# *nido*-Carborane-Containing Compounds Resulting from the Reaction of *closo*-Carboranes with Transition Metal Complexes

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The reaction of *closo* derivatives of 1,2-dithio-1,2-dicarba-*closo*-dodecaborane with $[MCl(PPh_3)_2]$ (M = Cu, Ag) in ethanol, produces complexes of the corresponding *nido* derivatives of 7,8-dithio-7,8-dicarba-*nido*-undecaborate(1−). These *nido* ligands form via formal $B^+$ elimination in the *closo* precursors, becoming anionic, i.e., they have a negative charge which greatly enhances their coordinating capabilities. As a consequence, the dithio *closo* derivatives which are neutral dithioethers, and hence weak ligands, tend to modify themselves upon coordination, losing a boron atom and becoming anionic, to produce the strongly coordinating 7,8-dithio-7,8-dicarba-*nido*-undecaborate(1−) derivative ligands. The $B^+$ removal has been proven by the X-ray analysis of the resulting $[Cu\{7,8\text{-}\mu\text{-}S(CH_2CH_2OCH_2CH_2OCH_2CH_2)SC_2B_9H_{10}\}(PPh_3)]$ and $[Ag\{7,8\text{-}\mu\text{-}S(CH_2CH_2OCH_2CH_2)SC_2B_9H_{10}\}(PPh_3)]$. Crystal structure data for $[Cu\{7,8\text{-}\mu\text{-}S(CH_2CH_2OCH_2CH_2OCH_2CH_2)SC_2B_9H_{10}\}(PPh_3)]$: mol wt 637.5; space group $P\bar{1}$, Z = 2; $a$ = 10.880(3) Å, $b$ = 12.784(3) Å, $c$ = 13.707(5) Å, $\alpha$ = 64.31(2)°, $\beta$ = 68.09(2)°, $\gamma$ = 84.64(2)° $R_w(F_o)$ = 0.061. Crystal structure data for $[Ag\{7,8\text{-}\mu\text{-}S(CH_2CH_2OCH_2CH_2)SC_2B_9H_{10}\}(PPh_3)]$ mol wt 637.8, space group $P2_1/n$; Z =8; $a$ = 14.578(9) Å, $b$ = 23.557(9) Å, $c$ = 18.322(6) Å, $\beta$ = 108.73(3)°, $R_w(F_o)$ = 0.077.

The incorporation of S,S′-connected chains to the moiety 7,8-dithio-7,8-dicarba-*nido*-undecaborate(1−) is being thoroughly studied in our group.[1] These macrocyclic compounds generally coordinate via the S atoms, though in a few cases (Hg(II), Ag(I)) $C_2B_3$–M bonding has also been found.[2] The length of the chain appears to be relevant to produce additional B(3)–H⇀M or B(3)–M bonds, which have been found with short strings.[3] These 7,8-dithio-7,8-dicarba-*nido*-undecaborate(1−) derivatives can be thought of as being anionic dithioethers. This anionic character bestows greater stability to the resulting complexes. Common thioethers are usually considered to be fairly poor ligands, not strongly bound to metals, and easily displaced by other ligands.[4] In their complexes, the normal coordination number of the metal ion is usually maintained, and metal–halogen coordination is dominant over metal–thioether coordination.[5] To better understand the influence of the negative charge in the anionic dithioether carborane ligands, presented here, the coordinating capability of the neutral *closo* precursors have been studied in this work. The *closo* and *nido* species (Figure 1) are structurally similar, however, the *nido* species is anionic and with a $C_2B_9$ cluster while the *closo* species is neutral and with a $C_2B_{10}$ cluster. Formal elimination of a $B^+$ fragment in the former $C_2B_{10}$ derivatives is the reason for the negative charge in the $C_2B_9$ derivatives.

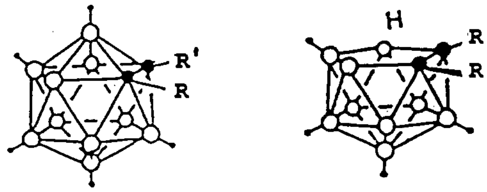

**Figure 1.** Neutral 1,2-RR′-1,2-dicarba-*closo*-dodecaborane and the anionic 7,8-RR′-7,8-dicarba-*nido*-undecaborate(1−) clusters.

**Table 1.** *closo*- and *nido*-Carborane Ligands and Their Abbreviations

| | |
|---|---|
| **Lc12** | 1,2-(1′,10′-dithia-4′,7′-dioxadecane-1′,10′-diyl)-1,2-dicarba-*closo*-dodecaborane |
| **Lc9** | 1,2-(1′,7′-dithia-4′-oxapentane-1′,7′-diyl)-1,2-dicarba-*closo*-dodecaborane |
| **Ln12** | 7,8-(1′,10′-dithia-4′,7′-dioxadecane-1′,10′-diyl)-7,8-dicarba-*nido*-undecaborate |
| **Ln9** | 7,8-(1′,7′-dithia-4′-oxapentane-1′,7′-diyl)-7,8-dicarba-*nido*-undecaborate |

We here report the reactions of *closo* derivatives of 1,2-dithio-1,2-dicarba-*closo*-dodecaborane with $[MCl(PPh_3)_2]$ (M = Cu, Ag) in ethanol. These reactions produce the *nido* derivatives, which imply the partial degradation of the initial *closo* cluster and the breaking of the metal–halogen and metal–phosphorus bonds in the $[MCl(PPh_3)_2]$ complexes to get the new metal–thioether coordination. The crystal structures of the resulting compounds, $[Ag\{7,8\text{-}\mu\text{-}S(CH_2CH_2OCH_2CH_2)S\text{-}C_2B_9H_{10}\}(PPh_3)]$ and $[Cu\{7,8\text{-}\mu\text{-}S(CH_2CH_2OCH_2CH_2OCH_2CH_2)S\text{-}C_2B_9H_{10}\}(PPh_3)]$, corroborate this reaction path.

## Results and Discussion

The ligands studied and the abbreviations used are schematically indicated in Table 1. The ligands are defined as follows: **Lc** means the moiety 1,2-dithio-1,2-dicarba-*closo*-dodecaborane; **Ln** means the moiety 7,8-dithio-7,8-dicarba-*nido*-undecaborate; the cycle size is indicated by a number—e.g., **Lc12** means a 1,2-

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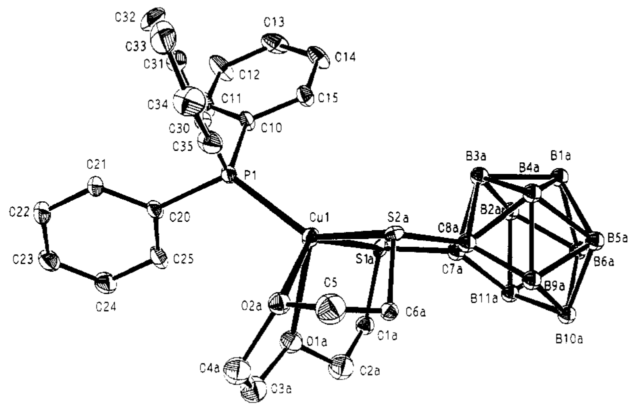


**Figure 2.** Molecular structure of configuration A of [**Cu(Ln12)(PPh$_3$)**]. Radii are drawn at 30% level and H atoms have been omitted.

