"Synthesis, Characterization and Reactivity of Exo-heterodisubstituted Carborane Ligands"

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Derivatives of *o*-carborane 1-R-1,2-$C_2B_{10}H_{11}$ bearing a nitrogen-containing substituent R attached to the cage carbon atom (C_c), have attracted attention as potential medicinal agents for use in boron neutron capture therapy (BNCT) and as potentially-chelating carboranyl ligand precursors.[1-10]

The synthesis and crystal structure of 1-(2'-pyridyl)-1,2-*closo*-$C_2B_{10}H_{11}$, and 1-(2'-pyridyl)-2-SH-1,2-*closo*-$C_2B_{10}H_{10}$, **1**, have been recently reported.[11] The latter is the first derivative of *o*-carborane containing a mercapto group, –SH, that has been structurally characterized.[12] This compound is a potential ligand for metal complexes requiring 6-member C3NMS chelating rings.

Our group has been concerned with the synthesis of dithioether 1,2-$(SR)_2$-1,2-*closo*-$C_2B_{10}H_{10}$,[13-16] monothioether 1-SR-2-R'-1,2-*closo*-$C_2B_{10}H_{10}$,[17] diphosphino 1,2-$(PR)_2$-1,2-*closo*-$C_2B_{10}H_{10}$,[18-23] monophosphino 1-PR_2-2-R'-1,2-*closo*-$C_2B_{10}H_{10}$[24-26] and S, P heterodisubstituted 1-PR_2-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$ compounds.[27, 28]

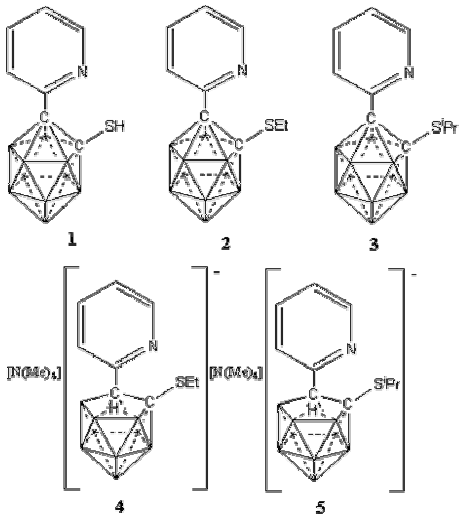


Figure 1.- Compounds **1**-**5** discussed in this study. Each naked cluster vertex represents B-H.

This paper describes the synthesis of N, S heterodisubstituted 1-(2'-pyridyl)-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$ compounds and their partial degradation which leads to [7-(2'-pyridyl)-8-SR-7,8-*nido*-$C_2B_9H_{10}]^-$ derivatives. Also, in order to know more on the influence of electron rich elements bonded to the carborane cluster we have studied the reactions of **1** with Au(I), Pd(II) and Rh(III). The different coordination requirements demanded by these metals allow to compare the role of N and S in the complexation reaction.

Results and Discussion

Reactivity of 1-(2'-pyridyl)-2-SH-1,2-*closo*-$C_2B_{10}H_{10}$ species.

1.- Synthesis and characterization of 1-(2'-pyridyl)-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$ (R= alkyl group) species.

Starting from **1** the synthesis of *closo* C_c-heterodisubstituted 1-(2'-pyridyl)-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$ (R= Et, **2** ^{i}Pr, **3**) compounds has been achieved after deprotonation with KOH in ethanol followed by alkylation with the appropriate alkyl bromide (R= Et, ^{i}Pr) in 81 and 88% yields respectively (see Figure 2 A). These compounds contain two coordinating sites, C_c-C-N and C_c-SR, in the same carborane cluster. This is the first time that bidentate ligands with these functional groups are reported and it is the result of advances in the development of easy routes to alkylate the mercapto group in carborane chemistry. The existence of one available C_c-SH unit has allowed the introduction of a second and different functional group. These ligands complement the 1,2-$(SR)_2$-1,2-*closo*-$C_2B_{10}H_{10}$[29], 1,2-$(PR_2)_2$-1,2-*closo*-$C_2B_{10}H_{10}$[30] and 1-PPh_2-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$[28] series and allows to study the reactivity of chelating S,N heterodisubstituted [1-(2'-pyridyl)-2-S-1,2-*closo*-$C_2B_{10}H_{10}]^-$ with metal complexes.

Compounds **2** and **3** have been characterized by elemental analyses, IR and NMR techniques. The IR spectra show the typical ν(B-H) absorption at frequencies above 2550 cm^{-1}, characteristic for 1-R-2-R'-1,2-*closo*-$C_2B_{10}H_{10}$ derivatives.[31] The $^{11}B\{^1H\}$-NMR of **2** and **3** present spectral data in the typical -2.0/-10.5 ppm range for a *closo*-C_2B_{10} cluster. This is even more compressed than the spectral range observed for 1-SR-1,2-*closo*-$C_2B_{10}H_{11}$ and 1-PPh_2-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$ compounds that appear in the range 0/-10.5 ppm and -1/-13 ppm, respectively. The nature of the R alkyl group does not greatly influence the $^{11}B\{^1H\}$-NMR spectrum. In this way a 1:1:2:2:4 pattern for **2** and 1:1:2:6 pattern for **3** are observed as it was expected for non-symmetrical carborane derivatives.

