

“Synthesis and Characterization of the [7-(2'-pyridyl)-7,8-*nido*-C₂B₉H₁₁]⁻ ligand”

A. Laromaine, F. Teixidor, C. Viñas*, R. Vespalec,^d H. Horáková,^b I. Mata,^a E. Molins^a.

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

^b Institute of Analytical Chemistry, Academy of Sciences of the Czech Republic, Veveří 97, Brno, Czech Republic

RECEIVED DATE (automatically inserted by publisher); clara@icmab.es

This paper describes the partial degradation reaction of 1-(2'-pyridyl)-1,2-*closo*-C₂B₁₀H₁₁ that leads to [7-(2'-pyridyl)-7,8-*nido*-C₂B₉H₁₁]⁻, **1**. As there are two possible sites to accommodate an extra proton producing 7-(2'-pyridyl)-7,8-*nido*-C₂B₉H₁₂, **2**, experiments have been conducted to learn which site is the more basic in **1**, the pyridine or the open cluster face. Furthermore, as **1** is obtained as a racemic mixture, experiments leading to the analytical separation of its enantiomers by capillary electrophoresis have been carried out.

Synthesis and characterization of [7-(2'-pyridyl)-7,8-*nido*-C₂B₉H₁₁]⁻ ligand

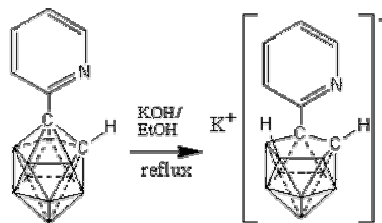


Figure 1.- Partial degradation reaction of 1-(2'-pyridyl)-1,2-*closo*-C₂B₁₀H₁₁.

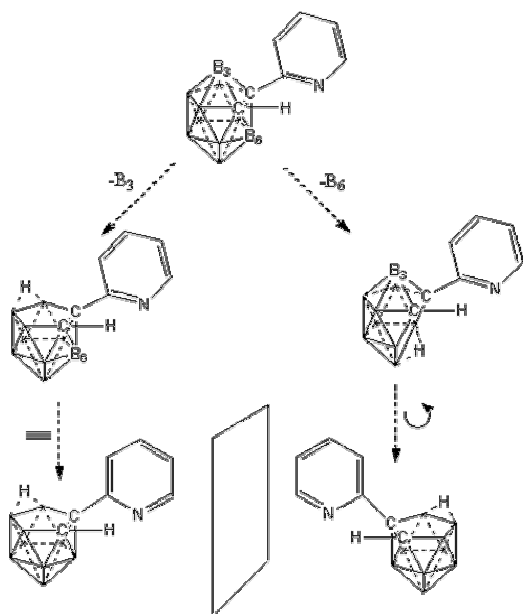


Figure 2 Isomers of **1**.

Partial degradation or the formal removal of a B⁺ from 1-(2'-pyridyl)-1,2-*closo*-C₂B₁₀H₁₁ to yield the corresponding anionic species [7-(2'-pyridyl)-7,8-*nido*-C₂B₉H₁₁]⁻ was readily accomplished using KOH in ethanol (see Figure 1).¹ This anionic ligand has been isolated as [NMe₄][7-

(2'-pyridyl)-7,8-*nido*-C₂B₉H₁₁] [NMe₄][**1**] in stoichiometric but not in isomeric purity (see Figure 2).

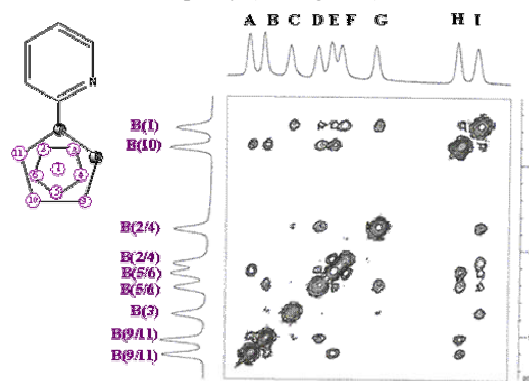


Figure 3.- ¹¹B{¹H}-¹¹B{¹H} 2D COSY NMR spectrum of [NMe₄][**1**].