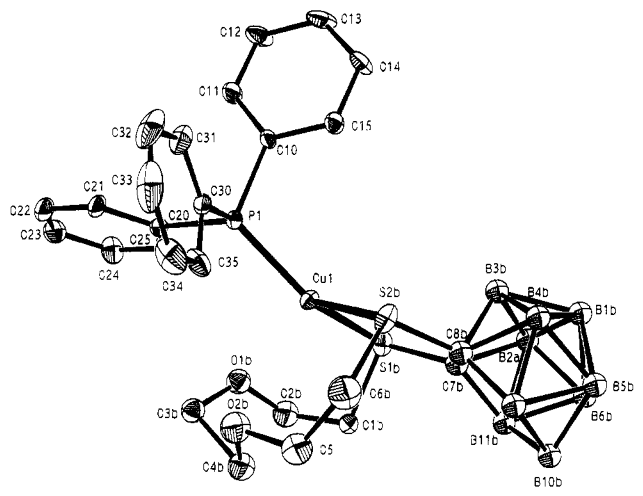


**Figure 3.** Molecular structure of configuration B of [**Cu(Ln12)(PPh$_3$)**]. Radii are drawn at 30% level and H atoms have been omitted.

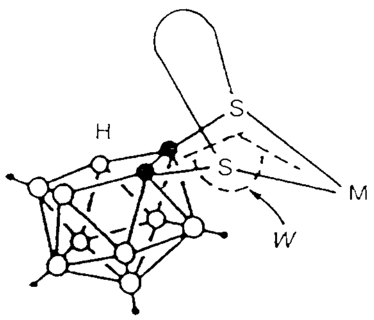
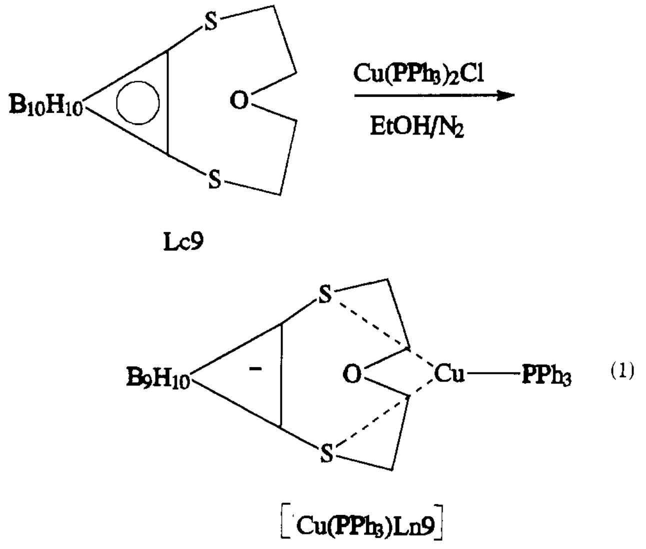


**Figure 4.** The **w** angle concept.

$S_2C_2B_{10}H_{10}$ moiety externally joined by a chain producing a cycle of total size 12.

The reaction of the *closo* ligands **Lc12** and **Lc9** with [CuCl(PPh$_3$)$_2$] in ethanol yields off-white solids. The IR spectra show B–H stretching absorptions at 2540 cm$^{-1}$ which are indicative of *nido* species. (Higher values, close to 2580 cm$^{-1}$, are encountered for closo species.) This interpretation is further supported by the $^1$H-NMR, −2.5 ppm absorption attributed to B–H–B bonding and the $^{11}$B-NMR pattern, 2:1:4:1:1, in the range between −9 and −37 ppm characteristic of *nido*-$C_2B_9$ derivatives. Similar results are obtained when [AgCl(PPh$_3$)$_2$] was allowed to react with **Lc12** and **Lc9**, demonstrating the strong tendency of these ligands to undergo boron elimination to acquire the negative charge, and consequently produce **Ln9**$^-$ and **Ln12**$^-$. Equation 1 shows an example of this reaction.



The X-ray crystal structures clearly confirm the *nido* nature of the resulting copper and silver complexes. The X-ray analysis of [**Cu(Ln12)(PPh$_3$)**] establishes the partial degradation of the *closo*-carborane cage and the partial disordering of the structure. Figures 2 and 3 show the molecular structure. Table 2 lists positional parameters and Table 3 selected bond lengths and angles. Only the Cu–PPh$_3$ moiety is ordered while the rest exhibit two configurations, **A** and **B**. A population parameter of 0.5 has been calculated from X-ray data. In **A** two sulfur atoms, one phosphorus atom and both oxygen atoms of the exocluster macrocyclic chain are coordinated to copper in a highly distorted square-pyramidal arrangement (Cu–S distances, 2.351(6), 2.289(10); Cu–P, 2.199(4) Å; Cu–O, 2.31(2), 2.56(2) Å). In **B**, the Cu–O distances are longer than in **A** and the O atoms do not appear to be included in the coordination sphere. Thus, the copper atom in **B** is only three-coordinated (Cu–S distances, 2.327(9), 2.33(1) Å; Cu–P, 2.199(4) Å; Cu–O, 2.80(2), 3.01(2) Å). In both configurations, **A** and **B**, the copper atom is anti with regard to the $C_2B_3$ open face. The dihedral angle **w**, see Figure 4, between the planes S(1)–Cu(1)–S(2) and S(1)–C(7)–C(8)–S(2), has values of 178.1(5)° for conformer **A** and 176.7(6)° for conformer **B** which are in agreement with other values found for this type of ligand.[6]

The molecular structure of the complex [**Ag(Ln9)(PPh$_3$)**] is shown in Figures 5 and 6. Table 4 lists positional parameters, and Table 5 lists selected bond lengths and angles. Unlike [**Cu(Ln12)(PPh$_3$)**], [**Ag(Ln9)(PPh$_3$)**] is not disordered and only one type of coordination is encountered about the Ag atom even though two different conformers (**A** and **B**) are found in this crystal. The first molecule presents a highly distorted tetrahedral environment with vertexes occupied by two sulfur atoms of the pseudosymmetrically acting carborane ligand (Ag–S distances, 2.505(5), 2.611(4) Å), and the string's oxygen (Ag–O distance, 2.627(9) Å). The fourth position is occupied by the phosphorus atom of the PPh$_3$ group (Ag–P distance; 2.377(5) Å). The other molecule presents similar distance values but quite different angles, e.g. the Ag–P distances are 2.377(5) and 2.364(5) Å, quite similar, but the P(1)–Ag(1)–S(1) and P(1)–Ag(1)–S(2) angles are 151.6(2) and 120.4(2)°, respectively, while the P(2)–Ag(2)–S(3) and P(2)–Ag(2)–S(4) angles are 136.4(2) and 133.3(2)°, respectively. Also it is clearly seen by comparing Figures 4 and 5 that the propellers of the PPh$_3$ groups have different orientations. This implies that within the crystal two conformers of [**Ag(Ln9)(PPh$_3$)**] are encountered. The **w** angle found has values of 162.2 and 164.9°, respectively which is considerably smaller than those found in [**Cu(Ln12)(PPh$_3$)**] (see Table 7), as was expected since shorter strings produce smaller **w** angles.[6] The Ag is anti with regard to the $C_2B_3$ open face, which is common with other complexes of this type of ligands.

