

Carborane to enhance chelating capacity *S,S'*-Thioether– thioester coordination and its transition metal stability

C. Viñas^a, M^a.R. Cirera^a, F. Teixidor^{a,*}, R. Sillanpää^b, R. Kivekäs^c

^a Institut de Ciència de Materials de Barcelona, Campus U.A.B., E-08193, Bellaterra, Spain

^b Department of Chemistry, University of Turku, FIN-20500 Turku, Finland

^c Department of Chemistry, PO Box 55, University of Helsinki, FIN-00014 Helsinki, Finland

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Abstract

An *S,S'*-thioether–thioester chelating ligand $[7,8-\mu\text{-SCH}_2\text{C(O)S-7,8-C}_2\text{B}_9\text{H}_{10}]^-$ (L_1), incorporating the unit $[-(\text{C})_2\text{B}_9\text{H}_{10}]^-$ has been synthesized. Reactions have been conducted with $\text{RhCl}(\text{PPh}_3)_3$ and $\text{PdCl}_2(\text{PPh}_3)_2$ complexes in ethanol. With Rh, L_1 maintains its original cyclic nature and most probably chelation via thioether–thioester takes place. The carborane negative charge may stabilize this original thioether–thioester complex. The other two Rh positions are occupied by two PPh_3 ancillary ligands forming $[\text{Rh}(L_1)(\text{PPh}_3)_2]$. The reaction of L_1 with Pd induces ligand modifications and the cyclic nature of L_1 is lost. A transesterification process leading to a dianionic ligand L_2 , $[7\text{-S-8-SCH}_2\text{C(O)OCH}_2\text{CH}_3\text{-7,8-C}_2\text{B}_9\text{H}_{10}]^{2-}$ has taken place. In this way L_2 is capable of compensating the dipositive Pd charge. The other two Pd positions are occupied by two PPh_3 . This reaction has been extended to methanol and isopropanol solvents. The crystal structure of $[\text{Pd}(L_2)(\text{PPh}_3)_2]$ has been determined.

Keywords: Carborane; Cluster; Palladium; Rhodium; Metalloboranes; Thiolate

1. Introduction

Thioethers are weak ligands; however, the coordinating capacity of polythiaethers is improved due to a higher number of participating thio groups. Thus a relatively rich chemistry has been found with 1,4,7-trithiacyclononane (9S3) [1–3], 1,5,9-trithiacyclododecane (12S3) [2–6], and the similar 12S4 [7] and 18S6 [8], and other trithiacompounds [9,10]. Dithioethers, having only two thio groups show weak bonding capacity; however, we have proven in earlier publications that the bonding capacity of dithioether ligands can be dramatically improved if a negative charge bearing fragment is incorporated in the dithioether molecule. In our case this fragment was the $[-(\text{C})_2\text{B}_9\text{H}_{10}]^-$ unit. The thio groups were directly connected to the cluster carbon atoms and

cycles of different size were synthesized. These molecules have different coordinating possibilities. In addition to the η^5 [11,12] and *exo-nido* coordination [13], the sulfur atoms provide the more plausible ways of bonding. The metal coordination number of six in these dithio compounds forces the participation of a B–H group in bonding [14]. With a coordination number of four this B–H participation has never been found [15]. If the chelating capacity of dithioethers is weak, that of *S,S'*-thioether–thioester is even lower, and no examples are found. Owing to the exalted chelating capacity found in dithioether derivatives of $[\textit{exo}\text{-S}_2\text{-C}_2\text{B}_9\text{H}_{10}]^-$ we expected that a correlation could be found with *S,S'*-thioether–thioester compounds bearing the $[\text{C}_2\text{B}_9\text{H}_{10}]^-$ unit. This new type of ligand could be of interest when chelation with a distinct degree of bonding by the participating elements along with a greater rigidity is sought. In this paper we present the results obtained with the new ligand $[7,8-\mu\text{-SCH}_2\text{C(O)S-7,8-C}_2\text{B}_9\text{H}_{10}]^-$, which has the *S,S'*-thioether–thioester chelating possibility.

* Corresponding author. Fax: (+34) 3 5805729; e-mail teixidor@icmab.es.