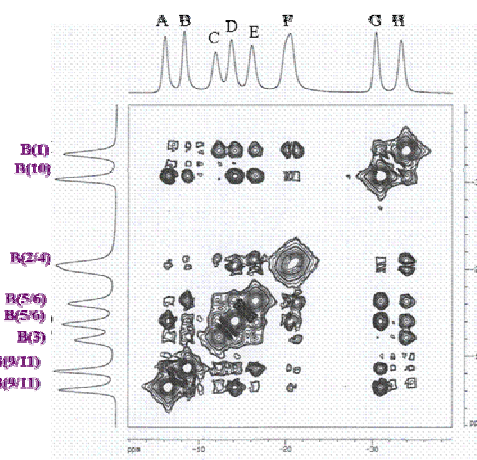


Figure 4.- ¹¹B{¹H}-¹¹B{¹H} 2D COSY NMR spectrum of **2**.

This *nido* species has been characterized by elemental analyses, MALDI-TOF-MS, IR and NMR techniques. Strong IR ν (B-H) resonances near 2520 cm⁻¹, in agreement with a *nido* [C₂B₉] cluster, have been observed.¹¹ The ¹¹B{¹H} NMR spectrum of [NMe₄][**1**] displays a 1:1:1:1:1:1:1:1:1 pattern in the range -7.5 / -34.1 ppm with the resonances sufficiently separated to permit their unambiguous assignment by means of ¹¹B{¹H}-¹¹B{¹H} COSY 2D NMR. The peak at -31.8 ppm is easily assigned to B(10) since it appears as a doublet of doublets in the ¹¹B NMR due to coupling with the H bridge as well as the *exo*-cluster H atom. The peak at -34.1 ppm, at the highest field, corresponds to B(1), the position antipodal to the open face. With the resonances due to B(1) and B(10) thus established, analysis of the cross peaks easily allowed the assignment of the remaining B resonances (see Figure 3).

The [7-(2'-pyridyl)-7,8-*nido*-C₂B₉H₁₁], **1** ligand has a negative charge that could be located at the *nido* cluster or dissipated throughout the pyridinyl group. In order to know on this, the protonated 7-(2'-pyridyl)-7,8-*nido*-C₂B₉H₁₂ (**2**) species was isolated after addition of HCl solution to the reaction media.

The ¹¹B{¹H} NMR spectrum of **2** appears at the same range as [NMe₄][**1**] but displays a 1:1:1:1:2:1:1 pattern. The ¹¹B{¹H}-¹¹B{¹H} COSY 2D NMR indicated that the overlapping signal corresponds to B(2) and B(4) that have moved from -18.2 and -22.3 ppm in the latter to -20.3 in 7-(2'-pyridyl)-7,8-*nido*-C₂B₉H₁₂ (See Figure 4). This may suggest that the extra proton is interacting with the *nido* cluster.ⁱⁱⁱ

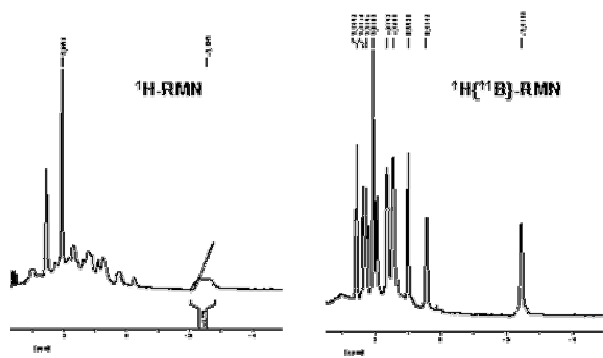


Figure 5.- ¹H and ¹H{¹¹B} NMR spectra of **2**.

The ¹H NMR spectra of **2** and [NMe₄][**1**] display, in addition to the corresponding organic groups, three very similar areas: i) resonances between 9.00 and 6.50 ppm corresponding to the pyridinyl group, ii) resonances between 2.60-0.00 ppm corresponding to the hydrogen atoms bonded to boron and iii) a resonance at high field between -2.00 to -3.00 ppm characteristic of the B-H-B hydrogen bridge.

