

Mercury coordination to Exo-dithio-7,8-dicarba-*nido*-undecaborate derivatives

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Received 9 February 1994

Abstract

Ligands incorporating two sulphur atoms directly connected to the carbon atoms of the unit 7,8-dicarba-*nido*-undecaborate (1-) have been shown to coordinate *via* the sulfur groups, and for Ru^{II} or Rh^{III} additional participation of the unit B(3)–H in the coordination is observed. Mercury (II) is an exception, and Hg–C₂B₃ (metal-to-open-face bonding) has been demonstrated regardless of the presence of the two sulfur atoms. This coordination has been proved unambiguously by the crystal structure of [Hg(L_{s2c5})(PPh₃)] where L_{s2c5}²⁻ = {7,8-μ-(SCH₂S)-7,8-C₂B₉H₉}²⁻.

Keywords: Mercury compounds; Carborane ligands; Boron compounds; π-bonding; Metallacarborane; X-ray structure

1. Introduction

The participation of electron-rich elements, S or P, connected to the cluster carbon atoms in 7,8-dicarba-*nido*-undecaborate(1-) has substantially modified the chemistry of this anion. Furthermore, the coordinating capabilities of the resulting exo-dithiocarborane [1] compounds can be modified by the length of the exo-cluster cyclic chain [2]. In Fig. 1(A) the cycle with the six-membered ring, HL_{s2c6}⁻ is represented, showing the two sulphur atoms connected to the carborane cage.

Silver coordination to 7,8-dicarba-*nido*-undecaborate(1-) derivatives was not recognized until our description of [NMe₄][Ag{7,8-μ-(SCH₂CH₂S)-7,8-C₂B₉H₁₀}₂] [3]. The Ag⁺ is S-coordinated in this case, but a structurally different Ag⁺ compound was obtained when the anion with a five-membered ring, HL_{s2c5}⁻ was used. Our interpretation of the spectroscopic data [3] led us to propose a Ag–C₂B₃ coordination (metal-open-face interaction) (Fig. 3) but this was not fully proved due to the lack of crystals suitable for

X-ray analysis. As indicated, every other complex studied had produced S–M coordination.

Both Hg²⁺ and Au⁺, were suitable ions to test metal-to-open-face coordination as they are very simi-

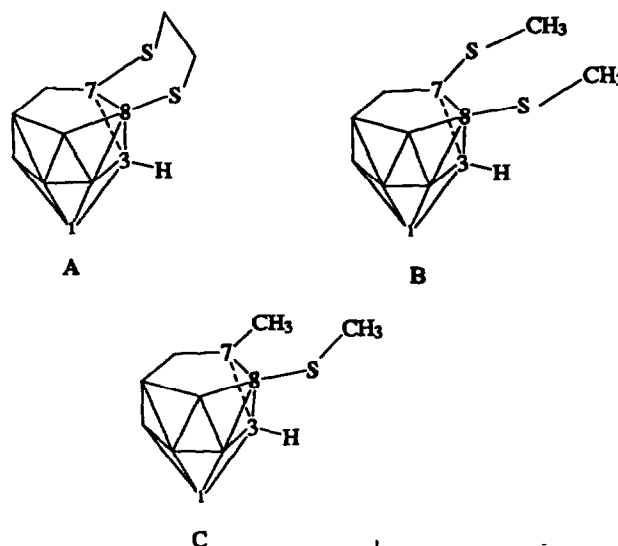


Fig. 1. Schematic representation of A = HL_{s2c6}⁻, B = HL_{s2n}⁻ and C = HL_{s1}⁻.

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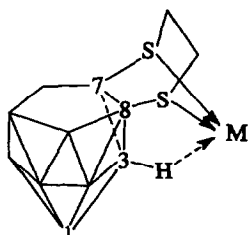


Fig. 2. The B(3)-H \rightarrow M interaction with HL_{s2c6}^- .

lar in many aspects to Ag^+ (e.g. linear coordination is common in all three ions) and Hg^{2+} -B(10) coordination was reported some time ago [4].