2.- Partial Degradation or Deboronation Reaction of 1-(2'-pyridyl)-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$ (R= Et, ^{i}Pr) species.

Partial degradation or the formal removal of a B^+ from 1-(2'-pyridyl)-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$ derivatives to yield the corresponding anionic species [7-(2'-pyridyl)-8-SEt-7,8-*nido*-$C_2B_9H_{10}]^-$ (**4**) and [7-(2'-pyridyl)-8-S^{i}Pr-7,8-*nido*-$C_2B_9H_{10}]^-$ (**5**) was readily accomplished using KOH in ethanol (see Figure 2B).[32-34] These species were isolated as the tetramethylammonium salts in stoichiometric but not in isomeric purity (see Figure 3). Chirality is the consequence of unequivalent substitution on both cluster carbon atoms. These heterosubstituted compounds show a similar reactivity towards EtO^- nucleophilic attack than this reported for 1-SR-1,2-*closo*-$C_2B_{10}H_{11}$. The existence of the pyridyl group has not affected the stability of the C_c-S bond towards a strong nucleophile such as EtO^-.

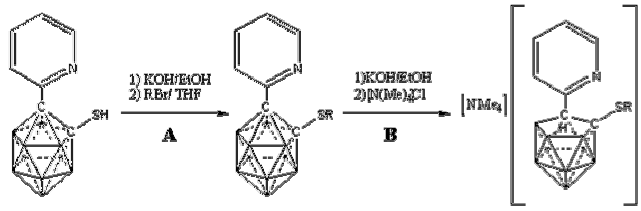


Figure 2.- Synthetic pathway to *closo*-heterodisubstituted *o*-carborane derivatives, **A**, and their partial degradation, **B**.

The *nido* species have been characterized by elemental analyses, MALDI-TOF-MS, IR and NMR techniques. For both **4** and **5**, strong IR ν (B-H) resonances near 2520 cm^{-1}, in agreement with a *nido* $[C_2B_9]^-$ cluster, have been observed.[31] The $^{11}B\{^1H\}$-NMR signals for **4** and **5** appear in the range -8/-36 ppm with patterns 2:1:1:2:1:1:1 and 2:1:2:1:1:1:1 for **4** and **5**, respectively, that are in agreement with an asymmetric *nido* $[C_2B_9H_{10}]^-$ cluster. The X-ray crystallographic analysis of $[NMe_4][7\text{-}(2'\text{-pyridyl})\text{-}8\text{-}S^iPr\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]$ confirms the above indicated data (see Figure 4).

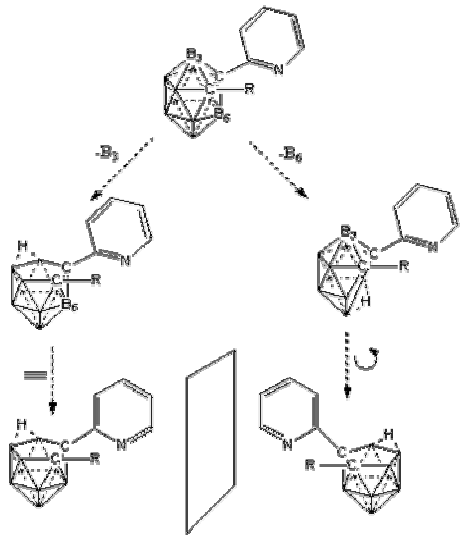


Figure 3.- Isomers of the anionic compounds.

Albeit the different substituents on cluster carbon atoms, the molecular structure of $[NMe_4]$[**5**] reminds very much this for $[NMe_4][7\text{-}PPh_2\text{-}8\text{-}S^iPr\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]$[35]. The S-$C_c$ bond lengths are comparable in both compounds despite that large discrepancies are found in the non-common substituent. In this regard, the C_c-pyridinyl distance in $[NMe_4][7\text{-}(2'\text{-pyridyl})\text{-}8\text{-}S^iPr\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]$, (1.511Å) is appreciably smaller than the C_c-P (1.857 Å) in $[NMe_4][7\text{-}PPh_2\text{-}8\text{-}S^iPr\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-$.

3.- Metal complexation studies of 1-(2'-pyridyl)-2-SH-1,2-*closo*-$C_2B_{10}H_{10}$.

The chelating properties of 1,2-$(PR_2)_2$-1,2-*closo*-$C_2B_{10}H_{10}$,[30, 36-50] 1,2-$(SR)_2$-1,2-*closo*- $C_2B_{10}H_{10}$,[29] 1-PPh_2-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$ and 1-PPh_2-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$[51] have already been studied. As we had demonstrated earlier[52, 53] the reaction of *exo*-heterodisubstituted carborane derivatives with transition metal complexes, $[MCl(PPh_3)_n]$ in methanol or ethanol, leads to deboronation of the *closo* cluster producing an 11-vertex monoanionic *nido* species.[27] A nucleophilic attack by ethanol to the more positive boron atoms, either B(3) or B(6), takes place producing a mononegative chelating ligand as a result of one Boron atom removal. Therefore special care, avoiding possible nucleophiles, needs to be taken in attempting the synthesis of transition metal complexes in which the *closo* C_2B_{10} fragment is retained. Preserving the closo nature of the cluster is not a simple task[44, 48, 53] but [1-(2'-pyridyl)-2-S-1,2-*closo*-$C_2B_{10}H_{10}]^-$ offered a unique chance to study a S^-/pyridine 6-member chelating bidentate ligand. To this aim coordination was addressed towards transition metals Pd(II), Rh(III), Au(I) with different coordinating site demands.

