1B), –36.5 (d, ^1J(B,H) = 146 Hz, 1B). Anal. Calcd for $C_{14}H_{22}AgB_9N_2S_2$: C, 34.48; H, 4.55; S, 13.15; N, 5.74. Found: C, 34.54; H, 4.86; S, 13.26; N, 5.46.

Synthesis of $[Ag(\mathbf{L}_{s2c12})]$. To 20 cm^3 of deoxygenated methanol containing 132 mg (0.341 mmol) of $[NMe_4](\mathbf{L}_{s2c12})$ was added $AgNO_3$ (58 mg, 0.341 mmol) dissolved in 20 cm^3 of deoxygenated methanol. A white solid precipitate was obtained. This solid was separated by filtering the mixture. The solid was dissolved in 20 cm^3 of acetonitrile and 30 cm^3 of butanol. After slow evaporation of the solvent a crystalline solid was obtained. The solid was separated by filtration to yield an analytically pure solid of $[Ag(\mathbf{L}_{s2c12})]$ (85 mg, 60%). FTIR (KBr): ν [cm^{-1}] = 2540, 2538 (B–H). ^1H-FTNMR (400 MHz, CD_2Cl_2, 25 °C, TMS): δ –2.6 (br, 1, B*H*B), 3.13 (br, 4, –C*H*$_2$), 3.54 (br, 2, –OC*H*$_2$), 3.65 (br, 4, –OC*H*$_2$). ^{11}B-FTNMR (128 MHz, CH_3CN, 25 °C, $BF_3 \cdot Et_2O$): δ = –8.4 (d, ^1J(B,H) = 139 Hz, 2B), –13.3 (1B), –15.6 (4B), –32.8 (d, ^1J(B,H) = 92 Hz, 1B), –35.8 (d, ^1J(B,H) = 142 Hz, 1B). Anal. Calcd for $C_8H_{22}AgB_9O_2S_2$: C, 22.90; H, 5.29; S, 15.28. Found: C, 23.16; H, 5.24; S, 15.11.

Synthesis of $[Ag(\mathbf{L}_{s2c15})]$. To 10 cm^3 of deoxygenated methanol containing 55 mg (0.145 mmol) of $Na(\mathbf{L}_{s2c15})$ was added $AgNO_3$ (24 mg, 0.141 mmol) dissolved in 10 cm^3 of deoxygenated methanol. A white solid precipitate was obtained. This solid was separated by filtering the mixture. The solid was washed with methanol to yield an analytically pure solid of $[Ag(\mathbf{L}_{s2c15})]$. Yield: 60 mg (92%). FTIR (KBr): ν [cm^{-1}] = 2578, 2537, 2528, 2478 (B–H). ^1H-FTNMR (400 MHz, CD_3CN, 25 °C, TMS): δ –2.6 (br, 1, B*H*B), 3.05 (br, 2, S–C*H*$_2$), 3.18 (br, 2, S–C*H*$_2$), 3.63 (br, 12, –OC*H*$_2$). ^{11}B-FTNMR (128 MHz, CH_3CN, 25 °C, $BF_3 \cdot Et_2O$): δ = –7.6 (d, ^1J(B,H) = 141 Hz, 2B), –12.6 (d, ^1J(B,H) = 148 Hz, 1B), –15.6 (d, ^1J(B,H) = 146 Hz, 2B), –17.4 (2B), –33.4 (d, ^1J(B,H) = 98 Hz, 1B), –35.9 (d, ^1J(B,H) = 141 Hz, 1B). Anal. Calcd for $C_{10}H_{26}AgB_9O_3S_2$: C, 25.91; H, 5.65; S, 13.83. Found: C, 25.83; H, 5.62; S, 13.71.