In this paper, we report the coordination characteristics of this type of ligand towards Hg^{2+} . Dithio, cyclic HL_{s2c} , non-cyclic HL_{s2n} , and monothio HL_{s1} anions have been studied and all show $\text{Hg-C}_2\text{B}_3$ coordination.

The anions are defined as follows: L stands the moiety 7,8-dicarba-nido-undecaborate, the subindexes for the carborane external fragment, e.g. s1 and s2 indicate one or two exocluster sulphur atoms, respectively, and c or n stands for the cyclic or non-cyclic nature of the exocluster unit. In the case of HL_{s2c} the cycle size is indicated by a number, e.g. HL_{s2c6}^- means a 7,8- $\text{C}_2\text{B}_9\text{H}_{10}$ moiety with two sulphur atoms connected to the cage at the 7,8 positions and externally joined by a spacer producing a six-membered cycle.

2. Experimental details

2.1. General

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

o-Carborane (Dexsil Chemical Corp.) was sublimed under high vacuum before use and HL_{s2c5}^- , HL_{s2c6}^- and

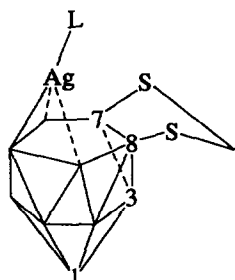


Fig. 3. Schematic representation of the $\text{Ag-C}_2\text{B}_9$ interaction with HL_{s2c5}^- .

HL_{s2n}^- were prepared from *o*-carborane according to the literature [1,5]. A 1.6 M solution of *n*-butyllithium in hexane (Fluka) was used as purchased. Ethanol was reagent grade.

2.2. Synthesis of $[\text{Hg}(\text{NO}_3)_2(\text{PPh}_3)]$

$\text{Hg}(\text{NO}_3)_2$ (0.570 g, 1.66 mmol) in methanol/ HNO_3 (60%) (10 $\text{cm}^3/0.5 \text{ cm}^3$) was added to a methanol solution (40 cm^3) of triphenylphosphine (0.450 g, 1.72 mmol). The mixture was stirred for 15 min. Diethyl ether/hexane (1:1) was added until turbidity appeared. One hour later, the white crystalline precipitate was filtered and washed with hexane (yield 0.78 g, 80%). Anal. Found: C, 37.01; H, 2.72; N, 4.74. $\text{C}_{18}\text{H}_{15}\text{HgN}_2\text{O}_6\text{P}$ calc.: C, 36.88; H, 2.56; N, 4.77%.

2.3. Synthesis of $[\text{Hg}(\text{L}_{s2c5})(\text{PPh}_3)]$

To 15 cm^3 of deoxygenated methanol containing 50.0 mg (0.176 mmol) of $[\text{NMe}_4](\text{HL}_{s2c5}^-)$ was added a methanol solution of $[\text{Hg}(\text{NO}_3)_2(\text{PPh}_3)]$ (105 mg, 0.179 mmol in 15 cm^3 of methanol). The yellow solution was kept at 4°C for 24 h. A green-yellow, crystalline solid was obtained. After filtering, the solid was washed with methanol. An analytically pure solid $[\text{Hg}(\text{L}_{s2c5})(\text{PPh}_3)]$ was obtained. Yield 72 mg (61%). FTIR (KBr): $\nu(\text{B-H})$ 2588, 2566, 2535, 2519, 2508, 2486, 2478 cm^{-1} . ^1H FTNMR (400 MHz, CDCl_3 , 25°C, TMS): δ 3.13 (d, $J = 11.0$ Hz, 1, $-\text{CH}_2-$); 3.39 (d, $J = 11.0$ Hz, 1, $-\text{CH}_2-$); 7.60–7.80 (m, 15, $\text{P}(\text{C}_6\text{H}_5)_3$). ^{11}B FTNMR (128 MHz, CH_2Cl_2 , 25°C, $\text{BF}_3 \cdot \text{Et}_2\text{O}$): δ -12.8 (1B); -14.4 (2B); -15.4 (4B); -22.1 (d, $^1J(\text{B}, \text{H}) = 112$ Hz, 1B); -29.9 (d, $^1J(\text{B}, \text{H}) = 141$ Hz, 1B). Anal. Found: C, 37.48; H, 3.92; S, 9.37 $\text{C}_{21}\text{H}_{26}\text{B}_9\text{-HgPS}_2$ calc.: C, 37.57; H, 3.90; S, 9.55%.