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**Table 2.** Non-Hydrogen Atomic Position Parameters and Isotropic Thermal Parameters for **[Cu(Ln12)(PPh$_3$)]**[a]

| | $x/a$ | $y/b$ | $z/c$ | $U_{\mathrm{eq}}$,[b] Å$^2$ |
|---|---|---|---|---|
| Cu(1) | 0.1667(1) | 0.2546(1) | 0.1498(1) | 0.048(2)* |
| S(1A)$^{i}$ | 0.1204(5) | 0.3703(4) | −0.0184(4) | 0.037(7)* |
| S(1B)$^{i}$ | 0.0635(6) | 0.2584(6) | 0.0272(5) | 0.063(9)* |
| S(2A)$^{i}$ | 0.3056(8) | 0.1475(7) | 0.0635(9) | 0.040(9)* |
| S(2B)$^{i}$ | 0.3587(9) | 0.1904(9) | 0.050(1) | 0.07(1)* |
| P(1) | 0.1944(3) | 0.3452(2) | 0.2456(2) | 0.047(4)* |
| O(1A)$^{i}$ | −0.049(2) | 0.181(1) | 0.215(2) | 0.071(5) |
| O(1B)$^{i}$ | −0.092(2) | 0.153(2) | 0.294(2) | 0.081(6) |
| O(2A)$^{i}$ | 0.138(2) | 0.038(2) | 0.291(2) | 0.062(6) |
| O(2B)$^{i}$ | 0.097(3) | 0.005(2) | 0.330(2) | 0.11(1) |
| C(1A)$^{i}$ | −0.051(2) | 0.319(2) | 0.031(2) | 0.054(6) |
| C(1B)$^{i}$ | −0.050(2) | 0.124(2) | 0.118(2) | 0.052(6) |
| C(2A)$^{i}$ | −0.093(3) | 0.206(3) | 0.122(3) | 0.094(9) |
| C(2B)$^{i}$ | −0.149(3) | 0.138(3) | 0.220(3) | 0.096(9) |
| C(3A)$^{i}$ | −0.112(3) | 0.073(3) | 0.323(3) | 0.09(1) |
| C(3B)$^{i}$ | −0.078(3) | 0.067(2) | 0.389(2) | 0.075(8) |
| C(4A)$^{i}$ | −0.016(4) | −0.008(3) | 0.378(3) | 0.09(1) |
| C(4B)$^{i}$ | −0.019(3) | −0.025(3) | 0.331(3) | 0.10(1) |
| C(5) | 0.214(1) | −0.035(1) | 0.244(1) | 0.108(5) |
| C(6A)$^{i}$ | 0.224(2) | 0.002(2) | 0.138(2) | 0.040(5) |
| C(6B)$^{i}$ | 0.351(3) | 0.041(3) | 0.153(3) | 0.12(1) |
| C(10) | 0.242(1) | 0.4996(8) | 0.1520(8) | 0.05(1)* |
| C(11) | 0.198(1) | 0.586(1) | 0.189(1) | 0.08(2)* |
| C(12) | 0.237(1) | 0.700(1) | 0.117(1) | 0.10(2)* |
| C(13) | 0.325(1) | 0.732(1) | 0.007(1) | 0.09(2)* |
| C(14) | 0.368(1) | 0.650(1) | −0.0353(9) | 0.07(2)* |
| C(15) | 0.327(1) | 0.5341(9) | 0.0377(9) | 0.06(2)* |
| C(20) | 0.056(1) | 0.3414(9) | 0.3722(9) | 0.05(1)* |
| C(21) | 0.070(1) | 0.335(1) | 0.470(1) | 0.06(2)* |
| C(22) | −0.038(1) | 0.339(1) | 0.562(1) | 0.08(2)* |
| C(23) | −0.159(1) | 0.351(1) | 0.556(1) | 0.08(2)* |
| C(24) | −0.178(1) | 0.359(1) | 0.461(1) | 0.08(2)* |
| C(25) | −0.067(1) | 0.355(1) | 0.3667(9) | 0.07(2)* |
| C(30) | 0.327(1) | 0.297(1) | 0.3013(9) | 0.06(2)* |
| C(31) | 0.401(1) | 0.365(1) | 0.314(1) | 0.08(2)* |
| C(32) | 0.497(2) | 0.320(2) | 0.363(2) | 0.13(4)* |
| C(33) | 0.524(2) | 0.210(2) | 0.386(2) | 0.14(4)* |
| C(34) | 0.450(2) | 0.138(1) | 0.378(1) | 0.10(2)* |
| C(35) | 0.353(1) | 0.181(1) | 0.334(1) | 0.07(2)* |
| B(1A)$^{i}$ | 0.439(1) | 0.351(1) | −0.3053(9) | 0.047(2) |
| B(2A)$^{i}$ | 0.289(2) | 0.4091(7) | −0.2581(9) | 0.047(2) |
| B(3A)$^{i}$ | 0.382(1) | 0.345(1) | −0.169(1) | 0.047(2) |
| B(4A)$^{i}$ | 0.452(1) | 0.223(1) | −0.191(1) | 0.047(2) |
| B(5A)$^{i}$ | 0.399(1) | 0.2132(9) | −0.2936(8) | 0.047(2) |
| B(6A)$^{i}$ | 0.298(1) | 0.328(1) | −0.3343(8) | 0.047(2) |
| C(7A)$^{i}$ | 0.213(1) | 0.307(1) | −0.1169(8) | 0.047(2) |
| C(8A)$^{i}$ | 0.303(1) | 0.2061(9) | −0.0823(7) | 0.047(2) |
| B(9A)$^{i}$ | 0.319(2) | 0.1225(7) | −0.1451(9) | 0.047(2) |
| B(10A)$^{i}$ | 0.227(1) | 0.183(1) | −0.240(1) | 0.047(2) |
| B(11A)$^{i}$ | 0.1558(9) | 0.305(2) | −0.210(1) | 0.047(2) |
| B(1B)$^{i}$ | 0.378(2) | 0.314(1) | −0.2962(9) | 0.067(3) |
| B(2B)$^{i}$ | 0.207(2) | 0.302(2) | −0.222(1) | 0.067(3) |
| B(3B)$^{i}$ | 0.320(3) | 0.327(1) | −0.168(1) | 0.067(3) |
| B(4B)$^{i}$ | 0.457(1) | 0.245(2) | −0.198(1) | 0.067(3) |
| B(5B)$^{i}$ | 0.427(1) | 0.170(2) | −0.269(1) | 0.067(3) |
| B(6B)$^{i}$ | 0.271(1) | 0.206(1) | −0.283(1) | 0.067(3) |
| C(7B)$^{i}$ | 0.190(1) | 0.218(2) | −0.080(1) | 0.067(3) |
| C(8B)$^{i}$ | 0.327(1) | 0.187(1) | −0.0681(9) | 0.067(3) |
| B(9B)$^{i}$ | 0.398(2) | 0.097(2) | −0.119(1) | 0.067(3) |
| B(10B)$^{i}$ | 0.289(3) | 0.0678(9) | −0.179(1) | 0.067(3) |
| B(11B)$^{i}$ | 0.149(1) | 0.151(2) | −0.142(1) | 0.067(3) |

[a] Key: i denotes a population parameter = 0.5. [b] Asterisks denote isotropic *B*'s.