2. Experimental section

2.1. General methods

1,2-(SH)₂-1,2-C₂B₁₀H₁₀ was synthesized from *o*-carborane (Dexsil Chemical Corp.) according to the literature [16]. RhCl(PPh₃)₃ and PdCl₂(PPh₃)₂ were prepared by the published procedure [17,18]. Bromoacetyl bromide was used as-purchased (Aldrich). Ethanol, methanol, isopropanol, dimethoxyethane and ethyl ether were of reagent quality. Dimethoxyethane was deoxygenated and distilled from sodium. All reactions were carried out under a dinitrogen atmosphere employing Schlenk techniques. Microanalyses were performed in our analytical laboratory by using a Perkin Elmer 240B microanalyzer. IR spectra (KBr disk) were measured on a Nicolet 710-FT spectrophotometer. The ¹H NMR, ¹¹B NMR, ¹³C NMR and ³¹P NMR spectra were recorded on a Bruker ARX-300 instrument.

2.2. Synthesis of [NMe₄][7,8-μ-SCH₂C(O)S-7,8-C₂B₉H₁₀] or **1**

To a three-necked round bottom flask (250 ml), fitted with a dinitrogen inlet/outlet, containing deoxygenated dry dimethoxyethane (50 ml) was added 1,2-(SH)₂-1,2-C₂B₁₀H₁₀ (1.00 g, 4.8 mmol) and anhydrous Na₂CO₃ (1.02 g, 9.6 mmol). After stirring for 30 min at room temperature bromoacetyl bromide was added (2 ml, five-times excess).

After stirring for 3 h at room temperature the NaHCO₃ and the NaBr were filtered. The solvent was evaporated and 10 ml of water were added. Insolubles were separated by filtering through Celite. Excess of tetramethylammonium chloride (or cesium chloride to get a better characterization of L₁) was added to the aqueous solution, resulting in the formation of a white precipitate. This was washed with water and ethyl ether and dried in vacuum to yield an analytically pure solid. Yield of **1** was 1.20 g (93%). Anal. Found: C, 30.68; H, 7.71; N, 4.34; S, 19.22. C₈H₂₄B₉O₂N. Calc.: C, 30.83; H, 7.76; N, 4.49; S, 20.57%. FTIR(KBr), ν(cm⁻¹): 2530 (B–H); 1655 (C=O). ¹H NMR (300 MHz, CD₃COCD₃, 25 °C, TMS): –2.5 (br, B–H–B), 3.41 (br, N(CH₃)₄ and –CH₂). ¹¹B{¹H} NMR (96 MHz, CD₃COCD₃, 25 °C, BF₃·Et₂O): –7.46 (1B), –8.12 (1B), –9.55 (1B), –17.36 (2B), –18.96 (1B), –19.64 (1B), –32.26 (1B), –34.77 (1B). ¹³C{¹H} NMR (75 MHz, CD₃COCD₃, 25 °C, TMS): 39.91 (s, CH₂), 54.00 (t, N(CH₃)₄), 198 (s, C=O). ¹H NMR for the Cs(L₁): (300 MHz, CD₃COCD₃, 25 °C, TMS): –2.5 (br, B–H–B), 3.34 (d, 1, CH^α, J(H^α,H^β) = 15.44 Hz), 3.45 (d, 1, CH^β, J(H^α,H^β) = 15.44 Hz).

2.3. Synthesis of [Rh(L₁)(PPh₃)₂] or **2**

To 10 ml of deoxygenated boiling ethanol containing **1** (34 mg, 0.109 mmol) was added RhCl(PPh₃)₃ (100 mg,

0.109 mmol) and the mixture was refluxed for 1.5 h. A red solid was separated by filtering the warm mixture. The solid was washed with water, warm ethanol and ethyl ether to yield an analytically pure solid [Rh(L₁)(PPh₃)₂]. Yield 70 mg (75%). Anal. Found: C, 55.17; H, 4.91; S, 6.83. C₄₀H₄₂B₉OP₂RhS₂. Calc.: C, 55.54; H, 4.89; S, 7.41%. FTIR (KBr), ν(cm⁻¹): 2535 (B–H); 1756 (C=O), 1435, 692, 520 (PPh₃). ¹H NMR (300 MHz, CD₂Cl₂, 25 °C, TMS): –2.47 (br, B–H–B), 3.47 (d, 1, CH^α, J(H^α,H^β) = 15.75 Hz), 3.8 (d, 1, CH^β, J(H^α,H^β) = 15.75 Hz), 7.2 (m, 30, C_{aryl}–H). ¹¹B{¹H} NMR (96 MHz, CD₂Cl₂, 25 °C, BF₃·Et₂O): –8.85 (1B), –11.17 (1B), –15.59 (1B), –18.37 (4B), –29.77 (1B), –33.53 (1B). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂, 25 °C, H₃PO₄, 85%): 18.5 (dd, 1, J(P,P)_C = 27.0 Hz, J(P,Rh) = 146.7 Hz), 37.03 (d, 1, J(P,P)_C = 27.0 Hz, J(P,Rh) = 146.7 Hz).