2.4. Synthesis of $[\text{Hg}(\text{L}_{s2c6})(\text{PPh}_3)]$

To 15 cm^3 of deoxygenated methanol containing 50.0 mg (0.168 mmol) of $[\text{NMe}_4](\text{HL}_{s2c6}^-)$ was added a methanol solution of $[\text{Hg}(\text{NO}_3)_2(\text{PPh}_3)]$ (100 mg, 0.170 mmol in 15 cm^3 of methanol). The colourless solution was kept at 4°C for 24 h. A green-yellow crystalline solid was obtained. After filtering, the solid was washed with methanol. An analytically pure solid $[\text{Hg}(\text{L}_{s2c6})(\text{PPh}_3)]$ was obtained. Yield 52 mg (45%). FTIR (KBr): $\nu(\text{B-H})$ 2608, 2542, 2486, 2474, 2426 cm^{-1} . ^1H FTNMR (400 MHz, CD_2Cl_2 , 25°C, TMS): δ 2.21 (d, $J = 8.0$ Hz, 2, $-\text{CH}_2-$); 2.99 (d, $J = 8.0$ Hz, 2, $-\text{CH}_2-$); 7.60–7.80 (m, 15, $\text{P}(\text{C}_6\text{H}_5)_3$). ^{11}B FTNMR (128 MHz, CH_2Cl_2 , 25°C, $\text{BF}_3 \cdot \text{Et}_2\text{O}$): δ -13.6 (7B); -25.3 (d, $^1J(\text{B}, \text{H}) = 103$ Hz, 1B); -31.1 (d, $^1J(\text{B}, \text{H}) = 149$ Hz, 1B). Anal. Found: C, 38.29; H, 4.29; S, 8.91. $\text{C}_{22}\text{H}_{28}\text{B}_9\text{-HgPS}_2$ calc.: C, 38.55; H, 4.12; S, 9.36%.

2.5. Synthesis of $[Hg(L_{s2n})(PPh_3)]$

To 10 cm³ of deoxygenated methanol containing 25.0 mg (0.083 mmol) of $[NMe_4](HL_{s2n})$ was added a methanol solution of $[Hg(NO_3)_2(PPh_3)]$ (50.0 mg, 0.085 mmol in 10 cm³ of methanol). The colourless solution was kept at -20°C for 24 h. A white solid was obtained. After filtering the solid was washed with methanol. An analytically pure solid $[Hg(L_{s2n})(PPh_3)]$ was obtained. Yield 25 mg (43%). FTIR (KBr): $\nu(B-H)$ 2586, 2557, 2547, 2536, 2499, 2452 cm⁻¹. ¹H FTNMR (400 MHz, CD₂Cl₂, 25°C, TMS): δ 2.21 (s, 6, -S-CH₃); 7.68 (m, 15, P(C₆H₅)₃). ¹¹B FTNMR (128 MHz, CH₂Cl₂, 25°C, BF₃·Et₂O): δ = -11.3 (d, ¹J(B, H) = 141 Hz, 1B); -14.7 (d, ¹J(B, H) = 132 Hz, 4B); -18.3 (d, ¹J(B, H) = 142 Hz, 2B); -26.8 (d, ¹J(B, H) = 124 Hz, 1B); -31.6 (d, ¹J(B, H) = 142 Hz, 1B). Anal. Found: C, 38.11; H, 4.48; S, 9.09. C₂₂H₃₀B₉HgPS₂ calc.: C, 38.43; H, 4.40; S, 9.33%.