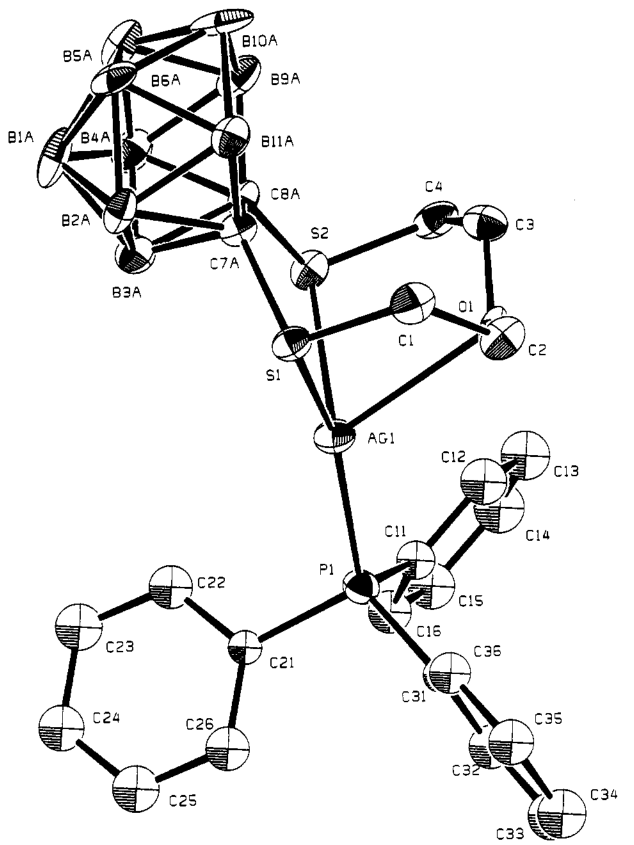

**Figure 5.** Molecular structure of conformer A of **[Ag(Ln9)(PPh$_3$)]**. Radii are drawn at 30% level and H atoms have been omitted.

**Table 3.** Selected Distances (Å) and Angles (deg) with Esd's in Parentheses for **[Cu(Ln12)(PPh$_3$)]**

| | | | |
|---|---|---|---|
| Cu(1)–S(1a) | 2.351(6) | S(1a)–C(7a) | 1.81(1) |
| Cu(1)–S(2a) | 2.29(1) | S(2a)–C(6a) | 1.81(2) |
| Cu(1)–P(1) | 2.199(4) | S(2a)–C(8a) | 1.82(2) |
| Cu(1)–O(1a) | 2.31(2) | P(1)–C(10) | 1.820(9) |
| Cu(1)–O(2a) | 2.56(2) | P(1)–C(20) | 1.81(1) |
| S(1a)–C(1a) | 1.81(2) | P(1)–C(30) | 1.81(1) |
| Cu(1)–S(1b) | 2.327(9) | S(1b)–C(1b) | 1.85(2) |
| Cu(1)–S(2b) | 2.33(1) | S(1b)–C(7b) | 1.82(2) |
| Cu(1)–P(1) | 2.199(4) | S(2b)–C(6b) | 1.81(3) |
| Cu(1)–O(1b) | 2.80(2) | S(2b)–C(8b) | 1.79(2) |
| Cu(1)–O(2b) | 3.01(2) | | |
| | | | |
| S(1a)–Cu(2)–S(2a) | 92.7(3) | Cu(1)–S(1a)–C(7a) | 102.4(4) |
| S(1a)–Cu(1)–P(1) | 116.4(2) | C(1a)–S(1a)–C(7a) | 105(1) |
| Cu(1)–P(1)–C(10) | 111.4(4) | Cu(1)–S(2a)–C(6a) | 106.4(7) |
| S(1a)–Cu(1)–O(1a) | 81.4(5) | Cu(1)–S(2a)–C(8a) | 105.2(5) |
| Cu(1)–P(1)–C(20) | 118.6(5) | S(1b)–Cu(1)–S(2b) | 91.7(4) |
| S(1a)–Cu(1)–O(2a) | 136.9(6) | S(1b)–Cu(1)–P(1) | 144.4(2) |
| Cu(1)–P(1)–C(30) | 115.0(5) | S(2b)–Cu(1)–P(1) | 115.4(4) |
| S(2a)–Cu(1)–P(1) | 131.3(3) | Cu(1)–S(1b)–C(1b) | 102.4(9) |
| S(2a)–Cu(1)–O(1a) | 108.4(6) | Cu(1)–S(1b)–C(7b) | 104.4(6) |
| S(2a)–Cu(1)–O(2a) | 68.2(5) | C(1b)–S(1b)–C(7b) | 101(1) |
| P(1)–Cu(1)–O(1a) | 113.6(6) | Cu(1)–S(2b)–C(6b) | 102(1) |
| P(1)–Cu(1)–O(2a) | 104.5(6) | Cu(1)–S(2b)–C(8b) | 104.7(7) |
| Cu(1)–S(1a)–C(1a) | 100.3(7) | | |

As a result we may conclude that the dithio *closo* derivatives, which are neutral dithioethers and hence weak ligands, tend to modify themselves upon coordination. This produces the negative, strongly coordinating 7,8-dithio-7,8-dicarba-*nido*-undecaborate(1−) ligands. In addition, no stereochemical differences in the final complex are observed, using either the *nido* or *closo* compounds as started materials. That is to say, the anti configuration of the metal versus the $C_2B_3$ open face is always encountered. We interpret this in a manner similar to the partial degradation observed in the formation of this type of *exo*-dithiocarborane derivatives,[7] where both the *closo* and the *nido* species are formed (see Scheme 1). Through S-M coordination (see Figure 7), electron density from the metal is transferred to the cage, which produces a pseudoreduction of the cluster and leads to the opening of the cage. In that situation the apical boron atom, which is the less coordinated, is susceptible to nucleophilic attack and partial cluster opening takes place. The presence of a nucleophile, e.g. ethanol, is then sufficient enough to remove the less coordinated open face boron atom to produce