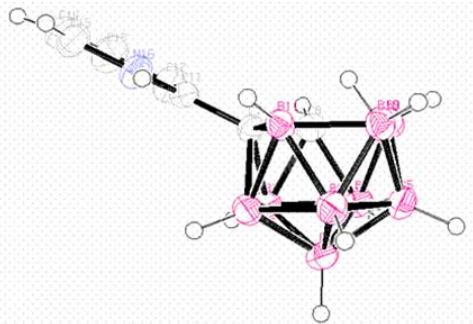


Figure 6.- ORTEP plot of **2**.

Figure 5 shows the ¹H and ¹H{¹¹B}NMR of **2**. As the ¹H{¹¹B}NMR of **2** at room temperature was not conclusive on the position of the extra proton, efforts to grow good crystals for X-ray diffraction were done. Crystallization by slow evaporation of an acetone solution of **2** at controlled temperature (4°C) afforded air and moisture insensitive yellow plate-shaped monocrystals suitable for X-ray analysis. The X-ray diffraction study of **2** revealed that in solid state the extra proton was bonded to the N atom of the pyridinyl group. A drawing of the molecular structure of **2** is shown in Figure 6.

Although definitive evidence for N··H⁺ interaction in the solid state is given by the X-ray analysis of **2**, no proof of its existence in solution has been found in the ¹H{¹¹B} NMR spectrum at room temperature. There could be a fast dynamic

exchange of the two proton atoms. To solve this question low temperature experiments with the aim to freeze out the specific H⁺ interaction were done. The set of ¹H{¹¹B} NMR spectra recorded in the range 298°K to 203°K, using acetone as a solvent, are shown in Figure 7. Remarkable is the high dependence of the chemical shift of the B-H-B signal on temperature. At room temperature this signal is a broad doublet that becomes a well defined singlet as the temperature decreases while a new resonance at 13.77 ppm appears. These spectroscopic data suggest that at room temperature there is an interaction between the proton and the C₂B₃ cluster open face but when temperature decreases proton moves to a N··H⁺ interaction, the one corresponding to this observed in the solid state.

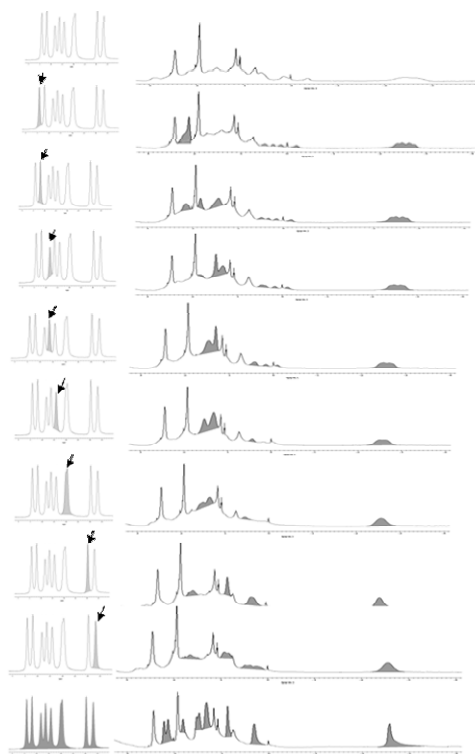


Figure 7.- ¹H{¹¹B} NMR spectra for **3** as a function of temperature.

As the ¹H{¹¹B} NMR spectrum discerns all nine hydrogen atoms bonded to the Boron cluster atoms as well as ¹¹B{¹H} NMR does with the boron atoms, ¹¹B selective irradiation ¹H NMR spectra were run (see Figure 8). This systematic study has indicated that the magnetic shielding of *exo*-cluster hydrogen atoms increases with the increasing shielding of the adjacent B atoms, i.e. ¹H shifts correlate well with the ¹¹B chemical shift as shown in Figure 9.