2.6. Synthesis of $[Hg(L_{s1})(PPh_3)]$

To 10 cm³ of deoxygenated methanol containing 25.0 mg (0.093 mmol) of $[NMe_4](HL_{s1})$ was added a methanol solution of $[Hg(NO_3)_2(PPh_3)]$ (55.0 mg, 0.094 mmol in 10 cm³ of methanol). The yellow solution was kept at -20°C for 24 h. A green-yellow, crystalline solid was obtained. After filtering the solid was washed with methanol. An analytically pure solid $[Hg(L_{s1})(PPh_3)]$ was obtained. Yield 43 mg (70%). FTIR (KBr): $\nu(B-H)$ 2585, 2560, 2552, 2540, 2526, 2515, 2495, 2484, 2472, 2432 cm⁻¹. ¹H FTNMR (400 MHz, CD₂Cl₂, 25°C, TMS): δ 1.22 (s, 3, -CH₃); 1.90 (s, 3, S-CH₃); 7.60–7.80 (m, 15, P(C₅H₅)₃). ¹¹B FTNMR (128 MHz, CH₂Cl₂, 25°C, BF₃·Et₂O): δ -10.4 (d, ¹J(B, H) = 155 Hz, 1B); -14.7 (4B); -15.7 (1B); -17.7 (d, ¹J(B, H) = 157 Hz, 1B); -26.6 (d, ¹J(B, H) = 108 Hz, 1B); -31.4 (d, ¹J(B, H) = 135 Hz, 1B). Anal. Found: C, 40.18; H, 4.54; S, 4.75. C₂₂H₃₁B₉HgPS calc.: C, 40.26; H, 4, 76; S, 4.88%.

2.7. X-Ray structure determination for $[Hg(L_{s2c5})(PPh_3)]$

The unit cell parameters were determined by least-squares refinement from 25 carefully centred reflections measured on a Nicolet P3F diffractometer. The data were corrected for Lorentz and polarization effects, and absorption (empirical correction). Scattering factors and dispersion corrections were taken from [6]. Crystal data are presented in Table 4. Intensity variation of the three standard reflections was negligible during the data collection.

The structure was solved by heavy-atom method using the SHELXS 86 program [7] and subsequent Fourier synthesis. Least-squares refinements were performed

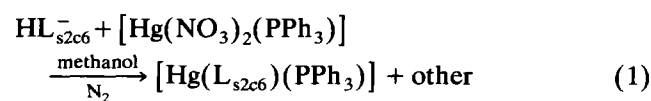
Table 1
nido-Carborane anions with their abbreviations, and the complexes obtained

HL_{s2c5}^-	$\{7,8-\mu-(SCH_2S)-7,8-C_2B_9H_{10}\}^-$
L_{s2c5}^{2-}	$\{7,8-\mu-(SCH_2S)-7,8-C_2B_9H_9\}^{2-}$
HL_{s2c6}^-	$\{7,8-\mu-(SCH_2CH_2S)-7,8-C_2B_9H_{10}\}^-$
L_{s2c6}^{2-}	$\{7,8-\mu-(SCH_2CH_2S)-7,8-C_2B_9H_9\}^{2-}$
HL_{s2n}^-	$\{7,8-(SCH_3)_2-7,8-C_2B_9H_{10}\}^-$
L_{s2n}^{2-}	$\{7,8-(SCH_3)_2-7,8-C_2B_9H_9\}^{2-}$
HL_{s1}^-	$\{7-(SCH_3)-8-(CH_3)-7,8-C_2B_9H_{10}\}^-$
L_{s1}^{2-}	$\{7-(SCH_3)-8-(CH_3)-7,8-C_2B_9H_9\}^{2-}$
$[Hg(L_{s2c5})(PPh_3)]$	
$[Hg(L_{s2c6})(PPh_3)]$	
$[Hg(L_{s2n})(PPh_3)]$	
$[Hg(L_1)(PPh_3)]$	