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**Table 4.** Atomic Position Parameters and Equivalent Isotropic Temperature Factors for **[Ag(Ln9)(PPh$_3$)]** Where the Equivalent Isotropic Temperature Factors for Non-Hydrogen Atoms Are of the Form $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}a_i\cdot a_j$

| atom | $x$ | $y$ | $z$ | $B$(eq), Å$^2$ | atom | $x$ | $y$ | $z$ | $B$(eq), Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| Ag(1) | 0.6020(1) | 0.37185(5) | 0.48766(8) | 3.95(6) | B(10B) | 1.038(1) | 0.3557(8) | 0.624(1) | 5(1) |
| Ag(2) | 1.1313(1) | 0.14717(5) | 0.48404(8) | 4.71(7) | B(11A) | 0.476(1) | 0.2033(8) | 0.585(1) | 3.7(9) |
| S(1) | 0.4765(3) | 0.3202(2) | 0.5285(2) | 3.2(2) | B(11B) | 1.109(1) | 0.34912(8) | 0.558(1) | 4(1) |
| S(2) | 0.7001(3) | 0.2771(2) | 0.5111(2) | 3.3(2) | C(11) | 0.7636(6) | 0.4397(4) | 0.4143(6) | 3.7(3) |
| S(3) | 1.1558(3) | 0.2538(2) | 0.4728(2) | 3.7(2) | C(12) | 0.7468(6) | 0.3929(4) | 0.3651(6) | 5.3(4) |
| S(4) | 1.0546(4) | 0.1719(2) | 0.5857(3) | 5.1(2) | C(13) | 0.8163(8) | 0.3766(4) | 0.3317(6) | 5.9(4) |
| P(1) | 0.6715(3) | 0.4568(2) | 0.4589(2) | 3.2(2) | C(14) | 0.9025(7) | 0.4070(5) | 0.3475(6) | 6.3(5) |
| P(2) | 1.2003(3) | 0.0632(2) | 0.4541(2) | 3.4(2) | C(15) | 0.9193(6) | 0.4538(4) | 0.3967(6) | 5.4(4) |
| O(1) | 0.5149(7) | 0.3048(4) | 0.3716(5) | 3.7(5) | C(16) | 0.8499(8) | 0.4701(4) | 0.4302(5) | 4.6(4) |
| O(2) | 0.9627(8) | 0.1864(5) | 0.4079(7) | 6.1(7) | C(21) | 0.7408(6) | 0.4952(4) | 0.5451(5) | 2.9(3) |
| C(1) | 0.393(1) | 0.2934(7) | 0.438(1) | 4.4(8) | C(22) | 0.8030(7) | 0.4625(3) | 0.6039(6) | 4.7(4) |
| C(2) | 0.418(1) | 0.3105(7) | 0.366(1) | 4.2(8) | C(23) | 0.8585(6) | 0.4883(4) | 0.6724(5) | 5.5(4) |
| C(3) | 0.548(1) | 0.2451(7) | 0.380(1) | 3.9(8) | C(24) | 0.8519(7) | 0.5467(5) | 0.6821(5) | 5.1(4) |
| C(4) | 0.652(1) | 0.2446(7) | 0.416(1) | 4.6(9) | C(25) | 0.7897(8) | 0.5793(3) | 0.6233(6) | 5.4(4) |
| C(5) | 1.049(1) | 0.2739(9) | 0.394(1) | 6(1) | C(26) | 0.7342(6) | 0.5536(4) | 0.5548(5) | 4.8(4) |
| C(6A)[I] | 0.984(2) | 0.226(1) | 0.359(2) | 5.4(6) | C(31) | 0.5891(6) | 0.5053(4) | 0.3959(5) | 2.8(3) |
| C(6B)[II] | 0.941(4) | 0.247(3) | 0.401(3) | 6(1) | C(32) | 0.6210(5) | 0.5445(4) | 0.3524(6) | 4.7(4) |
| C(7A) | 0.5398(9) | 0.2563(6) | 0.5734(8) | 2.7(6) | C(33) | 0.5555(8) | 0.5821(4) | 0.3038(5) | 5.6(4) |
| C(7B) | 1.133(1) | 0.2822(6) | 0.5572(8) | 3.0(7) | C(34) | 0.4580(7) | 0.5805(4) | 0.2987(5) | 5.8(4) |
| C(8A) | 0.642(1) | 0.2382(6) | 0.5675(8) | 2.5(6) | C(35) | 0.4260(5) | 0.5413(4) | 0.3423(6) | 5.1(4) |
| C(8B) | 1.086(1) | 0.2438(6) | 0.6074(8) | 3.0(7) | C(36) | 0.4916(7) | 0.5037(4) | 0.3909(5) | 4.2(4) |
| C(9A)[I] | 0.911(2) | 0.212(1) | 0.451(2) | 6.5(7) | C(41) | 1.2940(6) | 0.0753(4) | 0.4111(5) | 3.3(3) |
| C(9B)[II] | 0.897(4) | 0.163(3) | 0.445(3) | 5(1) | C(42) | 1.3750(8) | 0.0404(4) | 0.4249(5) | 5.0(4) |
| C(10) | 0.926(1) | 0.1762(8) | 0.525(1) | 8(1) | C(43) | 1.4462(6) | 0.0530(4) | 0.3916(6) | 6.4(5) |
| B(1A) | 0.652(1) | 0.220(1) | 0.717(1) | 5(1) | C(44) | 1.4363(7) | 0.1006(5) | 0.3443(6) | 5.2(4) |
| B(1B) | 1.224(1) | 0.310(1) | 0.705(1) | 6(1) | C(45) | 1.3552(8) | 0.1355(4) | 0.3304(5) | 6.1(5) |
| B(2A) | 0.534(1) | 0.2491(8) | 0.666(1) | 3.7(9) | C(46) | 1.2840(6) | 0.1229(4) | 0.3638(6) | 4.2(4) |
| B(2B) | 1.221(1) | 0.3236(9) | 0.612(1) | 5(1) | C(51) | 1.2604(7) | 0.0254(4) | 0.5432(5) | 2.9(3) |
| B(3A) | 0.642(1) | 0.2735(8) | 0.650(1) | 4(1) | C(52) | 1.2367(7) | −0.0302(4) | 0.5561(6) | 6.2(5) |
| B(3B) | 1.208(1) | 0.2561(8) | 0.642(1) | 4(1) | C(53) | 1.2804(8) | −0.0557(3) | 0.6277(7) | 7.2(5) |
| B(4A) | 0.720(1) | 0.2140(8) | 0.655(1) | 4(1) | C(54) | 1.3479(8) | −0.0255(5) | 0.6862(5) | 5.4(4) |
| B(4B) | 1.138(2) | 0.2531(9) | 0.702(1) | 5(1) | C(55) | 1.3716(6) | 0.0302(5) | 0.6732(5) | 6.0(5) |
| B(5A) | 0.663(1) | 0.154(1) | 0.669(1) | 5(1) | C(56) | 1.3278(7) | 0.0556(3) | 0.6017(6) | 5.5(4) |
| B(5B) | 1.106(1) | 0.3288(8) | 0.710(1) | 4(1) | C(61) | 1.1183(7) | 0.0121(4) | 0.3933(6) | 4.2(4) |
| B(6A) | 0.547(1) | 0.1737(8) | 0.676(1) | 4(1) | C(62) | 1.0205(8) | 0.0152(4) | 0.3872(6) | 5.9(4) |
| B(6B) | 1.159(1) | 0.3711(8) | 0.653(1) | 5(1) | C(63) | 0.9547(6) | −0.0235(5) | 0.3411(7) | 7.8(6) |
| B(9A) | 0.661(1) | 0.1689(8) | 0.576(1) | 4(1) | C(64) | 0.9867(8) | −0.0654(4) | 0.3011(6) | 6.6(5) |
| B(9B) | 1.022(2) | 0.2830(8) | 0.645(1) | 5(1) | C(65) | 1.0844(9) | −0.0685(4) | 0.3072(6) | 7.5(5) |
| B(10A) | 0.552(2) | 0.1389(8) | 0.594(1) | 6(1) | C(66) | 1.1502(6) | −0.0297(5) | 0.3533(6) | 5.4(4) |