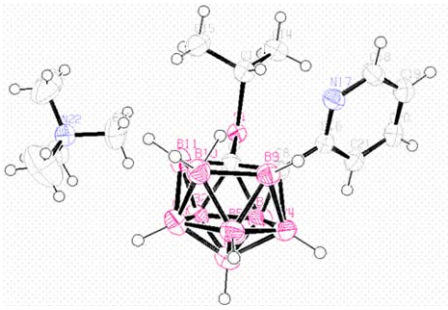
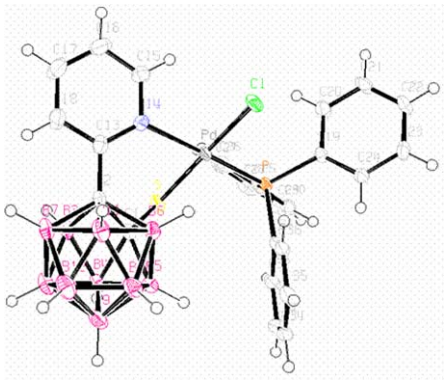


Figure 4.- ORTEP plot of $[NMe_4][7\text{-}(2'\text{-pyridyl})\text{-}8\text{-}S^iPr\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]$, $[NMe_4]$[**5**] .

Diethylether was the solvent of choice to avoid competing reactions caused by nucleophiles. The requirement for the absence of any nucleophile was even applied in the purification process. These restrictions were applied in the synthesis of $[PdCl(1\text{-}(2'\text{-pyridyl})\text{-}2\text{-}S\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10})(PPh_3)]$ (**6**); $[Rh(1\text{-}(2'\text{-pyridyl})\text{-}2\text{-}S\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10})(PPh_3)_2]$ (**7**) and $[Au\ (1\text{-}(2'\text{-pyridyl})\text{-}2\text{-}S\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10})(PPh_3)]$ (**8**). The syntheses of these complexes was achieved by reacting $[RhCl(PPh_3)_3]$, $[PdCl_2(PPh_3)_2]$ or $[AuClPPh_3]$ with the "in situ" prepared $[1\text{-}(2'\text{-pyridyl})\text{-}2\text{-}S\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}]^-$ in diethyl ether.

Figure 5.- ORTEP plot of [PdCl{1-(2'-pyridyl)-2-S-1,2-*closo*-



$C_2B_{10}H_{10}\}(PPh_3)]$ (**6**).

The IR spectra of **6**-**8** have shown ν(B-H) resonances near 2560 cm^{-1} that agree with a retention of the *closo* structure in the complexes. The ^{11}B-NMR spectrum in the range -1.9/-13.3 ppm points to the same conclusion, with a pattern 2:2:2:2:2 for **6**, 1:1:2:2:2:2 for **7** and 1:4:5 for **8**.

Unambiguous determination of the molecular structures of **6** and **8**, was possible after good crystals of these complexes were obtained from acetone/*n*-hexane and acetone/chloroform, respectively. Perspective views of the complex units are presented in Figs. 5 and 6. The common moieties of compounds **6** and **8** are very similar. In **6** the carborane cage is co-ordinated bidentately through N and S atoms to the Pd(II) ion, and the Cl ion and the PPh_3 group in *cis* positions complete the distorted square-planar co-ordination around the metal. The X-ray analysis of **8**, shown in Figure 6, clearly confirmed the *closo*

nature of the resulting gold complex and the ligand's monodentate behaviour toward Au(I) with no participation of the pyridyl group in bonding.

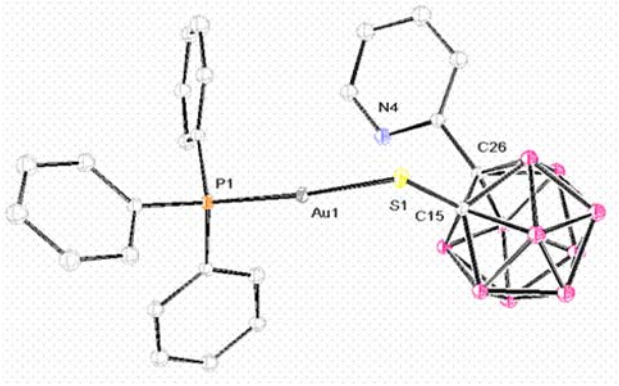


Figure 6.- ORTEP plot of [AuCl{1-(2'-pyridyl)-2-S-1,2-*closo*-$C_2B_{10}H_{10}$}(PPh_3)] (**8**).