by using the XTAL 2.6 program system [8], which minimized the function $w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. After refinement of all non-hydrogen atoms with anisotropic temperature factors, approximate positions of the hydrogen atoms could be picked from subsequent difference Fourier map. Refinement of all atoms, with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms, reduced the *R* value to 0.031 (*R_w* = 0.028). The greatest maximum and minimum residuals of 1.2 and -0.7 e Å⁻³ were at the vicinity of Hg. Full lists of all parameters are available from the Cambridge Crystallographic Data Centre.

3. Results and discussion

The anions studied and the abbreviations used are schematically indicated in Table 1. The reactions of the *nido* anions HL_{s2c5}^- and HL_{s2c6}^- with $[Hg(NO_3)_2(PPh_3)]$ in methanol at room temperature yield yellow-green crystalline precipitates, moderately air-stable, with the stoichiometries $[Hg(L_{s2c5})(PPh_3)]$ and $[Hg(L_{s2c6})(PPh_3)]$, respectively. A similar reaction with the open ligand HL_{s2n}^- (non-connecting S,S'-string) was also conducted to yield $[Hg(L_{s2n})(PPh_3)]$. The compound $[Hg(L_{s1})(PPh_3)]$ was obtained upon reaction of HL_{s1}^- with $[Hg(NO_3)_2(PPh_3)]$ in methanol. Equation (1) exemplifies these reactions for HL_{s2c6}^- .



Attempts to produce these compounds starting from $[HgCl_2(PPh_3)]$ did not succeed.

The stoichiometries indicated are consistent with elemental analysis and the ¹H NMR integrations. The

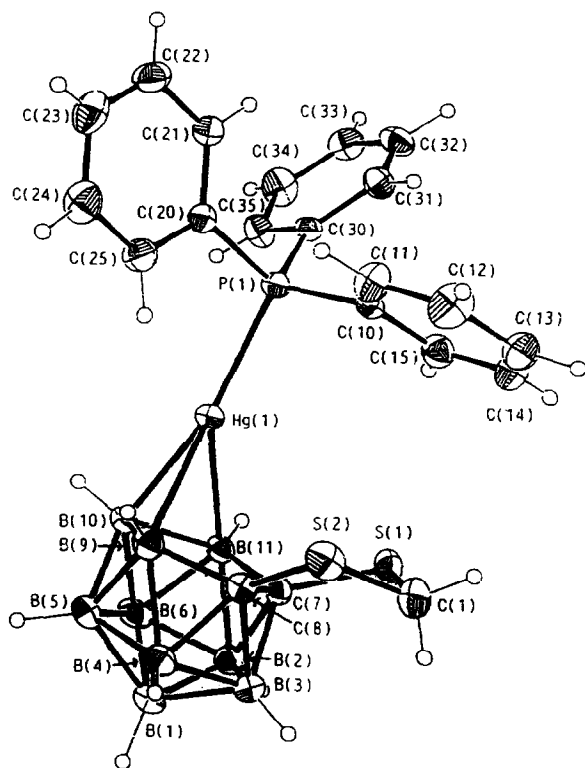


Fig. 4. ORTEP view of $[\text{Hg}(\text{L}_{s2c5})(\text{PPh}_3)]$ showing 40% thermal ellipsoids.