2.4. Reaction of **1** with PdCl₂(PPh₃)₂ in alcohols

To 10 ml of deoxygenated boiling alcohol (methanol, ethanol or isopropanol) containing **1** (34 mg, 0.109 mmol) was added PdCl₂(PPh₃)₂ (77 mg, 0.109 mmol) and the mixture was refluxed for 1 h. A red solid was separated by filtering the warm mixture. The solid was washed with water, warm alcohol and ethyl ether to yield an analytically pure solid. Data for [Pd(7-S-8-SCH₂C(O)OCH₂CH₃-7,8-C₂B₉H₁₀)(PPh₃)₂]: yield 82 mg (83%). Anal. Found: C, 54.8; H, 5.19; S, 6.77. C₄₂H₄₇B₉O₂P₂PdS₂. Calc.: C, 55.2; H, 5.19; S, 7.02%. FTIR (KBr) ν(cm⁻¹): 2537 (B–H), 1730, 1090, (C=O). ¹H NMR (300 MHz, CD₂Cl₂, 25 °C, TMS): –2 (br, B–H–B), 1.44 (t, 3, OCH₂CH₃), 2.78 (dd, 1, SCH), 4.00 (dd, 1, SCH), 4.28 (q, 2, OCH₂CH₃), 7.46 (m, 15, C_{aryl}–H). ¹¹B{¹H} NMR (96 MHz, CD₂Cl₂, 25 °C, BF₃·Et₂O): –8.74 (1B), –13.22 (1B), –15.95 (3B), –16.05 (1B), –20.71 (1B), –30.95 (1B),

Table 1
Crystallographic data for [Pd(7-S-8-SCH₂C(O)OCH₂CH₃-7,8-C₂B₉H₁₀)(PPh₃)₂]

Chemical formula	C ₄₂ H ₄₇ B ₉ O ₂ P ₂ PdS ₂
Fw	913.55
<i>a</i> (Å)	13.300(3)
<i>b</i> (Å)	17.478(5)
<i>c</i> (Å)	19.119(3)
β (deg)	93.74(2)
<i>V</i> (Å ³)	4435(2)
<i>Z</i>	4
Space group	monoclinic, P2 ₁ /n (No. 14)
<i>T</i> (°C)	23
λ (Å)	0.71069
ρ g cm ⁻³	1.368
μ (cm ⁻¹)	6.2
Transm. coeff.	0.894–1.000
<i>R</i> (<i>F</i> _o)	0.049
<i>R</i> _w (<i>F</i> _o)	0.047

Table 2

Final positional parameters and isotropic displacement parameters (\AA^2) with e.s.d. values in parentheses for $[\text{Pd}\{7\text{-S-}8\text{-SCH}_2\text{C}(\text{O})\text{OCH}_2\text{CH}_3\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}\}(\text{PPh}_3)_2]$