Comparison of configuration of the carborane ligand in [PdCl(1-(2'-pyridyl)-2-S-1,2-$C_2B_{10}H_{10}$)(PPh_3)] with the free (1-(2'-pyridyl)-2-SH-1,2-$C_2B_{10}H_{10}$) ligand reveals noticeable differences. For the free ligand the N-Cpyr-C1-C2 torsion angle is 96.41º.[12] Coordination of the ligand to Pd (II) changes orientation of the pyridyl group which is coplanar with the cluster; the torsion angle is -44.12º. In addition, due to coordination, the C1-C2 distance shortens from 1.730(3) Å in the free ligand to 1.706 Å in the complex.

Conclusions

The synthesis of *closo* and *nido* C_c heterodisubstituted 1-(2'-pyridyl)-2-SR-1,2-$C_2B_{10}H_{10}$ (R= Et, ^{i}Pr) and [7-(2'-pyridyl)-8-SR-7,8-$C_2B_9H_{10}$]$^-$ (R= Et, ^{i}Pr) derivatives has been conducted. They contain the C_c-C_5H_4N and C_c-S bonds in the same carborane cluster. The heterosubstituted 1-(2'-pyridyl)-2-SR-1,2-*closo*-$C_2B_{10}H_{10}$ ligands are able to coordinate to metals producing pure samples of complexes with *closo* cluster retention by using dry non-nucleophilic solvents to perform the reaction. The two coordinating moieties C_c-C_5H_4N and C_c-S are not equivalent, as has been demonstrated upon reaction to Au(I), where the C_c-S moiety is more reactive. With metals requiring a higher coordination number than one, as Pd(II) and Rh(I), both C_c-C_5H_4N and C_c-S moieties coordinate to metal.

Experimental Section

Materials and Methods. 1-pyridyl-2-SH-1,2-*closo*-carborane was synthesized according to the literature.[12] A 1.6 M solution of *n*-butyl lithium in *n*-hexane was used as purchased. [$RhCl(PPh_3)_3$],[54] [$PdCl_2(PPh_3)_2$],[55] [$AuClPPh_3$][56] were synthesized as described elsewhere. All organic compounds and inorganic salts were analytical reagent grade and were used as received. The solvents were reagent grade. All reactions were carried out under a dinitrogen atmosphere using standard Schlenck techniques. Microanalyses were performed on a Carlo Erba EA1108 microanalyzer. The mass spectra were recorded in the negative ion mode using a Bruker Biflex MALDI-TOF-MS [N_2 laser; λ_{exc} 337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)]. IR spectra were obtained as KBr pellets on a Nicolet 710-FT spectrophotometer. The ^{1}H-NMR (300.0 MHz), ^{11}B-NMR (96.3 MHz), ^{13}C{^{1}H}-NMR (75.0 MHz) and ^{31}P{^{1}H}-NMR (121.5 MHz) spectra were recorded on a Bruker ARX 300 spectrometer. Chemical Shift values for ^{1}H-NMR, ^{13}C{^{1}H}-NMR, ^{11}B-NMR and ^{31}P{^{1}H}-NMR were referenced relative to external $SiMe_4$, $BF_3.OEt_2$ and 85% H_3PO_4 respectively. Chemical shifts are reported in units of parts per million, and all coupling constants are reported in Hz.

Synthesis of 1-(2'-pyridyl)-2-SEt-1,2-*closo*-$C_2B_{10}H_{10}$ (2)

To a two necked round bottom flask (50 ml), containing a solution of KOH (25 mg, 0.45 mmol) in deoxygenated ethanol (10 ml), was added (1-C_5H_4N-2-SH-1,2-*closo*-$C_2B_{10}H_{10}$) (115 mg, 0.45 mmol). After stirring for 1 hour at room temperature the solvent was evaporated and the residue redissolved in dry THF (10ml). Bromoethane (0.013 ml, 0.90 mmol) was added and the mixture was refluxed for two hours. All volatiles were evaporated in vacuum, and the residue was treated with diethyl ether (10 ml) and water 10ml, the organic layer was separated and washed with KOH (3x10 ml, 0.5N), dried over anhydrous $MgSO_4$ and evaporated in vacuum resulting a yellow solid. Yield: 112 mg (88%). Anal. Calcd for $C_9H_{19}B_{10}NS$: N, 4.97 %; C, 38.41 %; H, 6.8 %; S, 11.4 %; Found: N, 4.95 %; C, 38.20 %; H, 6.50 %; S, 11.15 %. IR: ν[cm^{-1}]= 2965, 2924 (C_{aryl}-H/ C_{alkyl}-H); 2569 (B-H); 2364, 2338 (S-R); 1584 (C=N); 1463, 1433 (C-N); 1081, 1014 (C-N-C); 811 (CH_3); 774, 740 (C_{aryl}-H). ^{1}H{^{11}B}-RMN (CD_3COCD_3): δ= 8.67 (d, ^{3}J(H,H)= 4.7, C_{pyr}-**H$_6$**, 1H), 7.95 (ddd, ^{3}J(H,H)=7.6, ^{4}J(H,H)=7.7, ^{5}J(H,H)=1.5, C_{pyr}-**H$_4$**, 1H), 7.89 (ddd, ^{3}J(H,H)= 7.7, ^{4}J(H,H)= 4.7, C_{pyr}-**H$_5$**, 1H), 7.5 (ddd, ^{3}J(H,H)= 7.2, ^{4}J(H,H)=4.6, ^{5}J(H,H)= 0.6, C_{pyr}-**H$_3$**, 1H), 2.77 (q, ^{3}J(H,H)= 7.5, S-C**H$_2$**CH_3, 2H), 3.00 (s, B-**H**, 1H), 2.53 (s, B-**H**, 1H), 2.45 (s, B-**H**, 4H), 2.37 (s, B-**H**, 2H), 2.22 (s, B-**H**, 2H), 0.90 (t, ^{3}J(H,H)= 7.5, C**H$_3$**, 3H).^{11}B-RMN (CD_3COCD_3): δ= -2.0 (d, ^{1}J(B,H)= 196, 1B), -2.9 (d, ^{1}J(B,H)= 144, 1B), -7.6 (d, ^{1}J(B,H)= 172, 2B), -9.1 (2B), -9.8 (d, ^{1}J(B,H)= 132, 4B). ^{13}C{^{1}H}-RMN (CD_3COCD_3): δ= 148.8 (s, **C**$_{2pyr}$), 148.1 (s, **C**$_{6pyr}$), 139.1 (s, **C**$_{4pyr}$), 125.5 (s, **C**$_{3pyr}$), 124.9 (s, **C**$_{5pyr}$), 87.51 (s, **C**$_c$-Py), 85.2 (s, **C**$_c$-SEt), 30.0 (s, **C**$_{CH2}$), 11.9 (s, **C**$_{CH3}$).