$^{11}\text{B}\{\text{H}\}$ NMR spectra of the complexes do not resemble those of HL_{s2c5}^- , HL_{s2c6}^- and HL_{s2n}^- (2:1:2:2:1:1 pattern). Resonances in the range (δ) between -13 and -31 ppm are observed in the $^{11}\text{B}\{\text{H}\}$ NMR spectra of the L_{s2c5}^- , L_{s2c6}^- and L_{s2n}^- complexes. The $^{11}\text{B}\{\text{H}\}$ NMR pattern of the HL_{s1}^- complexes is slightly wider, between -10 and -31 ppm. These signal distributions suggest boron-cage-to-metal interaction. The comparison of these ^{11}B NMR spectra with that of $\text{B}_9\text{C}_2[\text{Hg}(\text{PPh}_3)]\text{H}_{11}$ [4] supports Hg-open face coordination. The ^1H NMR spectra do not display the resonance at $\delta -2.5$ ppm attributed to the open face B–H–B proton [9]. Its absence implies that in the complexes, this proton has been replaced by a metal ion.

To prove unambiguously the nature of these compounds the X-ray analysis of $[\text{Hg}(\text{L}_{s2c5})(\text{PPh}_3)]$ was undertaken. Figure 4 shows its molecular structure. Table 2 lists positional parameters and Table 3 lists selected interatomic distances and angles. The mercury atom is coordinated almost linearly by triphenylphosphine and a unique boron atom B(10) of the open face: $\text{Hg}(1)\text{--P}(1) = 2.405(1)$, $\text{Hg}(1)\text{--B}(10) = 2.208(6)$ Å, $\text{P}(1)\text{--Hg}(1)\text{--B}(10) = 165.8(1)^\circ$. Additional, although relatively weak, bonding is suggested by the other boron atoms of the open face, B(9) and B(11), since

interatomic distances of 2.630(6) and 2.500(5) Å are found for $\text{Hg}(1)\text{--B}(9)$ and $\text{Hg}(1)\text{--B}(11)$, respectively. Thus, the complex is perhaps best described as pseudo-sigma-bonded. Interatomic distances between the mercury atom and the carbon cluster atoms, 2.997(4) and 3.043(4) Å, correspond essentially to non-bonded interactions. The molecule is very similar to $[\text{3-PPh}_3 - 3,1,2\text{-HgC}_2\text{B}_9\text{H}_{11}]$ [4] but for minor differences, e.g. $[\text{Hg}(\text{L}_{s2c5})(\text{PPh}_3)]$ how a less linear P–Hg–B(10) unit $165.8(1)^\circ$ versus $172.5(4)^\circ$. In addition, Hg in $[\text{Hg}(\text{L}_{s2c5})(\text{PPh}_3)]$ is less face-bonded than Hg in $[\text{3-PPh}_3 - 3,1,2\text{-HgB}_9\text{C}_2\text{H}_{11}]$ since the $\text{Hg}(1)\text{--B}(9)$, $\text{Hg}(1)\text{--B}(11)$ and $\text{Hg}(1)\text{--C}(7)$, $\text{Hg}(1)\text{--C}(8)$ distances are longer in $[\text{Hg}(\text{L}_{s2c5})(\text{PPh}_3)]$ than in $[\text{3-PPh}_3 - 3,1,2\text{-HgC}_2\text{B}_9\text{H}_{11}]$.

Although the structures of $[\text{Hg}(\text{L}_{s2c5})(\text{PPh}_3)]$ and $[\text{3-PPh}_3 - 3,1,2\text{-HgC}_2\text{B}_9\text{H}_{11}]$ are very similar, they were produced in very different manners. The latter was obtained from $\text{Tl}[3,1,2\text{-TlC}_2\text{B}_9\text{H}_{11}]$. This, in turn, was