	x	y	z	U_{eq}^a
Pd	0.74499(4)	0.72706(4)	0.60941(3)	0.0271(2)
S(1)	0.5813(1)	0.7057(1)	0.5616(1)	0.0340(7)
S(2)	0.6641(1)	0.7276(1)	0.7186(1)	0.0332(6)
P(1)	0.9046(1)	0.7550(1)	0.6615(1)	0.0293(7)
P(2)	0.7860(1)	0.7111(1)	0.4953(1)	0.0333(7)
O(1)	0.7225(5)	0.5892(4)	0.8175(3)	0.072(3)
O(2)	0.7303(5)	0.5306(4)	0.7151(4)	0.094(3)
C(1)	0.6115(6)	0.6323(5)	0.7265(5)	0.055(4)
C(2)	0.6938(6)	0.5776(5)	0.7519(5)	0.054(4)
C(3)	0.8043(8)	0.5416(7)	0.8465(6)	0.103(6)
C(4)	0.8196(8)	0.5588(7)	0.9199(6)	0.108(6)
C(7)	0.5141(5)	0.7701(5)	0.6140(3)	0.031(2)
C(8)	0.5503(4)	0.7768(5)	0.6926(3)	0.030(2)
C(12)	0.9587(5)	0.8454(4)	0.6369(4)	0.034(3)
C(13)	0.9076(6)	0.8949(5)	0.5914(4)	0.053(4)
C(14)	0.9462(7)	0.9681(5)	0.5795(5)	0.069(4)
C(15)	1.0365(7)	0.9896(6)	0.6130(6)	0.084(5)
C(16)	1.0884(6)	0.9427(5)	0.6587(5)	0.068(4)
C(17)	1.0498(6)	0.8707(5)	0.6707(5)	0.051(3)
C(18)	0.9051(5)	0.7721(5)	0.7555(4)	0.035(3)
C(19)	0.8548(5)	0.8369(5)	0.7780(4)	0.046(3)
C(20)	0.8567(6)	0.8549(5)	0.8477(5)	0.056(4)
C(21)	0.9074(6)	0.8091(6)	0.8967(4)	0.059(4)
C(22)	0.9564(6)	0.7455(5)	0.8762(4)	0.060(4)
C(23)	0.9571(6)	0.7257(5)	0.8050(4)	0.048(3)
C(24)	0.9943(5)	0.6787(5)	0.6507(4)	0.035(3)
C(25)	0.9618(6)	0.6047(5)	0.6651(4)	0.045(3)
C(26)	1.0256(6)	0.5428(5)	0.6610(5)	0.052(4)
C(27)	1.1233(6)	0.5549(5)	0.6403(5)	0.058(4)
C(28)	1.1552(6)	0.6269(5)	0.6254(5)	0.050(3)
C(29)	1.0910(5)	0.6883(5)	0.6303(4)	0.040(3)
C(30)	0.9184(5)	0.6995(5)	0.4755(4)	0.039(3)
C(31)	0.9610(6)	0.6290(6)	0.4684(5)	0.062(4)
C(32)	1.0600(7)	0.6223(7)	0.4514(6)	0.091(5)
C(33)	1.1170(6)	0.6840(7)	0.4441(6)	0.095(5)
C(34)	1.0769(6)	0.7568(6)	0.4518(5)	0.074(4)
C(35)	0.9773(6)	0.7647(5)	0.4684(4)	0.052(3)
C(36)	0.7459(5)	0.7891(4)	0.4375(4)	0.034(3)
C(37)	0.7724(6)	0.7894(5)	0.3686(4)	0.043(3)
C(38)	0.7446(6)	0.8490(5)	0.3227(4)	0.049(3)
C(39)	0.6910(6)	0.9093(5)	0.3470(4)	0.045(3)
C(40)	0.6633(6)	0.9091(5)	0.4154(4)	0.048(3)
C(41)	0.6910(6)	0.8495(5)	0.4605(4)	0.038(3)
C(42)	0.7233(5)	0.6238(5)	0.4639(4)	0.039(3)
C(43)	0.7241(7)	0.5615(5)	0.5095(5)	0.063(4)
C(44)	0.6715(8)	0.4951(5)	0.4874(5)	0.071(4)
C(45)	0.6201(7)	0.4900(6)	0.4259(5)	0.074(4)
C(46)	0.6176(7)	0.5508(6)	0.3813(5)	0.072(4)
C(47)	0.6713(6)	0.6184(5)	0.4000(5)	0.052(3)
B(1)	0.4728(6)	0.9165(5)	0.6580(5)	0.040(4)
B(2)	0.4672(7)	0.8570(5)	0.5828(5)	0.039(4)
B(3)	0.5729(6)	0.8546(5)	0.6416(5)	0.035(3)
B(4)	0.5336(6)	0.8645(6)	0.7282(5)	0.037(3)
B(5)	0.4019(7)	0.8712(6)	0.7232(5)	0.047(4)
B(6)	0.3599(7)	0.8661(6)	0.6309(6)	0.050(4)
B(9)	0.4600(6)	0.7813(6)	0.7447(4)	0.039(3)
B(10)	0.3445(7)	0.7882(6)	0.6873(5)	0.048(4)
B(11)	0.3931(6)	0.7749(6)	0.6000(4)	0.039(3)

^a $U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

Table 3

Selected bond lengths (\AA) and angles (deg) for $[\text{Pd}\{7\text{-S-}8\text{-SCH}_2\text{C}(\text{O})\text{OCH}_2\text{CH}_3\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}\}(\text{PPh}_3)_2]$