Synthesis of 1-(2'-pyridyl)-2-S^{i}Pr-1,2-*closo*-$C_2B_{10}H_{10}$ (3)

In the same manner as the compound **2** was added solution of KOH (6 mg, 0.11 mmol) in deoxygenated ethanol (5 ml), was added (1-C_5H_4N-2-SH-1,2-*closo*-$C_2B_{10}H_{10}$) (28 mg, 0.11 mmol). After stirring for 1 hour at room temperature the solvent was evaporated and the residue redissolved in dry THF (5ml). Bromoisopropyl (0.02 ml, 0.22 mmol) was added and the mixture was refluxed for two hours. All volatiles were evaporated in vacuum, and the residue was treated with diethyl ether (10 ml) and water 10ml, the organic layer was separated and washed with KOH (3x10 ml, 0.5N), dried over anhydrous $MgSO_4$ and evaporated in vacuum resulting a yellow oil.. Yield: 29 mg (81%). Anal. Calcd for $C_{10}H_{21}B_9NS$: N, 4.92 %; C, 42.20 %; H, 7.44 %; S, 11.27 %. Found: N, 4.64 %; C, 42.2 %; H, 7.70 %; S, 10.91 %. IR: ν[cm^{-1}]= 2932 (C_{aryl}-H/ C_{alkyl}-H); 2577 (B-H); 2352, 2361 (S-R); 1464, 1434 (C-N); 1081, 1012 (C-N-C). ^{1}H{^{11}B}-RMN ($CDCl_3$): δ= 8.65 (d, ^{3}J(H,H)= 4.5, C_{pyr}-**H**, 1H), 7.75 (m, C_{pyr}-**H**, 2H), 7.39 (ddd, ^{3}J(H,H)= 5.3, ^{4}J(H,H)= 1.8, C_{pyr}-**H**, 1H), 3.25 (h, ^{3}J(H,H)= 6.9, CH, 1H), 2.95 (s, B-**H**, 2H), 2.57 (s, B-**H**, 2H), 2.47 (s, B-**H**, 4H), 2.27 (s, B-**H**, 2H), 1.12 (d, ^{3}J(H,H)= 6.9, CH_3, 6H). ^{11}B-RMN ($CDCl_3$): δ= -2.4 (d, ^{1}J(B,H)= 156, 1B), -3.6 (d, ^{1}J(B,H)= 138, 1B), -8.5 (d, ^{1}J(B,H)= 159, 2B), -10.4 (d, ^{1}J(B,H)= 126, 6B). ^{13}C{^{1}H}-RMN ($CDCl_3$): δ= 149.1 (s, **C**$_{pyr}$), 136.9 (s, **C**$_{pyr}$), 126.1 (s, **C**$_{pyr}$), 124.7 (s, **C**$_{pyr}$), 121.5 (s, **C**$_{pyr}$), 87.5 (s, **C**$_c$-Py), 85.7 (s, **C**$_c$-S^{i}Pr), 42.6 (s, S-**C**H), 23.8 (s, CH-**C**H_3).

Synthesis of [NMe_4][7-(2'-pyridyl)-8-SEt-7,8-*nido*-$C_2B_9H_{10}$], [NMe_4][4]

In a Schlenck flask containing a solution of KOH (70 mg, 1.2 mmol) in deoxygenated ethanol (5 ml), was added 1-(2'-C_5H_4N)-2-SEt-1,2-*closo*-$C_2B_{10}H_{10}$ (71 mg, 0.25 mmol). The mixture was refluxed for 3 hours, cooled down to room temperature and evaporated. The residue was dissolved in water (2 ml) and treated with the solution of tetramethylammonium chloride. The white solid was filtered off and washed with water and diethyl ether. Yield: (61 mg, 0.17 mmol), (70 %). Anal. Calcd for $C_{13}H_{31}B_9N_2S$: N, 8.13 %; C, 45.29 %; H, 9.06 %; S, 9.30 %. Found: N, 8.01 %; C, 45.41 %; H,9.17 %, S, 9.51 %. IR: ν[cm^{-1}]= 2937 (C_{aryl}-H); 2534 (B-H), 2362, (S-R); 1472