Table 2

Final positional parameters and isotropic thermal parameters with e.s.d.s in parentheses for $[\text{Hg}(\text{L}_{s2c5})(\text{PPh}_3)]$

	x	y	z	U_{eq} (Å ²)
Hg(1)	0.21614(2)	0.14341(1)	0.05365(0)	0.03794(9)
S(1)	0.5206(1)	−0.0289(1)	0.09346(7)	0.0537(7)
S(2)	0.4597(2)	0.0918(1)	0.20807(6)	0.0564(8)
P(1)	0.3278(1)	0.29505(8)	0.02136(5)	0.0349(6)
C(1)	0.5881(6)	0.0109(5)	0.1749(3)	0.065(4)
C(10)	0.4976(5)	0.3046(3)	0.0677(2)	0.036(2)
C(11)	0.5206(6)	0.3733(4)	0.1181(3)	0.053(3)
C(12)	0.6499(7)	0.3728(5)	0.1546(3)	0.066(4)
C(13)	0.7534(6)	0.3066(5)	0.1410(3)	0.058(3)
C(14)	0.7277(6)	0.2391(5)	0.0916(3)	0.056(3)
C(15)	0.6011(6)	0.2358(4)	0.0551(3)	0.048(3)
C(20)	0.2233(5)	0.4000(3)	0.0450(2)	0.038(2)
C(21)	0.2272(5)	0.4895(4)	0.0108(3)	0.046(3)
C(22)	0.1535(6)	0.5715(4)	0.0344(3)	0.058(3)
C(23)	0.0826(6)	0.5638(5)	0.0904(3)	0.060(4)
C(24)	0.0769(6)	0.4753(5)	0.1226(3)	0.060(3)
C(25)	0.1462(6)	0.3932(4)	0.1006(2)	0.049(3)
C(30)	0.3526(5)	0.3056(3)	−0.0659(2)	0.035(2)
C(31)	0.4688(5)	0.3517(4)	−0.0887(2)	0.045(3)
C(32)	0.4810(6)	0.3630(4)	−0.1563(2)	0.054(3)
C(33)	0.3762(6)	0.3292(4)	−0.2008(3)	0.056(3)
C(34)	0.2604(7)	0.2834(5)	−0.1787(3)	0.064(4)
C(35)	0.2478(6)	0.2696(4)	−0.1112(2)	0.050(3)
B(1)	0.1370(6)	−0.1405(5)	0.1756(3)	0.053(3)
B(2)	0.2481(6)	−0.1508(4)	0.1096(3)	0.048(3)
B(3)	0.3146(6)	−0.1066(4)	0.1878(3)	0.045(3)
B(4)	0.1868(6)	−0.0346(5)	0.2219(3)	0.049(3)
B(5)	0.0403(6)	−0.0277(5)	0.1667(3)	0.052(3)
B(6)	0.0789(7)	−0.1024(4)	0.0937(3)	0.050(3)
C(7)	0.3424(4)	−0.0425(3)	0.1152(2)	0.037(2)
C(8)	0.3086(5)	0.0217(3)	0.1762(2)	0.037(2)
B(9)	0.1565(6)	0.0732(4)	0.1699(3)	0.044(3)
B(10)	0.0737(6)	0.0299(4)	0.0912(3)	0.042(3)
B(11)	0.2192(6)	−0.0431(4)	0.0566(3)	0.038(3)

Table 3
Selected interatomic distances (Å) and angles (°) with e.s.d.s in parentheses for [Hg(L_{s2c5})(PPh₃)]