Pd–S(1)	2.335(2)	P(2)–C(42)	1.821(8)
Pd–S(2)	2.411(2)	O(1)–C(2)	1.30(1)
Pd–P(1)	2.337(2)	O(1)–C(3)	1.45(1)
Pd–P(2)	2.300(2)	O(2)–C(2)	1.20(1)
S(1)–C(7)	1.784(7)	C(1)–C(2)	1.51(1)
S(2)–C(1)	1.817(9)	C(3)–C(4)	1.44(2)
S(2)–C(8)	1.783(7)	C(7)–C(8)	1.552(9)
P(1)–C(12)	1.812(8)	C(7)–B(11)	1.62(1)
P(1)–C(18)	1.821(7)	C(8)–B(9)	1.61(1)
P(1)–C(24)	1.811(8)	B(9)–B(10)	1.83(1)
P(2)–C(30)	1.836(7)	B(10)–B(11)	1.84(1)
P(2)–C(36)	1.814(8)		
S(1)–Pd–S(2)	83.23(7)	Pd–P(2)–C(36)	114.1(2)
S(1)–Pd–P(1)	176.22(8)	Pd–P(2)–C(42)	106.4(3)
S(1)–Pd–P(2)	83.24(7)	S(1)–C(7)–B(3)	118.4(5)
S(2)–Pd–P(1)	94.25(7)	S(1)–C(7)–B(11)	118.0(5)
S(2)–Pd–P(2)	165.69(7)	C(8)–C(7)–B(11)	113.5(6)
P(1)–Pd–P(2)	99.49(7)	S(2)–C(8)–C(7)	115.9(5)
Pd–S(1)–C(7)	99.7(2)	S(2)–C(8)–B(3)	111.4(4)
Pd–S(2)–C(1)	105.3(3)	S(2)–C(8)–B(4)	117.0(5)
Pd–S(2)–C(8)	100.3(2)	S(2)–C(8)–B(9)	120.3(5)
C(1)–S(2)–C(8)	98.1(4)	C(7)–C(8)–B(9)	113.9(5)
Pd–P(1)–C(12)	115.9(2)	C(8)–B(9)–B(10)	105.3(6)
Pd–P(1)–C(18)	113.6(2)	B(9)–B(10)–B(11)	101.7(6)
Pd–P(1)–C(24)	112.6(2)	C(7)–B(11)–B(10)	105.2(6)
Pd–P(2)–C(30)	120.0(2)		

–35.48 (1B). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂, 25 °C, H₃PO₄, 85%): 23.12 (d, 1, $J(\text{P,P})_{\text{C}} = 28.55$ Hz), 32.03 (d, 1, $J(\text{P,P})_{\text{C}} = 28.55$ Hz).

2.5. X-ray structure determination of $[\text{Pd}\{7\text{-S-}8\text{-SCH}_2\text{C}(\text{O})\text{OCH}_2\text{CH}_3\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}\}(\text{PPh}_3)_2]$

Single-crystal data collection was performed at ambient temperature on a Rigaku AFC5S diffractometer using graphite monochromatized Mo K α radiation. The unit cell parameters were determined by least squares refinement of 14 carefully centered reflections. The data obtained were corrected for Lorentz and polarization effects and for dispersion. A correction for empirical absorption (ψ scan) was also applied. A total of 6441 reflections giving 6090 unique reflections ($R_{\text{int}} = 0.066$) were collected by ω – 2θ scan mode ($2\theta_{\text{max}} = 50^\circ$). Of these, 3548 were considered as observed according to the criterion $F > 4\sigma(F)$. Crystallographic data are presented in Table 1.

The structure was solved by direct methods by using the MTRIL program [19]. Least squares refinements and all subsequent calculations were performed using the XTAL3.2 program system [20], which minimized the function $\sum w(\Delta F)^2 [1/w = \sigma^2(F_o)]$. Non-hydrogen atoms were refined with anisotropic displacement parameters in the final refinements. Hydrogen atoms of the carborane cage were refined with fixed isotropic

displacement parameters ($U(H)$ equal to $1.2 \times U$ of host atom) but the rest of the hydrogen atoms were placed at their calculated positions ($C-H = 0.95 \text{ \AA}$ and $U(H)$ equal to $1.2 \times U$ of host atom). Neutral atomic scattering factors were those included in the programs. The figure was plotted with XTAL-ORTEP. Final positional parameters and isotropic displacement parameters are listed in Table 2; selected bond lengths and angles are listed in Table 3.

2.5.1. Supplementary data

Tables including experimental details (1 page), bond lengths and angles (8 pages), positional and thermal parameters for hydrogen atoms (1 page), anisotropic displacement parameters for non-hydrogen atoms (1 page) are available.

3. Results and discussion

The reaction of 1,2-(SH)₂-1,2-C₂B₁₀H₁₀ with bromoacetyl bromide in dimethoxyethane (glyme) in the presence of Na₂CO₃ produced, after the addition of [NMe₄]Cl, the thioester containing nido derivative [NMe₄][7,8-μ-SCH₂C(O)S-7,8-C₂B₉H₁₀] or [NMe₄][L₁] (**1**). The reaction is indicated in Fig. 1.