(C-N); 1026 (C-N-C). ^{1}H-{^{11}B}RMN (CD_3COCD_3): δ= 8.37 (d, ^{3}J(H,H)= 4, C_{pyr}-**H**, 1H), 7.48 (t, ^{3}J(H,H)= 8, ^{4}J(H,H)= 2, C_{pyr}-**H**, 1H), 7.26 (d, ^{3}J(H,H)= 8, C_{pyr}-**H**, 1H), 7.00 (t, ^{3}J(H,H)= 6, ^{4}J(H,H)= 2, C_{pyr}-**H**, 1H), 3.44 (s, N(C**H$_3$)$_4$**, 12H), 2.92 (q, ^{3}J(H,H)= 7.5, C**H$_2$**-CH_3, 1H), 2.65 (q, ^{3}J(H,H)= 7.5, C**H$_2$**-CH_3, 1H), 2.47 (s, B-**H**, 1H), 2.23 (s, B-**H**, 1H), 2.20 (s, B-**H**, 1H), 1.73 (s, B-**H**, 2H), 1.48 (s, B-**H**, 1H), 1.38 (s, B-**H**, 1H), 0.83 (t, ^{3}J(H,H)= 7, CH_2-C**H$_3$**, 3H), 0.73 (s, B-**H**, 1H), 0.24 (s, B-**H**, 1H), -2.05 (s, B**H**B, 1H). ^{11}B-RMN (CD_3COCD_3): δ= -7.1 (d, ^{1}J(B,H)= 138, 2B), -12.1 (d, ^{1}J(B,H)=158, 1B), -15.9 (d, ^{1}J(B,H)=142, 3B), -18.48 (d, ^{1}J(B,H)=145, 1B), -32.6 (dd, ^{1}J(B,H)=132, ^{1}J(B,H)=29, B(10)), -35.1 (d, ^{1}J(B,H)=138, B(1)). ^{13}C{^{1}H}-RMN (CD_3COCD_3): δ= 155.9 (s, **C$_{py}$**), 147.4 (s, **C$_{pyr}$**), 135.2 (s, **C$_{4pyr}$**), 125.2 (s, **C$_{3pyr}$**), 120.4 (s, **C$_{5pyr}$**), 62.7 (s, **C$_c$**), 55.1 (s, N(**C**H$_3$)$_4$), 22.2 (s, **C**H$_2$), 13.4 (s, **C**H$_3$). MALDI-TOF-MS: 270.36 (47.5%, M), 208.27 (100%, M-SEt).

Synthesis of [NMe$_4$][7-(2'-pyridyl)-8-S^{i}Pr-7,8-*nido*-$C_2B_9H_{10}$], [NMe$_4$][5]

In a Schlenck flask containing a solution of KOH (11 mg, 0.20 mmol) in deoxygenated ethanol (5 ml), was added 1-(2'-Pyr)-2-S^{i}Pr-1,2-*closo*-$C_2B_{10}H_{10}$ (12 mg, 0.04 mmol). The mixture was refluxed for 3 hours, cooled down to room temperature and evaporated. The residue was dissolved in water (2 ml) and treated with the solution of tetramethylammonium chloride. The white solid was filtered off and washed with water and diethyl ether. Yield: 9 mg, 0.025 mmol, (64%). Anal. Calcd for $C_{14}H_{32}B_9N_2S$: N, 7.83 %; C, 47.00 %; H, 9.02 %, S, 8.96%. Found: N, 7.65 %; C, 47.12 %; H 9.14 %, S, 8.80 %. IR: ν[cm^{-1}]= 3035, 2970, 2922, 2866 (C_{aryl}-H); 2528 (B -H), 1587 (C=N); 1481, 1471 (C_{alkyl}). ^{1}H-{^{11}B}RMN (CD_3COCD_3): δ= 8.37 (d, ^{3}J(H,H)= 4, C_{pyr}-**H**, 1H), 7.49 (td, ^{3}J(H,H)= 8, ^{4}J(H,H)= 2, C_{pyr}-**H**, 1H), 7.31 (d, ^{3}J(H,H)= 8, C_{pyr}-**H**, 1H), 7.01 (td, ^{3}J(H,H)= 6, ^{4}J(H,H)= 2, C_{pyr}-**H**, 1H), 3.44 (s, N(C**H$_3$)$_4$**, 12H), 3.07 (h, ^{3}J(H,H)= 7, C**H**, 1H), 2.51 (s, B-**H**, 1H), 2.28 (s, B-**H**, 1H), 1.65 (s, B-**H**, 1H), 1.50 (s, B-**H**, 1H), 1.29 (s, B-**H**, 1H), 1.03 (d, ^{3}J(H,H)= 7, CH-C**H$_3$**, 3H), 0.85 (d, ^{3}J(H,H)= 7, CH-C**H$_3$**, 3H), 0.75 (s, B-**H**, 1H), 0.24 (s, B-**H**, 1H), -2.04 (s, B**H**B, 1H). ^{11}B-RMN (CD_3COCD_3): δ= -8.3 (d, ^{1}J(B,H)= 137, 2B), -13.4 (d, ^{1}J(B,H)= 154, 1B), -15.7 (d, ^{1}J(B,H)= 152, 1B), -17.7 (d, ^{1}J(B,H)= 131, 2B), -18.8 (d, ^{1}J(B,H)= 162 ,1B)-33.6 (d, ^{1}J(B,H)= 169, 1B), -36.0 (d, ^{1}J(B-H)=141, 1B). ^{13}C{^{1}H}-RMN (CD_3COCD_3): δ= 161.2 (s,**C$_{2py}$**), 147.4 (s, **C$_{6pyr}$**), 134.4 (s, **C$_{4pyr}$**), 125.9 (s, **C$_{3pyr}$**), 120.3 (s, **C$_{5pyr}$**), 69.8 (s, **C$_c$**), 55.1 (s, N(**C**H$_3$)$_4$), 38.7 (s, **C**H), 24.4 (s, **C**H$_3$), 23.1 (s, **C**H$_3$). MALDI-TOF-MS: 284.4 (100%, M), 238.3 (75.4%, M-^{i}Pr), 208.3 (55.2%, M-S^{i}Pr).