[a] Key: I denotes population parameter = 0.68; II denotes population parameter = 0.32.

the partially degraded species. Wallbridge and co-workers have previously used d$^{10}$ electron-rich complexes to "reduce" carborane compounds, e.g. in the synthesis of $[(Ph_3P)AgC_2B_8H_{11}]_2$[8] and $[AgCB_{11}H_{12}\cdot 2C_6H_6]$[9]

## 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 $^1$H-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; 1,2-(1′,7′-Dithia-4′-oxapentane-1′,7′-diyl)-1,2-dicarba-*closo*-dodecaborane (Lc9) and 1,2-(1′,10′-Dithia-4′,7′-dioxadecane-1′,10′-diyl)-1,2-dicarba-*closo*-dodecaborane (Lc12) were prepared from *o*-carborane according to the literature.[10] A 1.7 M solution of *n*-butyllithium in hexane from Fluka was used as purchased. $[CuCl(PPh_3)_2]$ and $[AgCl(PPh_3)_2]$ were synthesized according to the literature.[11] Ethanol was reagent grade.

**Synthesis of [Cu(Ln12)(PPh$_3$)].** $[CuCl(PPh_3)_2]$ (31 mg, 0.05 mmol) was added to a deoxygenated ethanol suspension (20 mL) containing 16.1 mg (0.05 mmol) of (Lc12). The mixture was refluxed under $N_2$ for 2.5 h. The resulting white solid was removed by filtration, and 11.8 mg (37%) of the analytically pure solid was obtained. FTIR (KBr): $\nu$ (cm$^{-1}$) = 2540 (B-H). $^1$H-FTNMR (400 MHz, $CD_3COCD_3$, 25 °C, TMS): $\delta$ −2.1 (s, br, B*H*B), 7.49 (m, 15, C$_{aryl}$–*H*), 3.8–3.1 (m, 12, C–*H*). $^{11}$B-FTNMR (128 MHz, THF, 25 °C, $BF_3\cdot Et_2O$): $\delta$ = −10.7 (2B), −14.0 (1B), −17.69 (4B), −33.5 (1B), −36.5 (1B). Anal. Calcd for $C_{26}H_{37}B_9O_2PS_2Cu$: C, 48.99; H, 5.85. Found: C, 47.7; H, 6.26.

A colorless crystal suitable for X-ray analysis was grown from an ethanol solution after partial evaporation of the solvent.

**Synthesis of [Ag(Ln12)(PPh$_3$)].** $[AgCl(PPh_3)_2]$ (33.3 mg, 0.05 mmol) was added to a deoxygenated ethanol suspension (20 mL) containing 16.1 mg (0.05 mmol) of **Lc12**. The mixture was refluxed under $N_2$ for 2.5 h. The resulting white solid was removed by filtration, and 14.8 mg (43.5%) of the analytically pure solid was obtained. FTIR (KBr): $\nu$ (cm$^{-1}$) = 2537 (B–H). $^1$H-FTNMR (400 MHz, $CD_3COCD_3$, 25 °C, TMS): $\delta$ −2.7 (s, br B*H*B), 7.53 (m, 15, C$_{aryl}$–*H*), 3.8–3.7 (m, 12, C–*H*). $^{11}$B-FTNMR (128 MHz, THF, 25 °C, $BF_3\cdot Et_2O$: $\delta$ = −9.07 (2B), −13.6 (1B), −16.33 (4B), −33.2 (1B), −36.3 (1B). Anal. Calcd for $C_{26}H_{37}B_9O_2PS_2Ag$: C, 45.80; H, 5.47. Found: C, 44.7; H, 5.26.

**Synthesis of [Cu(Ln9)(PPh$_3$)].** $[CuCl(PPh_3)_2]$ (231 mg, 0.37 mmol) was added to a deoxygenated ethanol suspension (50 mL) containing 103 mg (0.37 mmol) of **Lc9**. The mixture was refluxed under $N_2$ for 2.5 h. The resulting white solid was removed by filtration, and 97 mg (44.2%) of the analytically pure solid was obtained. FTIR (KBr): $\nu$ (cm$^{-1}$) = 2539, 2511 (B–H). $^1$H-FTNMR (400 MHz, $CD_3COCD_3$, 25 °C, TMS): $\delta$ −2.1 (s, br B*H*B), 7.49 (m, 15, C$_{aryl}$–*H*), 3.8–3.1 (m, 12, C–*H*). $^{11}$B-FTNMR (128 MHz, THF, 25 °C, $BF_3\cdot Et_2O$): $\delta$ = −9.75 (d, 3, $^1J$(B, H) = 136 Hz), −16.43 (d, 4, $^1J$(B, H) = 141 Hz), −32.23 (d, 1, $^1J$(B, H) = 117 Hz), −35.77 (d, 1, $^1J$(B, H) = 145 Hz). Anal. Calcd for $C_{24}H_{33}B_9OPS_2Cu$: C, 48.57; H, 5.60. Found: C, 48.3; H, 5.48.

**Synthesis of [Ag(Ln9)(PPh$_3$)].** $[AgCl(PPh_3)_2]$ (60 mg, 0.090 mmol) was added to a deoxygenated ethanol suspension (20 mL) containing 25 mg (0.090 mmol) of **Lc9**. The mixture was refluxed under $N_2$ for 2.5 h. The resulting white solid was removed by filtration, and 22 mg (38.3%)

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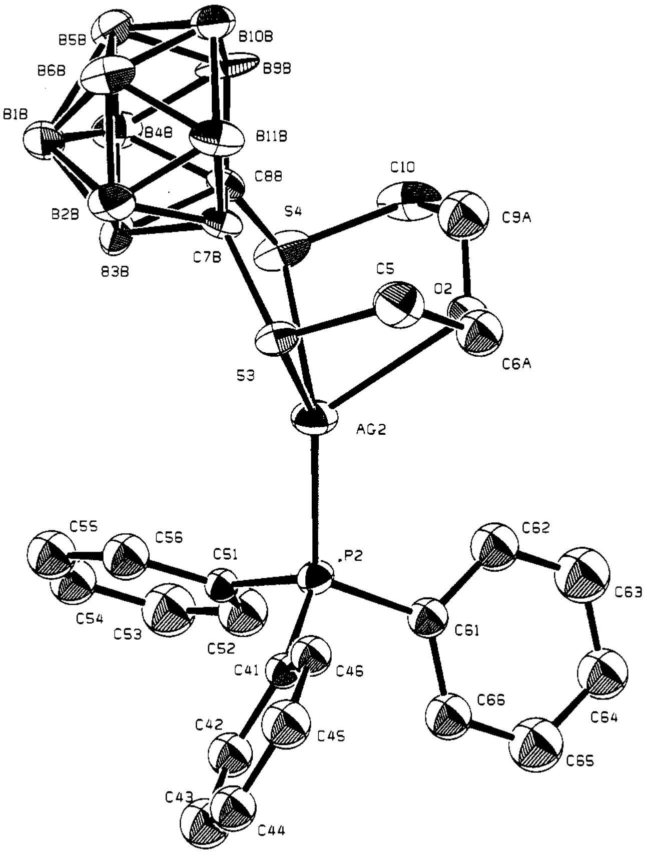


**Figure 6.** Molecular structure of conformer **B** of **[Ag(Ln9)(PPh$_3$)]**. Radii are drawn at 30% level and H atoms have been omitted.