Synthesis of $[Ag(\mathbf{L}_{s2a})(PPh_3)]$. To 15 cm^3 of deoxygenated methanol containing 76 mg (0.231 mmol) of $[NMe_4](\mathbf{L}_{s2a})$ was added $[Ag(NO_3)(PPh_3)]$ (100 mg, 0.231 mmol) dissolved in 10 cm^3 of deoxygenated methanol. Then 4 cm^3 of hexane was added to the solution. A crystalline white solid was obtained when the solution was left for 48 h at –20 °C. This solid was separated by filtering the cold mixture. The solid was washed with methanol and hexane to yield an analytically pure solid $[Ag(\mathbf{L}_{s2a})(PPh_3)]$. Yield: 130 mg. (90%). FTIR (KBr): ν [cm^{-1}] = 2578, 2565, 2533, 2527, 2467 (B–H). ^1H-FTNMR (400 MHz, CD_2Cl_2, 25 °C, TMS): δ –2.67 (br, 1, B*H*B), 1.19 (t, ^1J = 7.3 Hz, 6, –C*H*$_3$), 2.90 (m, 2, S–C*H*$_2$), 3.09 (m, 2, S–C*H*$_2$), 7.30–7.60 (m, 15, aryl–*H*). ^{11}B-FTNMR (128 MHz, CH_2Cl_2, 25 °C, $BF_3.Et_2O$): δ = –8.6 (d, ^1J(B,H) = 135 Hz, 2B), –12.7 (d, ^1J(B,H) = 152 Hz, 1B), –15.9 (d, ^1J(B,H) = 146 Hz, 2B), –17.4 (2B), –33.1 (d, ^1J(B,H) = 105 Hz, 1B), –36.4 (d, ^1J(B,H) = 144 Hz, 1B). Anal. Calcd for $C_{24}H_{35}AgB_9PS_2$: C, 46.21; H, 5.66; S, 10.28. Found: C, 46.30; H, 5.70; S, 10.30.

Synthesis of $[Ag(\mathbf{L}_{s2a})(bipy)]$. To 20 cm^3 of deoxygenated methanol containing 77 mg (0.235 mmol) of $[NMe_4](\mathbf{L}_{s2a})$ were added $AgNO_3$ (39 mg, 0.230 mmol) and 2,2′-bipyridine (390 mg, 0.250 mmol) dissolved in 20 cm^3 of deoxygenated methanol. A crystalline white solid was obtained when the solution was left for 24 h at 4 °C. This solid was separated by filtering the cold mixture. The solid was washed with methanol to yield an analytically pure solid $[Ag(\mathbf{L}_{s2a})(bipy)]$. Yield: 95 mg (80%). FTIR (KBr): ν [cm^{-1}] = 2530, 2506 (B–H). ^1H-FTNMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ –2.5 (br, 1, B*H*B), 1.30 (t, ^1J = 7.3 Hz, 6, –C*H*$_3$), 2.92 (m, 2, S–C*H*$_2$), 3.13 (m, 2, S–C*H*$_2$), 7.60 (t, ^1J = 5.5 Hz, 2, bipy (*H*: 5,5′)), 8.05 (t, ^1J = 8.3 Hz, 2, bipy (*H*: 4,4′)), 8.21 (d, ^1J = 7.4 Hz, 2, bipy (*H*: 3,3′)), 8.68 (d, ^1J = 5.6 Hz, 2, bipy (*H*: 6,6′)). ^{11}B-FTNMR (128 MHz, CH_3COCH_3, 25 °C, $BF_3 \cdot Et_2O$): δ = –7.6 (d, ^1J(B,H) = 142 Hz, 2B), –11.9 (d, ^1J(B,H) = 161 Hz, 1B), –14.9 (d, ^1J(B,H) = 146 Hz, 2B), –16.3 (d, ^1J(B,H) = 175 Hz, 2B), –32.8 (d, ^1J(B,H) = 110 Hz, 1B), –35.8 (d, ^1J(B,H) = 143 Hz, 1B). Anal. Calcd for $C_{16}H_{28}AgB_9N_2S_2$: C, 37.12; H, 5.45; S, 12.39; N, 5.41. Found: C, 37.42; H, 5.80; S, 12.72; N, 5.39.