The anionic *nido* compounds were also analyzed by MALDI-TOF-MS analysis. Figure 10 shows the MALDI-TOF-MS for [NMe₄][7-(2'-pyridyl)-7,8-*nido*-C₂B₉H₁₁]. The highest m/z peak displays a signal group with isotopic distribution centered at m/z 211 corresponding to the anionic molecular fragment [C₇H₁₅B₉N]⁻. The experimental peak position and isotopic distribution matches the theoretical calculations.

Attempts to separate the enantiomers have been made on [NMe₄][**1**] and **2** by using capillary electrophoresis (CE). Capillary electrophoresis (CE) is a single separation technique that proved effective in the discrimination of sterically different forms (atropisomers) of anionic boron cluster compounds^{iv} to date. This technique^{v,vi} was therefore used to the evidence the existence of [NMe₄][**1**] and **2** in two sterically different forms each. Main practical advantages of

CE are high separation efficiency, high separation speed, easy and fast change of separation conditions and of the separation mode, cheapness and, last but not least, negligible consumption of analysed samples that are injected in the separation capillary in submillimolar concentrations and in volumes of the order of nanoliters.

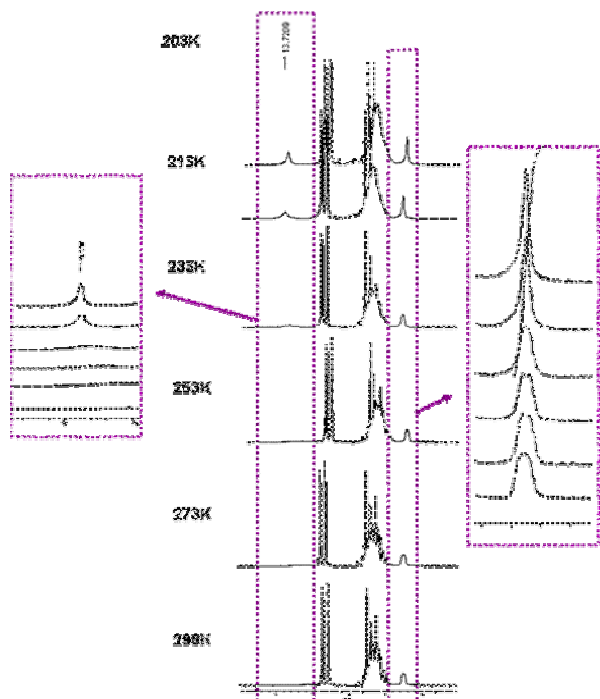


Figure 8.- ^{11}B selective irradiation ^1H NMR spectra of 2.

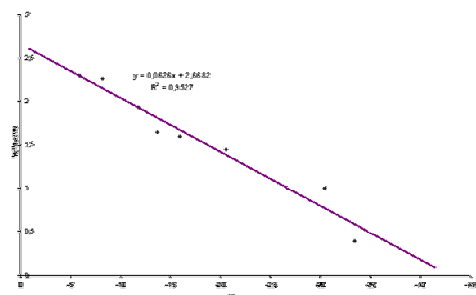


Figure 9.- A plot of ^1H versus ^{11}B chemical shifts for the individual BH_{exo} units for 2.

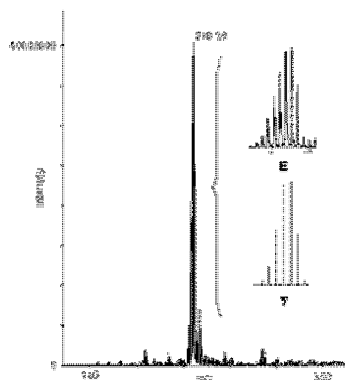
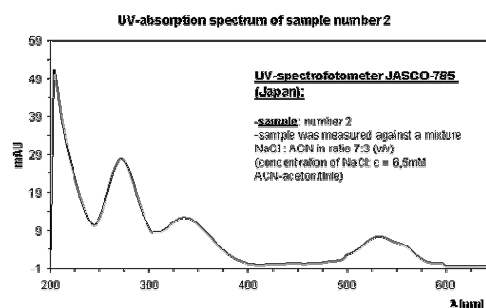


Figure 10.- MALDI-TOF- MS of $[\text{NMe}_4][1]$ (T=calculated, E=Experimental).