Hg(1)–P(1)	2.405(1)	P(1)–C(10)	1.816(4)
Hg(1)–C(7)	2.997(4)	P(1)–C(20)	1.807(5)
Hg(1)–C(8)	3.043(4)	P(1)–C(30)	1.801(4)
Hg(1)–B(9)	2.630(6)	C(7)–B(3)	1.736(7)
Hg(1)–B(10)	2.208(6)	C(7)–C(8)	1.556(6)
Hg(1)–B(11)	2.500(5)	C(7)–B(11)	1.606(7)
S(1)–C(1)	1.803(7)	C(8)–B(3)	1.735(7)
S(1)–C(7)	1.793(5)	C(8)–B(9)	1.602(7)
S(2)–C(1)	1.799(7)	B(9)–B(10)	1.820(8)
S(2)–C(8)	1.799(5)	B(10)–B(11)	1.872(8)
P(1)–Hg(1)–B(9)	132.3(1)	S(1)–C(7)–B(3)	117.4(3)
P(1)–Hg(1)–B(10)	165.8(1)	S(1)–C(7)–C(8)	113.0(3)
P(1)–Hg(1)–B(11)	147.8(1)	S(1)–C(7)–B(11)	118.4(3)
B(9)–Hg(1)–B(10)	43.1(2)	B(3)–C(7)–C(8)	63.3(3)
B(10)–Hg(1)–B(11)	46.3(2)	B(3)–C(7)–B(11)	118.2(4)
C(1)–S(1)–C(7)	95.1(2)	C(8)–C(7)–B(11)	113.9(4)
C(1)–S(2)–C(8)	95.8(3)	S(2)–C(8)–B(3)	116.8(3)
Hg(1)–P(1)–C(10)	108.3(1)	S(2)–C(8)–C(7)	111.5(3)
Hg(1)–P(1)–C(20)	108.9(2)	S(2)–C(8)–B(9)	120.0(3)
Hg(1)–P(1)–C(30)	115.0(1)	B(3)–C(8)–C(7)	63.4(3)
C(10)–P(1)–C(20)	107.3(2)	B(3)–C(8)–B(9)	117.3(4)
C(10)–P(1)–C(30)	109.0(2)	C(7)–C(8)–B(9)	114.3(3)
C(20)–P(1)–C(30)	108.1(2)	C(8)–B(9)–B(10)	105.4(4)
S(1)–C(1)–S(2)	108.1(3)	B(9)–B(10)–B(11)	101.9(4)
C(7)–B(3)–C(8)	53.3(3)	C(7)–B(11)–B(10)	104.2(4)

produced by the addition of aqueous solution of thallium(I) acetate to an aqueous alkaline solution [10] of (3)–1,2-C₂B₉H₁₂[−]. An alkaline solution was necessary to remove the open face B–H–B. In contrast,

[Hg(L_{s2c5})(PPh₃)] did not require the addition of base. This may be because the electron-rich C-connected elements with which we have obtained peculiar reactions are also responsible for this enhanced acidity.

As a conclusion, we have proved for the first time, that open-face coordination is possible in exo electron-rich C-connected derivatives of 7,8-dicarbido-undecaborate (1[−]). Such coordination is favoured over S-coordination for certain metal ions (e.g. Hg²⁺) that have a strong tendency to linear coordination and, in contrast to other metal ions, the cyclic, and non-cyclic, natures of HL_{s2c}[−] and HL_{s2nr}[−] and the presence of two or one electron-rich elements do not influence the coordination of the Hg²⁺ ion. Furthermore, it is found that the Hg²⁺-open-face coordination is so favoured that it is not necessary to remove the B–H–B open face proton by base.

Acknowledgements

The authors are grateful to the Spanish agencies CICYT and CIRIT for financial support.

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Table 4
Crystallographic data for [Hg(L_{s2c5})(PPh₃)]

Chemical formula	C ₂₁ H ₂₆ B ₉ HgPS ₂
FW	671.41
a (Å)	9.530(2)
b (Å)	13.400(3)
c (Å)	20.201(3)
β (°)	94.06(1)
V (Å ³)	2573.2 (7)
Z	4
Space group	P2 ₁ /n (alt. P2 ₁ /c)
T (°C)	23
λ (Å)	0.71069
ρ _{calcd} (g cm ^{−3})	1.733
μ (cm ^{−1})	63.3
Transmission coefficient	0.758–1.000
R(F _o)	0.031
R _w (F _o)	0.028
Total reflections	5923
Unique reflections	5341
Significant reflections (F > 2σ F)	4763