**Table 5.** Selected Distances (Å) and Angles (deg) with Esd's in Parentheses for **[Ag(Ln9)(PPh$_3$)]**

| | | | |
|---|---|---|---|
| Ag(1)–P(1) | 2.377(5) | Ag(1)–S(1) | 2.505(5) |
| Ag(1)–S(2) | 2.611(4) | Ag(1)–O(1) | 2.627(9) |
| Ag(2)–P(2) | 2.364(5) | Ag(2)–S(3) | 2.555(4) |
| Ag(2)–S(4) | 2.530(6) | Ag(2)–O(2) | 2.58(1) |
| S(1)–C(1) | 1.83(1) | S(1)–C(7A) | 1.82(1) |
| S(2)–C(4) | 1.82(2) | S(2)–C(8A) | 1.78(2) |
| S(3)–C(5) | 1.82(2) | S(3)–C(7B) | 1.81(2) |
| S(4)–C(8B) | 1.76(1) | S(4)–C(10) | 1.86(2) |
| P(1)–Ag(1)–S(1) | 151.6(2) | Ag(1)–S(1)–C(7A) | 102.9(5) |
| P(1)–Ag(1)–S(2) | 120.4(2) | Ag(1)–S(2)–C(4) | 100.4(5) |
| P(1)–Ag(1)–O(1) | 117.2(3) | Ag(1)–S(2)–C(8A) | 101.4(5) |
| S(1)–Ag(1)–S(2) | 87.1(1) | Ag(2)–S(3)–C(5) | 102.3(7) |
| S(1)–Ag(1)–O(1) | 74.9(3) | Ag(2)–S(3)–C(7B) | 103.0(5) |
| S(2)–Ag(1)–O(1) | 73.5(2) | Ag(2)–S(4)–C(8B) | 104.2(6) |
| P(2)–Ag(2)–S(3) | 136.4(2) | Ag(2)–S(4)–C(10) | 99.8(9) |
| P(2)–Ag(2)–S(4) | 133.3(2) | Ag(1)–P(1)–C(11) | 109.9(4) |
| P(2)–Ag(2)–O(2) | 125.3(3) | Ag(1)–P(1)–C(21) | 112.5(4) |
| S(3)–Ag(2)–S(4) | 86.5(2) | Ag(1)–P(1)–C(31) | 115.8(3) |
| S(3)–Ag(2)–O(2) | 74.8(3) | Ag(2)–P(2)–C(41) | 114.0(4) |
| S(4)–Ag(2)–O(2) | 75.3(3) | Ag(2)–P(2)–C(51) | 108.6(4) |
| Ag(1)–S(1)–C(1) | 103.6(6) | Ag(2)–P(2)–C(61) | 117.0(4) |

of the analytically pure solid was obtained. FTIR (KBr): $\nu$ (cm$^{-1}$) = 2551, 2502 (B–H). $^1$H-FTNMR (400 MHz, $CD_3COCD_3$, 25 °C, TMS): $\delta$ −2.5 (s, br B*H*B), 7.53 (m, 15, $C_{aryl}$–*H*), 3.75, 3.48, 3.24 (m, 8, C–*H*). Anal. Calcd for $C_{24}H_{33}B_9OPS_2Ag$: C, 48.57; H, 5.60. Found: C, 47.7; H, 5.46.

A colorless crystal suitable for X-ray analysis was grown from an ethanol solution after partial evaporation of the solvent.

## Crystal Structure Determination

**[Cu(Ln12)(PPh$_3$)].** The cell parameters were obtained by least-squares refinement of 25 accurately centred reflections using a Nicolet P3F diffractometer and Mo K$\alpha$ radiation. The triclinic symmetry and approximate unit cell parameters were checked also by photographic techniques. The crystal data are shown in Table 6. 5597 unique reflections were collected, of which 2756 were considered as observed according to the criterion $|F_o| \geq 4\sigma(F_o)$. The data were corrected for Lorentz and polarization effects and for dispersion. $\Psi$-Scans for several intense reflections verified the absence of noteworthy variable absorption.

The structure analysis was carried out in the centrosymmetric space group $P\bar{1}$. The structure was partially solved by direct methods with SHELXS.[12] The least-squares refinement using the XTAL program package[13] indicated that only the metal atom

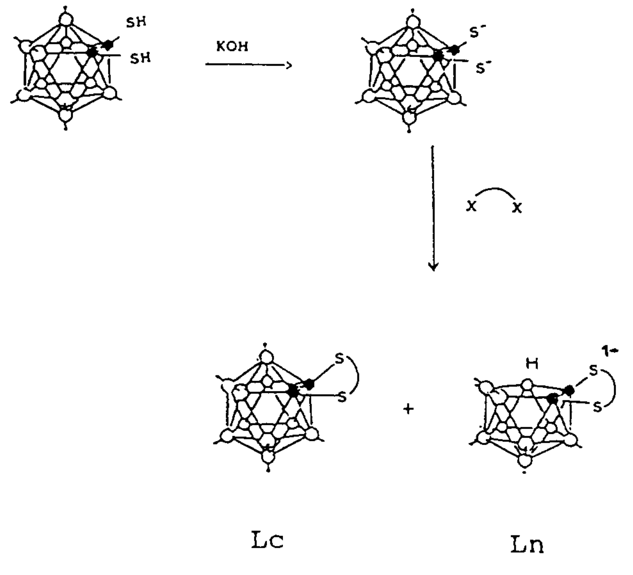
**Table 6.** Crystallographic Data for **[Cu(Ln12)(PPh$_3$)]** and **[Ag(Ln9)(PPh$_3$)]**

| compound | **[Cu(Ln12)(PPh$_3$)]** | **[Ag(Ln9)(PPh$_3$)]** |
|---|---|---|
| chem formula | $C_{26}H_{37}B_9CuO_2PS_2$ | $C_{24}H_{33}AgB_9OPS_2$ |
| fw | 637.5 | 637.8 |
| $a$, Å | 10.880(3) | 14.578(9) |
| $b$, Å | 12.784(3) | 23.557(9) |
| $c$, Å | 13.707(5) | 18.322(6) |
| $\alpha$, deg | 64.31(2) | 90.0 |
| $\beta$, deg | 68.09(2) | 108.73(3) |
| $\gamma$, deg | 84.64(2) | 90.0 |
| $V$, Å$^3$ | 1588.6(9) | 5959(5) |
| $Z$ | 2 | 8 |
| space group | triclinic, $P\bar{1}$ | monoclinic, $P2_1/n$ |
| T, °C | 23 | 23 |
| $\lambda$, Å | 0.71069 | 0.71069 |
| $\rho$, g cm$^{-3}$ | 1.332 | 1.422 |
| $\mu$, cm$^{-1}$ | 9.16 | 8.75 |
| transm coeff | 0.97–1.00 | 0.92–1.00 |
| $R(F_o)$ | 0.085 | 0.070 |
| $R_w(F_o)$ | 0.061 | 0.077 |