Chiral separation

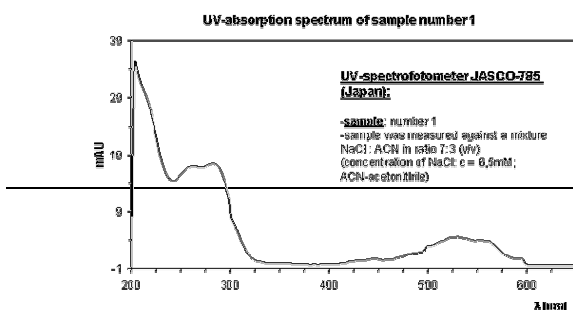
Reasonable sensitivity of the photometric detection is conditioned by the use of the light, which is maximally absorbed by a detected species (a compound or an ion). Therefore, UV-Vis spectra of $[\text{NMe}_4][1]$ and of 2 have been measured first (Figure 11). Approximately 1 mM samples of these compounds have been prepared for CE studies by the dissolution of calculated amounts of either $[\text{NMe}_4][1]$ or 2 in 6.5 mM solution of NaCl in the water-acetonitrile 7:3 (v/v) mixture. These samples have been consecutively injected in the separation capillary till the sample solution filled the capillary section acting as the detection cell. Then, the light absorption spectrum of the dissolved compound, corrected for the solvent background, was recorded (Figure 11). Detection wavelength of 200 nm was chosen for CE experiments based on obtained spectra.

Figure 11.- UV spectra of $[\text{NMe}_4][1]$ (A) and 2 (B) in 6.5 mM



solution of NaCl in the water-acetonitrile 7:3 (v/v) mixture.

Any species has to be analysed in the absence of a chiral selector in the background electrolyte before its chiral separation. There are two reasons for it. First, electrophoretic purity of an analysed compound and its mobility must be known. Second, the chiral discrimination of sterically different forms of the compound is verified by the identity of the peak area of the analysed compound or ion in the absence of a chiral selector with the sum of its peak areas in the presence of the chiral selector. Achiral separation of $[\text{NMe}_4][1]$ in sodium borate of pH 9 and ionic strength $I = 11$ mM, dissolved in the mixture water-methanol 45:55 (v/v), as the background electrolyte is in Figure 12. A narrow and symmetrical single main peak and much smaller peaks of impurities evidence that the injected sample does not contain two or more (detectable) constituents in comparable concentrations. Thus, this peak may be ascribed to $[\text{7-(2'-pyridyl)-7,8-nido-C}_2\text{B}_9\text{H}_{11}]^-$ without doubt. The main single peak splits to two peaks of (practically) identical height and area in the presence of β -cyclodextrin as the chiral selector^{vi,vii} in the separation system (Figure 13). Such a result has to be expected because there are no reasons for quantitative prevalence of some sterical form of $[\text{7-(2'-pyridyl)-7,8-nido-C}_2\text{B}_9\text{H}_{11}]^-$ to our knowledge.



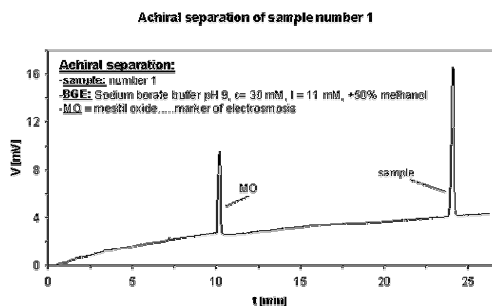
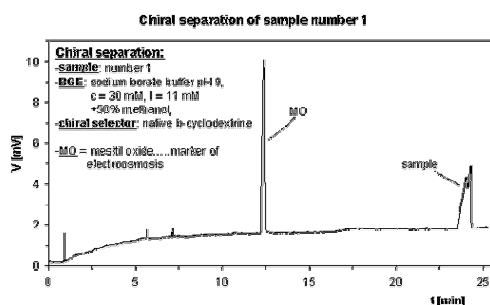


Figure 12.- Achiral separation of $[\text{NMe}_4][\mathbf{1}]$ with mesityloxide (MO) as an electroosmosis marker in sodium borate of pH 9 and ionic strength $I = 11$ mM, dissolved in the mixture water-methanol 45:55 (v/v), as the background electrolyte.