Synthesis of [PdCl(1-(2'-pyridyl)-2-S-1,2-*closo*-$C_2B_{10}H_{10}$)(PPh$_3$)] (6)

In a Schlenck flask containing a solution of 1-(2'-C_5H_4N)-1,2-*closo*-$C_2B_{10}H_{11}$ (41 mg, 0.18 mmol) in dried diethyl ether (5 ml), was added *n*-BuLi (0.12 ml, 0.18 mmol) at 0ºC and keeping stirring 30 minutes and 30 minutes at room temperature. S powder was added (6mg, 0.18 mmol) at 0ºC during 10 minutes and keep stirring 30 minutes at 0ºC and 30 minutes at r.t.. [$PdCl_2(PPh_3)_2$] (129mg, 0.18mmol) was added and stirred during 1h at r.t. A brown solid precipitated that no contain boron. The orange solution was filtered and dried. Yield: (97mg, 80%). Anal. Calcd for $C_{25}H_{29}B_{10}NSClPPd$: N, 2.13%; C, 45.74%; H, 4.45%; S, 4.88%. Found: N, 2.03 %; C, 45.88 %; H, 4.56 %, S, 5.01 %. IR: ν[cm^{-1}]= 2930 (C_{aryl}-H); 2607, 2592,2567 (B -H), 1433, 1101, 1018, 690, 515 (PPh$_3$). ^{1}H-{^{11}B}-NMR ($CDCl_3$): δ= 8.41 (s, C_{pyr}-**H**, 1H), 7.71-7.32 (m, 18H), 2.48-2.23 (m, B-**H**). ^{11}B-RMN ($CDCl_3$): δ= 0.4 (d, ^{1}J(B,H)= 158, 1B), -0.3 (d, ^{1}J(B,H)= 158, 1B), -4.8 (d, ^{1}J(B,H)= 140, 2B), -7.0 (d, ^{1}J(B,H)= 123, 2B), -7.8 (d, ^{1}J(B,H)= 191, 2B), -9.6 (d, ^{1}J(B,H)= 174, 2B) .^{13}C{^{1}H}-RMN ($CDCl_3$): δ= 150.9 (s, **C$_{pyr}$**), 148.7 (s, **C$_{pyr}$**), 137.4 (s, **C$_{pyr}$**), 132.2 (d, ^{1}J(C,P)= 11, **C$_{PPh3}$**), 131.6 (s, **C$_{PPh3}$**), 128.5 (d, ^{1}J(C,P)= 12.4, **C$_{PPh3}$**), 124.3 (s, **C$_{pyr}$**), 121.5 (s, **C$_{pyr}$**), 75.3 (s, **C$_c$**), 65.9 (s, **C$_c$**).^{31}P{^{1}H}-NMR ($CDCl_3$): δ= 44.7 (s, PPh$_3$).

Synthesis of [Rh(1-(2'-pyridyl)-2-S-1,2-*closo*-$C_2B_{10}H_{10}$)(PPh$_3$)$_2$] (7)