**Table 7.** The **w** Angle and C–C, C–S distances in **Lc9**, **[Ag(Ln9)(PPh$_3$)]**, **Lc12**, and **[Cu(Ln12)(PPh$_3$)]**

| compound | ring size | **w**, deg | $d_{C-C}$, Å | $d_{C-S}$ Å |
|---|---|---|---|---|
| **Lc9** | 9 | | 1.816 | 1.764 |
| **[Ag(Ln9)(PPh$_3$)]** conformer **A** | 9 | 162.2 | 1.59 | 1.82<br>1.78 |
| **[Ag(Ln9)(PPh$_3$)]** conformer **B** | 9 | 164.9 | 1.60 | 1.81<br>1.76 |
| **Lc12** | 12 | | 1.858 | 1.795<br>1.806 |
| **[Cu(Ln12)(PPh$_3$)]** conformer **A** | 12 | 178.1 | 1.555 | 1.81<br>1.82 |
| **[Cu(Ln12)(PPh$_3$)]** conformer **B** | 12 | 176.7 | 1.555 | 1.82<br>1.79 |

**Scheme 1.** Synthesis of Ligands



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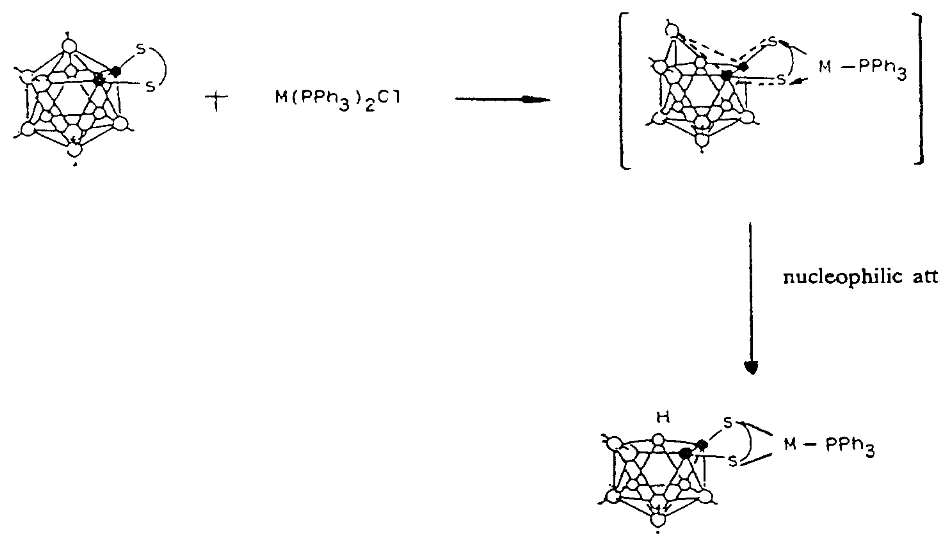

**Figure 7.** Proposed mechanism for the partial degradation of 1,2-dithio-*o*-carborane derivatives during the complexation with [MCl(PPh$_3$)$_2$] (M = Cu, Ag) in ethanol.

and the coordinated triphenylphosphine ligand are ordered. The rest of the molecule is disordered displaying two different configurations, labeled **A** and **B**, with the carborane cages partially superimposed. The approximate orientations of the cage could be concluded from the atom positions obtained after several Fourier map calculations, and the rest of the boron atoms were placed at estimated positions.

To obtain more suitable results for the cages, a rigid group refinement technique was used. The carborane cage of the compound [Pd(PPh$_3$)Cl{7,8-$\mu$-(SCH$_2$CH$_2$S)C$_2$B$_9$H$_{10}$}] was assumed to be "ideal" and this cage was fitted into the approximate positions. The two orientations for **A** and **B** of the cage were refined. The refinements resulted in a population parameter of 0.50(1) and thus the value 0.5 was adopted for both the cages.

The carbon atom C(5) occupies one position and is common for both configurations. In the final refinements the carbon atoms of the phenyl groups, the phosphorus atom, the copper atom, and the disordered sulfur atoms were refined anisotropically. The positions, orientations, and isotropic group temperature factors of the disordered cages were refined. The non-hydrogen atoms of the disordered chain between the sulfur atoms were refined isotropically. The hydrogen atoms of the phenyl groups were included in the calculation in the fixed positions. Refinement of this arrangement gave the final R value of 0.085 ($R_w$ = 0.061) for 2756 reflections and 291 parameters. The minimum and maximum residual peaks in the difference Fourier map were −0.5 and +0.8 e Å$^{-3}$. The quantity $w\sum(|F_o| - |F_c|)^2$ was minimized, where $w^{-1} = \sigma^2(F)$.

Critical examination of the bond parameters does not indicate abnormal values for the ordered part of the molecule. However, the bond parameters of the chain between the sulfur atoms are very inaccurate and do not allow any detailed discussion.

**[Ag(Ln9)(PPh$_3$)].** The lattice parameters were calculated by least-squares refinement of 24 centred reflections measured on a Rigaku AFC5S diffractometer with graphite monochromated MoK$_\alpha$ radiation. The crystal data are shown in Table 6. The data obtained were corrected for Lorentz and polarization effects. Absorption and decay corrections were also taken into account.

The structure of **[Ag(Ln9)(PPh$_3$)]** was solved by direct methods and refined by full-matrix least-squares techniques to an *R* value of 0.070 ($R_w$ = 0.077). The final cycle was based on 4200 independent, observed reflections [$I > 2\sigma(I)$]. The asymmetric unit contains two molecules. The chain of another molecule is disordered. The carbon atoms of the phenyl rings of the phosphine molecules were treated as rigid groups and were refined isotropically as well as the disordered carbon atoms. All other heavy atoms were refined anisotropically. The hydrogens of carbon atoms were included in calculated positions and the boron hydrogen atoms as they were found in difference maps with fixed temperature factors. Neutral atomic scattering and dispersion factors were taken from ref [14]. All calculations were performed using the TEXSAN[15] crystallographic software. Figures were drawn with ORTEP.[16] The final atomic positional coordinates and equivalent isotropic temperature factors are listed in Table 4.

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**Supplementary Material Available:** Tables of experimental details, hydrogen atom positional parameters and thermal parameters, anisotropic thermal parameters, interatomic distances and angles, and least-square planes for [Cu(Ln12)(PPh$_3$)] and tables of hydrogen atom positional parameters and thermal parameters, anisotropic thermal parameters, and interatomic distances and angles for [Ag(Ln9)(PPh$_3$)] (24 pages). Ordering information is given on any current masthead page.

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