Compound **1** was characterized by elemental analysis, ¹H, ¹³C and ¹¹B NMR. The partial degradation or boron removal from closo to nido [21] was clearly proven by the appearance of a ¹H resonance at -2.5 ppm attributed to the endohedral open face hydrogen. The shift of the IR ν(BH) from 2601 cm⁻¹ to 2530 cm⁻¹ is another clear indication of the nido formation. The 1:1:1:2:1:1:1:1 boron signal distribution at the ¹¹B{¹H} NMR in the range -7 to -37 ppm is also fully consistent with the partial degradation.

Ligand L₁ has been drawn as a cycle. In principle, cycles and macrocycles are not easily obtained and, to avoid polymerization, require the use of high dilution conditions. In the synthesis of the related compound [7,8-μ-SCH₂CH₂S-7,8-C₂B₉H₁₀]⁻, also containing a six-membered cycle, a good yield was obtained and no

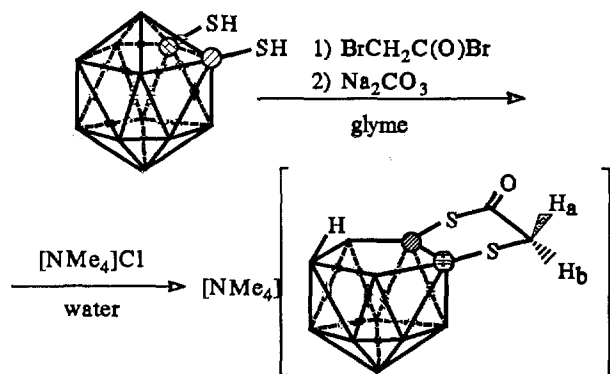


Fig. 1. Synthesis of [NMe₄][L₁], **1**.

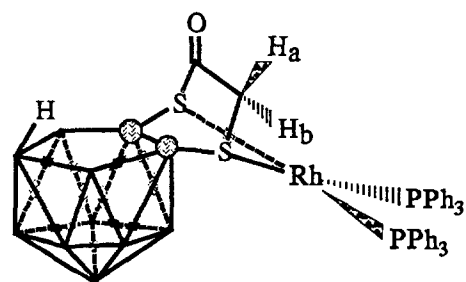


Fig. 2. Proposed structure for [Rh(L₁)(PPh₃)₂], **2**.

special care was taken in its synthesis. So, in principle, six-membered rings incorporating the moiety [*exo*-S₂-C₂B₉H₁₀]⁻ seem to be favored [22]. The ¹H NMR chemical shift difference between H_α and H_β in SCH_αH_βC(O)S support the cycle formation. The cycle rigidity and the presence of the open face in the molecule produces a differentiation of both proton atoms [23] which could not be accounted for in the case of a polymer. Furthermore, the nature of the complexes produced also supports this cycle formation. In forming L₁ the thioester group is produced readily while the thioether requires the addition of base. This was proved by carrying out the reaction in its absence, in which case only the thioester was formed.

Ligand L₁ is unique, in the sense that it has a negative charge and contains two distinct sulfur atoms, one a thioether and the second a thioester, in an ideal manner to act as a chelating group. The cluster rigidity forces the two sulfur atoms to be in an eclipsed conformation; so, in the case of the ligand acting as a chelating agent via the sulfur atoms, the metal would be placed syn or anti with regard to the open face, most probably the latter according to previous data with the above-mentioned [7,8-μ-SCH₂CH₂S-7,8-C₂B₉H₁₀]⁻. Besides, the sp² nature of the C(O) group fixes the SC(O)CH₂S moiety, too. Consequently, the mobility of this cycle would be highly restricted, only allowed in the dihedral angle defined by Cc-S-CH₂.

Ligand L₁ has different ways of bonding to metal. In addition to the η⁵ and *exo*-nido coordination, the sulfur atoms provide another alternative [24]. Ligand L₁ could provide, to the best of our knowledge, the first example of an S(thioether)S(thioester) chelating group in the literature (some mercapto thioesters have been reported, e.g. see Ref. [25]); however, it could also coordinate as an *exo*-monothioether carborane, supported by one or two agostic B-H → M bonds. To know how it would react to metal ions we planned the reaction with monovalent and divalent metal complexes.

The reaction of **1** with RhCl(PPh₃)₃ in ethanol produced complex **2** of formula [Rh(L₁)(PPh₃)₂]. The proposed structure is indicated in Fig. 2.