Achiral separation of **2** in sodium borate of pH 9 and ionic strength $I = 11$ mM gives again single main peak. The shape and the mobility of this peak are identical with those of the $[\text{7-(2'-pyridyl)-7,8-nido-C}_2\text{B}_9\text{H}_{11}]^-$, which is obtained after the injection of $[\text{NMe}_4][\mathbf{1}]$. Optical spectra of anionic zones obtained from $[\text{NMe}_4][\mathbf{1}]$ and from **2** are identical in the sodium borate buffer. Moreover, these spectra are identical with the spectrum of $[\text{NMe}_4][\mathbf{1}]$ dissolved in the 6.5 mM solution of NaCl in the water-acetonitrile 7:3 (v/v) mixture (Figure 11A). These results imply that ionization of $[\text{NMe}_4][\mathbf{1}]$ and **2** in weakly basic and in neutral water-acetonitrile solutions gives identical anion, $[\text{7-(2'-pyridyl)-7,8-nido-C}_2\text{B}_9\text{H}_{11}]^-$. This implication support identical results



of chiral separations of $[\text{NMe}_4][\mathbf{1}]$ and of **2** at conditions specified in Figure 13.

Figure 13.- Chiral separation of $[\text{NMe}_4][\mathbf{1}]$ with mesityloxide (MO) as an electroosmosis marker in background electrolyte consisting of sodium borate of pH 9 and ionic strength $I = 11$ mM, dissolved in the mixture water-methanol 45:55 (v/v), and of 2 mM β -cyclodextrin added as a chiral selector.

Experimental section

Materials and Methods. 1- $\text{C}_5\text{H}_4\text{N}$ -1,2-*closo*-carborane was synthesized according to the literature.^{viii} 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 Schlenk 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 $^1\text{H-NMR}$ (300.0 MHz), $^{11}\text{B-NMR}$ (96.3 MHz) and $^{13}\text{C}\{^1\text{H}\}$ -NMR (75.0 MHz) spectra were recorded on a Bruker ARX 300 spectrometer. Chemical Shift values for $^1\text{H-NMR}$, $^{13}\text{C}\{^1\text{H}\}$ -NMR and $^{11}\text{B-NMR}$ were referenced relative to external SiMe_4 and $\text{BF}_3\cdot\text{OEt}_2$. Chemical

shifts are reported in units of parts per million, and all coupling constants are reported in Hz.

Capillary electrophoresis (CE): The used laboratory set-up is based on a Spellman 1000R high-voltage power supply (Plainview, NY, USA) and on a JASCO 875 UV-Vis spectrophotometer (Tokyo, Japan) adapted for CZE experiments with thermostated fused silica capillaries.^v The spectrophotometer software allows either continual monitoring of the background electrolyte composition during analysis or recording of optical absorption spectrum of a compound present in a very short section of the radially illuminated separation capillary, which acts as the photometric detector cell.

Synthesis of $[\text{NMe}_4][\text{7-(2'-pyridyl)-7,8-nido-C}_2\text{B}_9\text{H}_{11}]$, $[\text{NMe}_4][\mathbf{1}]$