In a Schlenck flask containing a solution of 1-(2'-C_5H_4N)-1,2-*closo*-$C_2B_{10}H_{11}$ (37 mg, 0.16 mmol) in dried diethyl ether (4 ml), was added *n*-BuLi (0.1 ml, 0.16 mmol) at 0ºC and keeping stirring 30 minutes and 30 minutes at room temperature. S powder was added (5mg, 0.16 mmol) at 0ºC during 10 minutes and keep stirring 30 minutes at 0ºC and 30 minutes at r.t.. [$RhCl(PPh_3)_3$] (152mg, 0.16mmol) was added and stirred during 20h at r.t. The solution was concentrated and added hexane, and a brown solid precipitated without boron. The solution was dried and a brown solid was obtained. Yield: (54mg, 50%). Anal. Calcd for $C_{43}H_{44}B_{10}NSRhP_2$: N, 1.59 %; C, 58.70 %; H, 5.04 %; S, 3.64 %. Found: N, 1.70 %; C, 58.66 %; H, 5.33 %, S, 3.73 %. IR: ν[cm^{-1}]= 3059, 2962 (C_{aryl}-H); 2569 (B -H), 1435, 1118, 692, 542 (PPh$_3$). ^{1}H-{^{11}B }-NMR ($CDCl_3$): δ= 8.39 (d, ^{3}J(H,H)= 4, C_{pyr}-**H**, 1H), 7.74-7.1 (m, 30H), 2.46 (s, B-**H**, 1H), 2.33 (s, B-**H**, 8H), 2.25 (s, B-**H**, 1H). ^{11}B-RMN ($CDCl_3$): δ= -2.5 (d, ^{1}J(B,H)= 147, 1B), -3.1 (d, ^{1}J(B,H)= 151, 1B), -7.6 (d, ^{1}J(B,H)= 151, 2B), -9.9 (d, ^{1}J(B,H)= 129, 2B), -10.6 (d, ^{1}J(B,H)= 182, 2B), -12.5 (d, ^{1}J(B,H)= 160, 2B). ^{13}C{^{1}H}-RMN ($CDCl_3$): δ= 148.7 (s, **C$_{py}$**), 137.4 (s, **C$_{pyr}$**), 132.9 (s, **C$_{pyr}$**), 131.6 (s, **C$_{Ph}$**), 128.6 (s, **C$_{Ph}$**), 124.3 (s, **C$_{pyr}$**), 121.4 (s, **C$_{pyr}$**). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ= 44.7 (s, PPh$_3$), 30.93 (s, PPh$_3$).

Synthesis of [Au (1-(2'-pyridyl)-2-S-1,2-*closo*-$C_2B_{10}H_{10}$)(PPh$_3$)] (8)

In a Schlenck flask containing a solution of 1-(2'-C_5H_4N)-1,2-*closo*-$C_2B_{10}H_{11}$ (37 mg, 0.16 mmol) in dried diethyl ether (4 ml), was added *n*-BuLi (0.1 ml, 0.16 mmol) at 0ºC and keeping stirring 30 minutes and 30 minutes at room temperature. S powder was added (5mg, 0.16 mmol) at 0ºC during 10 minutes and keep stirring 30 minutes at 0ºC and 30 minutes at r.t.. [AuClPPh$_3$] (78mg, 0.16 mmol) was added and stirred during 2h at r.t. A brown solid was observed and fileterd off and not identified. To the organic fraction was added hexane (2 mL) and a paled brown solid precipitated and washed with hexane. Yield: (112 mg, 62 %). Anal. Calcd for $C_{25}H_{29}B_{10}AuNSP+0.1C_6H_{14}$: N, 1.86 %; C, 41.66 %; H, 4.46 %; S, 4.52 %. Found: N, 1.86 %; C, 41.73 %; H, 4.03 %, S, 3.95 %. IR: ν[cm^{-1}]= 3052 (C_{aryl}-H); 2597, 2578, 2561 (B -H), 2363 (S-R); 1583 (C=N); 1434, 1101, 752, 690, 540 (PPh$_3$). ^{1}H-{^{11}B}-NMR ($CDCl_3$): δ= 8.40 (d, ^{3}J(H,H)= 3, C_{pyr}-**H$_6$**, 1H), 7.73 (d, ^{3}J(H,H)= 8, C_{pyr}-**H$_3$**, 1H), 7.59 (t, ^{3}J(H,H)= 8, C_{pyr}-**H$_4$**, 1H), 7.42 (m, P**Ph**$_3$, 15H), 7.19 (m, C_{pyr}-**H**, 1H), 3.49 (s, B-**H**, 2H), 2.88 (s, B-**H**, 2H), 2.45 (s, B-**H**, 3H), 2.22 (s, B-**H**, 3H). ^{11}B-RMN ($CDCl_3$): δ= -1.9 (d, ^{1}J(B,H)= 152, 1B), -5.9 (d, ^{1}J(B,H)= 134, 4B), -9.6 (d, ^{1}J(B,H)= 153, 5B). ^{13}C{^{1}H}-RMN ($CDCl_3$): δ= 150.34 (s, **C$_{py}$**), 149.11 (s, **C$_{pyr}$**), 136.50 (s, **C$_{pyr}$**), 134.13 (d, ^{1}J(C,P)= 14, **C$_{Ph}$**), 131.90 (s, **C$_{Ph}$**), 129.31 (d, ^{1}J(C,P)= 11, **C$_{Ph}$**), 128.61 (s, **C$_{Ph}$**), 126.22 (s, **C$_{pyr}$**), 124.20 (s, **C$_{pyr}$**), 88.95 (s, **C$_c$**), 86.52 (s, **C$_c$**). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ= 38.13 (s, PPh$_3$). MALDI-TOF-MS: 251.25 (100%, M-AuPPh$_3$).

X-ray studies X-ray measurements for [NMe$_4$][7-(2'-pyridyl)-8-S^{i}Pr-7,8-*nido*-$C_2B_9H_{10}$], [$PdClPPh_2$(1-(2'-pyridyl)-2-S-1,2-*closo*-$C_2B_{10}H_{10}$], [$AuPPh_3$(1-(2'-pyridyl)-2-S-1,2-*closo*-$C_2B_{10}H_{10}$] were made on a Rigaku

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