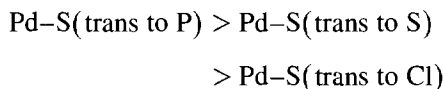
One indication of the intervening SC(O) group has been the IR frequency shift from 1655 cm⁻¹ in **1** to 1756 cm⁻¹ in **2**. In the complex the C(O) group has

acquired more double bond character, hence it is more independent of the *S*. The possibility of the $-\text{SC}(\text{O})\text{CH}_2\text{S}-$ behaving only as a monodentate thioether is excluded because no $\text{B}-\text{H} \rightarrow \text{Rh}$ resonances have been found in the ^1H NMR, a requisite for *exo*-monothioether carboranes bonded to Rh. The η^5 coordination is overruled by the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum which keeps many resemblances to carborane **1**.

The anionic charge of L_1 is very suitable for Rh(I). Now how would L_1 react with an M(II) ion? The reaction of **1** with $\text{PdCl}_2(\text{PPh}_3)_2$ in ethanol yielded a red solid **3**. The IR showed a $\text{C}=\text{O}$ frequency shift from 1655 cm^{-1} in **1** to 1730 cm^{-1} in **3**. Though a smaller shift than in **2** had been observed, a similar ligand behavior in **3** could, a priori, be postulated. However, and contrarily to **2**, the ^1H NMR displayed resonances attributable to an $-\text{OCH}_2\text{CH}_3$ fragment. The $^{11}\text{B}\{^1\text{H}\}$ NMR was similar to that of **1**, and the $^{31}\text{P}\{^1\text{H}\}$ NMR showed two non-equivalent phosphine ancillary ligands in a *cis* disposition ($^2J_{\text{P-P}} = 28.5\text{ Hz}$). The analytical data also supported the existence of an $-\text{OCH}_2\text{CH}_3$ unit. To fully understand the nature of **3** it was required to grow suitable crystals for X-ray diffraction analysis. The molecular structure is indicated in Fig. 3. The Pd(II) is coordinated, in a distorted planar arrangement, to two phosphorus atoms of two PPh_3 groups, and the carborane cage acting as a bidentate ligand. The cluster based bonds are formed by the sulfido group S(1) and the thioether group S(2). These coordination bonds are

oriented so that the Pd(II) atom occupies an anti disposition vs. the C_2B_9 open face of the carborane cage.

Neither the Pd–P nor the Pd–S bond lengths are similar. The Pd–P(1) bond (trans to S(1)) is ca. 0.04 \AA longer than the Pd–P(2) bond, and the Pd–S(2) is ca. 0.08 \AA longer than the Pd–S(1) bond. If we compare these distances with the equivalent ones in $[\text{Pd}\{7,8-\mu-(\text{S}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{S})\text{C}_2\text{B}_9\text{H}_{10}\}_2]$ [15] (**4**), $[\text{PdCl}\{7,8-\mu-(\text{SCH}_2\text{CH}_2\text{S})\text{C}_2\text{B}_9\text{H}_{10}\}(\text{PPh}_3)]$ [15] (**5**) and $[\text{PdCl}\{7\text{-SMe-8-Me-11-PPh}_2\text{-7,8-C}_2\text{B}_9\text{H}_{10}\}(\text{PPh}_3)]$ [26] (**6**), some significant features can be noticed. In **5** and **6** the Pd–P(PPh_3) bonds, being trans to thioether S, are $2.290(2)$ and $2.309(1)\text{ \AA}$ and thus they agree very well with the Pd–P(2) value of $2.300(2)\text{ \AA}$ in **3**. Thus it seems that the Pd–P(1) distance in **3** is lengthened by the increased trans influence of the sulfido group ($-\text{S}^-$) compared with that of the thioether group. The Pd–S bond lengths in the compared compounds vary from $2.296(2)$ to $2.411(2)\text{ \AA}$, and the length seems to depend on the trans substituents and on the nature of the sulfur atom. As for **3**, it was also expected that the Pd(II) would form a shorter bond to the sulfido group than to the thioether. In **3–6** the Pd–S(thioether group) bond lengths follow the order:



In **4** and **5** the group $\text{S}-\text{C}(\text{carb})-\text{C}(\text{carb})-\text{S}$ is planar, with torsion angles values of $-1(1)$ and $-0.9(7)^\circ$ respectively; however, in **3** the $\text{S}(1)-\text{C}(7)-\text{C}(8)-\text{S}(2)$ torsion angle value is $7.0(8)^\circ$. This slight non-planarity probably originates from the different nature of the S substituents. The different orientation of the thioether and sulfido groups with respect to the carborane cage is also reflected in the $\text{S}(1)-\text{C}(7)-\text{B}(3)$ and $\text{S}(2)-\text{C}(8)-\text{B}(3)$ values of $118.3(5)$ and $111.4(5)^\circ$.