In a Schlenk flask containing a solution of KOH (383 mg, 6.78 mmol) in deoxygenated ethanol (20 ml), was added 1- NC_5H_4 -1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (300 mg, 1.36 mmol). The mixture was refluxed for 3 hours, cooled down to room temperature and evaporated. The residue was dissolved in water (10 ml) and treated with the solution of tetramethylammonium chloride. The white solid was filtered off and washed with water and diethyl ether. Yield: 377.3 mg, 1.3 mmol, (98%). Anal. Calcd for $\text{C}_{11}\text{H}_{27}\text{B}_9\text{N}_2$: N, 9.84 %; C, 46.41 %; H, 9.56 %; trobat: N, 9.72 %; C, 46.59 %; H, 9.37 %. IR: $\nu[\text{cm}^{-1}] = 3045$ (C-H), 3007-2756 ($\text{C}_{\text{aryl}}\text{-H}$); 2545 (B-H), 1562 (C=N); 1427 (CH_3); 1283 (N-C); 1022 (C-N-C); 791, 766, 748 ($\text{C}_{\text{aryl}}\text{-H}$). $^1\text{H-NMR}$ (CD_3COCD_3): $\delta = 8.17$ (d, $^3\text{J}(\text{H,H}) = 3$, $\text{C}_{\text{pyr}}\text{-H}$, 1H), 7.42 (t, $^3\text{J}(\text{H,H}) = 9$, $^4\text{J}(\text{H,H}) = 3$, $\text{C}_{\text{pyr}}\text{-H}$, 1H), 7.26 (d, $^3\text{J}(\text{H,H}) = 11$, $\text{C}_{\text{pyr}}\text{-H}$, 1H), 6.89 (t, $^3\text{J}(\text{H,H}) = 9$, $\text{C}_{\text{pyr}}\text{-H}$, 1H), 3.44 (s, $\text{N}(\text{CH}_3)_4$, 12H), 2.82 (s, $\text{C}_c\text{-H}$, 1H), 2.28 (s, B-H, 1H), 2.18 (s, B-H, 1H), 1.78 (s, B-H, 1H), 1.77 (s, B-H, 1H), 1.41 (s, B-H, 1H), 0.87 (s, B-H, 1H), 0.86 (s, B-H, 1H), -2.37 (s, B-H-B, 1H). $^{11}\text{B-NMR}$ (CD_3COCD_3): $\delta = -7.5$ (d, $^1\text{J}(\text{B,H}) = 144$, 1B), -9.2 (d, $^1\text{J}(\text{B,H}) = 132$, 1B), -12.3 (d, $^1\text{J}(\text{B,H}) = 154$, 1B), -15.4 (d, $^1\text{J}(\text{B,H}) = 138$, 1B), -17.1 (d, $^1\text{J}(\text{B,H}) = 158$, 1B), -18.2 (d, $^1\text{J}(\text{B,H}) = 148$, 1B), -22.3 (d, $^1\text{J}(\text{B,H}) = 140$, 1B), -31.8 (d, $^1\text{J}(\text{B,H}) = 174$, $^1\text{J}(\text{B,H}) = 54$, 1B), -34.1 (d, $^1\text{J}(\text{B-H}) = 135$, 1B). $^{13}\text{C}\{^1\text{H}\}$ -NMR $\delta = 164.8$ (s, $\text{C}_{2\text{pyr}}$), 147.7 (s, $\text{C}_{6\text{pyr}}$), 137.7 (s, $\text{C}_{4\text{pyr}}$), 122.3 (s, $\text{C}_{3\text{pyr}}$), 121.2 (s, $\text{C}_{5\text{pyr}}$), 63.4 (s, $\text{C}_c\text{-Pyr}$), 56.7 (s, $\text{N}(\text{CH}_3)_4$), 43.5 (s, $\text{C}_c\text{-H}$). MALDI-TOF-MS: 210.3 (100%, M).

Synthesis of 7-(2'-pyridyl)-7,8-nido- $\text{C}_2\text{B}_9\text{H}_{12}$ (**2**)