Synthesis of $[Ag(\mathbf{L}_{s1})(PPh_3)]$. To 4 cm^3 of deoxygenated methanol containing 50 mg (0.187 mmol) of $[NMe_4](\mathbf{L}_{s1})$ was added $[Ag(NO_3)$-

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(14) (a) Teixidor, F.; Romerosa, A. M.; Rius, J.; Miravitlles, C.; Casabó, J.; Viñas, C.; Sánchez, E. *J. Chem. Soc., Dalton Trans.* **1990**, 525. (b) Teixidor, F.; Rudolph, R. *J. Organomet. Chem.* **1983**, 301. (c) Teixidor, F.; Rius, J.; Romerosa, A. M.; Miravitlles, C.; Escriche, Ll.; Sanchez, E.; Viñas, C.; Casabó, J. *Inorg. Chim. Acta* **1990**, 287.

(PPh_3)] (80 mg, 0.185 mmol) dissolved in 6 cm^3 of deoxygenated methanol. Then 2 cm^3 of hexane was added to the solution. A crystalline white solid was obtained when the solution was left for 24 h at −20 °C. This solid was separated by filtering the cold mixture. The solid was washed with methanol and hexane to yield an analytically pure solid [Ag(L_{s1})(PPh_3)]. Yield: 90 mg (86%). FTIR (KBr): ν [cm^{-1}] = 2577, 2533, 2500, 2403 (B–H). ^{1}H-FTNMR (400 MHz, CD_3CN, 25 °C, TMS): δ −2.5 (br, 1, B*H*B), 1.55 (s, 3, –C*H*$_3$), 2.29 (s, 3, S–C*H*$_3$), 7.35–7.60 (m, 15, aryl-*H*). ^{11}B-FTNMR (128 MHz, CH_3CN, 25 °C, $BF_3 \cdot Et_2O$): δ = −9.2 (d, ^1J(B,H) = 137 Hz, 2B), −11.9 (d, ^1J(B,H) = 160 Hz, 1B), -17.7 (d, ^1J(B,H) = 150 Hz, 2B), −18.9 (d, ^1J(B,H) = 147 Hz, 2B), −35.0 (d, ^1J(B,H) = 102 Hz, 1B), −37.1 (d, ^1J(B,H) = 140 Hz, 1B). Anal. Calcd for $C_{22}H_{31}AgB_9PS$: C, 46.88; H, 5.54; S, 5.69. Found: C, 46.97; H, 5.60; S, 5.47.

Synthesis of [Ag(L_{s1})(bipy)]. To 7 cm^3 of deoxygenated methanol containing 25.2 mg (0.094 mmol) of [NMe_4](L_{s1}) were added $AgNO_3$ (15.9 mg, 0.094 mmol) and 2,2′-bipyridine (15.0 mg, 0.096 mmol) dissolved in 15 cm^3 of deoxygenated methanol. A white solid precipitate was obtained. This solid was separated by filtering the mixture. The solid was washed with methanol to yield an analytically pure solid [Ag(L_{s1})(bipy)]. Yield: 40 mg (92%). FTIR (KBr): ν [cm^{-1}] = 2576, 2528, 2512 (B–H). ^{1}H-FTNMR (400 MHz, CD_2Cl_2, 25 °C, TMS): δ −2.5 (br, 1, B*H*B), 1.67 (s, 3, –C*H*$_3$), 2.69 (s, 3, S–C*H*$_3$), 7.63 (t, ^1J = 6.3 Hz, 2, bipy (*H*: 5,5′)), 8.07 (t, ^1J = 7.4 Hz, 2, bipy (*H*: 4,4′)), 8.20 (d, ^1J = 8.4 Hz, 2, bipy (*H*: 3,3′)), 8.86 (s, 2, bipy (*H*: 6,6′)). ^{11}B-FTNMR (128 MHz, CH_2Cl_2, 25 °C, $BF_3 \cdot Et_2O$): δ = −7.6 (d, ^1J(B,H) = 139 Hz, 1B), −9.5 (d, ^1J(B,H) = 139 Hz, 1B), −11.3 (d, ^1J(B,H) = 167 Hz, 1B), −15.3 (1B), −16.3 (1B), −17.2 (1B), −19.5 (d, ^1J(B,H) = 140 Hz, 1B), −33.9 (d, ^1J(B,H) = 120 Hz, 1B), −36.5 (d, ^1J(B,H) = 142 Hz, 1B). Anal. Calcd for $C_{14}H_{24}AgB_9N_2S$: C, 36.75; H, 5.29; S, 7.01; N, 6.12. Found: C, 36.84; H, 5.26; S, 6.92; N, 6.08.