The more striking point about **2** has been the $\text{S}-\text{C}(\text{O})$ bond breaking in L_1 to form a sulfido $-\text{S}^-$ and an ester group. The Pd(II) ion has induced modifications in L_1 . This is not strange in Pd chemistry, as we have recently shown with pyridine [27] derivatives. Given a possible pathway, the ligand rearranges or modifies itself to compensate the Pd(II) charge. If **1** is taken in ethanol, a transesterification process leading to a two negatively charged ligand L_2 may take place. The monoprotonated form of L_2 is $[\text{7-SH-8-SCH}_2\text{C}(\text{O})\text{OCH}_2\text{CH}_3\text{-7,8-C}_2\text{B}_9\text{H}_{10}]^-$ and is represented in Fig. 4. That the transesterification process was metal-induced was proven by refluxing **1** in ethanol in the absence of Pd for several hours, without any apparent modification of L_1 .

To know if the modification process was general in alcohol solvents, a similar reaction was conducted in MeOH and Me_2CHOH . In both cases the transesterification process took place, and complexes similar to **3**,

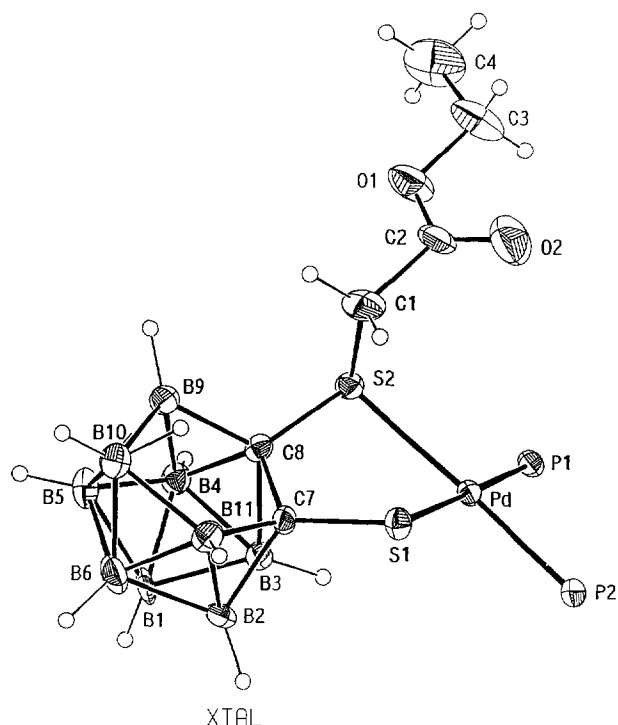


Fig. 3. Simplified ORTEP plot of $[\text{Pd}(7\text{-S,8-SCH}_2\text{C}(\text{O})\text{OCH}_2\text{CH}_3\text{-7,8-C}_2\text{B}_9\text{H}_{10})\text{(PPh}_3)_2]$ showing 30% displacement ellipsoids. Phenyl groups are omitted for clarity.

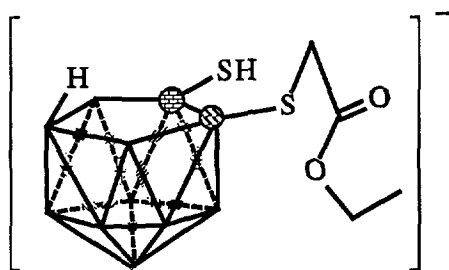


Fig. 4. Schematic view of $[HL_2]^-$.

now **7** and **8** with $-\text{OCH}_3$ and $-\text{OCH}(\text{CH}_3)_2$ groups, were obtained.

A quick, but most probably not too accurate, interpretation of the facts could be that ring loss in L_1 could be prevented depending on the charge of the metal ion; so, Rh(I), requiring only one negative charge, would maintain the ring as such, while Pd(II), requiring two negative charges, would induce ligand's alteration. We are not able, at present, to confirm the veracity of this hypothesis because our experience in dealing with L_1 with other metal ions has been quite limited. However, NMR data of the complex obtained from the reaction of **1** with $\text{AuCl}(\text{PPh}_3)_2$ in ethanol did show the existence of $-\text{OCH}_2\text{CH}_3$ resonances, too. Thus, it seems that the nature of the metal ion can be very relevant on the L_1 behavior. Owing to its apparent lability towards metal ions, we think that L_1 may be of interest in catalysis. The expected different bond strength between S(thioether)–Rh and S(thioester)–Rh could induce an extra empty position at the Rh neighborhood, so favoring insertion of reagents.

Acknowledgements

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