X-ray Data Collection for [Ag(L_{s2c15})] and [Ag(L_{s2c6})(PPh_3)]·0.5CH_2Cl_2]. Single-crystal data collections for the both compounds were performed at ambient temperature on a Nicolet P3F diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å). The crystal of **[Ag(L_{s2c15})]** was protected for light during the data collection. The unit cell parameters for the colorless needlelike crystals were determined by least-squares refinement of 25 carefully centred reflections. Data were corrected for both Lorentz and polarization effects but not for absorption or extinction. Crystallographic data for the both compounds are presented in Table 6.

Structure Determination and Refinement of [Ag(L_{s2c15})]. The structure was solved by the Patterson method[15] and successive Fourier maps. Space group $Pna2_1$ was confirmed through absent reflections and structure analysis. All non-hydrogen atoms were refined anisotropically, and only the hydrogen atoms bonded to carbon atoms C(12)–C(19) were included in the calculations in fixed positions (C–H = 0.95 Å and U = 0.05 Å^2). The final R value was 0.062 (R_w = 0.038). Refinement of the enantiomeric model did not decrease the R factor. Refinements were performed using the XTAL2.6 program system,[16] which minimized the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$. All calculations were carried out on a VAX 8650 computer.

Table 6. Crystallographic Data for **[Ag(L_{s2c15})]** and **[Ag(L_{s2c6})(PPh_3)]·0.5CH_2Cl_2**

	[Ag(L_{s2c15})]	**[Ag(L_{s2c6})(PPh_3)]·0.5CH_2Cl_2**
chem formula	$C_{10}H_{26}AgB_9O_3S_2$	[$C_{22}H_{29}AgB_9PS_2$]·0.5CH_2Cl_2
fw	463.6	636.2
a, Å	14.0211(7)	13.069(3)
b, Å	16.658(8)	17.414(5)
c, Å	8.196(3)	13.545(4)
β, deg	90.0	110.32(2)
V, Å^3	1914(2)	2891(1)
Z	4	4
space group	$Pna2_1$	$P2_1/n$
T, °C	23	23
λ, Å	0.710 69	0.710 69 Å
ρ_{calcd}, g cm^{-3}	1.609	1.461
μ, cm^{-1}	12.6	9.79
transm coeff	0.97–1.00	0.94–1.00
$R(F_o)$	0.062	0.068
$R_w(F_o)$	0.038	0.034

Structure Determination and Refinement of [Ag(L_{s2c6})(PPh_3)]·0.5CH_2Cl_2. The structure was solved by the Patterson method[15] and successive Fourier syntheses. Least-squares refinements were performed using the XTAL2.6 program system,[16] which minimized the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$. The structure is partly disordered. A disordered dichloromethane molecule occupies two positions in the vicinity of inversion center. Refinement of all non-hydrogen atoms of the complex molecule and the disordered solvent molecule (population parameter 0.5) revealed a maximum of 1.7 e Å^{-3} on the C_2B_3 open face of the carborane cage, thus indicating two orientations for the cage. Refinements of the two orientations resulted population parameters 0.72(1) and 0.28(1) for B(3A) and B(3B), respectively. The disordered boron atom B(3) and the carbon atom of the solvent molecule were refined isotropically and the rest of the non-H atoms anisotropically in the final refinements. Except for two hydrogen atoms of the disordered carborane cage, all hydrogen atoms of the complex unit were found from a difference Fourier map and refined isotropically. The final R value was 0.068 (R_w = 0.034). All calculations were performed on a VAX 8650 computer.

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Supplementary Material Available: Tables of experimental details, positional parameters and thermal parameters, interatomic distances and angles, and least-squares planes for **[Ag(L_{s2c6})(PPh_3)]·0.5CH_2Cl_2** and **[Ag(L_{s2c15})]** (46 pages). Ordering information is given on any current masthead page.

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(15) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(16) Hall, S. R., Stewart, J. M., Eds.; *XTAL2.6 User's Manual*; Universities of Western Australia and Maryland: Nedlands, Australia, and College Park, MD, 1989.