In a Schlenk flask containing a solution of KOH (370 mg, 6.61 mmol) in deoxygenated ethanol (20 ml), was added 1- NC_5H_4 -1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (290 mg, 1.32 mmol). The mixture was refluxed for 3 hours, cooled down to room temperature and evaporated. A HCl aqueous solution (1M) was added to the residue and a yellow solid was obtained. The solid was filtered off and washed with water and diethyl ether. Yield: 267.3 mg, 1.21 mmol, (96%). Anal. Calcd for $\text{C}_7\text{H}_{16}\text{B}_9\text{N}$: N, 6.62 %; C, 39.75 %; H, 7.62 %, found: N, 6.80 %; C, 39.46 %; H, 7.54 %. IR: $\nu[\text{cm}^{-1}] = 3103.2$ (C-H); 2597.9, 2537.2, 2493.8 (B-H); 1531.3 (C=N), 1293.2 (N-C); 1171.7 (C-N-C); 783.0, 737.7, 724.2 ($\text{C}_{\text{aryl}}\text{-H}$). $^1\text{H}\{^{11}\text{B}\}$ -NMR (CD_3COCD_3): $\delta = 13.77$ (s, H^+ , 1H), 8.66 (d, $^3\text{J}(\text{H,H}) = 8$, $\text{C}_{\text{pyr}}\text{-H}$, 1H), 8.43 (t, $^3\text{J}(\text{H,H}) = 8$, $\text{C}_{\text{pyr}}\text{-H}$, 1H), 7.88 (d, $^3\text{J}(\text{H,H}) = 8$, $\text{C}_{\text{pyr}}\text{-H}$, 1H), 7.80 (t, $^3\text{J}(\text{H,H}) = 6$, $\text{C}_{\text{pyr}}\text{-H}$, 1H), 2.55 (s, $\text{C}_c\text{-H}$, 1H), 2.35 (s, B-H, 1H), 2.26 (s, B-H, 1H), 1.95 (s, B-H, 1H), 1.64 (s, B-H, 2H), 1.47 (s, B-H, 2H), 1.00 (s, B-H, 1H), 0.45 (s, B-H, 1H), -2.43 (s, 1H). $^{11}\text{B-NMR}$ (CD_3COCD_3): $\delta = -6.0$ (d, $^1\text{J}(\text{B,H}) = 120$, 1B), -8.2 (d, $^1\text{J}(\text{B,H}) = 139$, 1B), -11.8 (d, $^1\text{J}(\text{B,H}) = 178$, 1B), -13.6 (d, $^1\text{J}(\text{B,H}) = 124$, 1B), -16.0 (d, $^1\text{J}(\text{B,H}) = 168$, 1B), -20.3 (d, $^1\text{J}(\text{B,H}) = 166$, 2B), -30.3 (dd, $^1\text{J}(\text{B,H}) = 138$, $^1\text{J}(\text{B,H}) = 21$, 1H, 1B), -33.2 (d, $^1\text{J}(\text{B,H}) = 168$, 1B). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CD_3COCD_3): $\delta = 159.8$ (s, $\text{C}_{2\text{pyr}}$), 146.0 (s, $\text{C}_{6\text{pyr}}$), 140.4 (s,

C_{4pyr}), 123.8 (s, C_{3pyr}), 122.9 (s, C_{5pyr}), 58.0 (s, C_{c-Pyr}), 39.3 (s, C_{c-H}). MALDI-TOF-MS: 210.3 (100%, M).

X-ray studies X-ray measurements for [NMe₄][7-(2'-pyridyl)-8-SⁱPr-7,8-*nido*-C₂B₉H₁₀].

Acknowledgment We are grateful to thank CICYT for MAT01-1575, Generalitat de Catalunya for 2001/SGR/0033.

SUPPORTING INFORMATION PARAGRAPH. supplied as Supporting Information should be included at the end of the at (<http://pubs.acs.org/instruct/jacsat.pdf>).

- ¹
- a) R.A. Weisboeck and M.F. Hawthorne, *J. Am. Chem. Soc.*, **1964**, 86, 1642. b) P.M. Garret, F.N. Tebbe and M.F. Hawthorne, *J. Am. Chem. Soc.*, 1964, 86, 5016. c) M.F. Hawthorne, D.C. Young, P.M. Garret, D.A. Owen, S.G. Schwerin, F.N. Tebbe and P.M. Wegner, *J. Am. Chem. Soc.*, 1968, 90, 862.
 - ii L. A. Leites *Chem. Rev.* 1992, 92, 279.
 - iii a) S. Hermánek *Chem. Rev.* 1992, 92, 325. b) S. Hermánek *Inorg. Chim. Acta* 1999, 289, 20. c) X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, K. Nestor, M. Thorton-Pett, S. Hermanek, T. Jelínek, B. Stibr, *J. Chem. Soc., Dalton Trans.*, 1990, 681. d) D. Reed *Chem.Soc.Rev.* 1993, 109.
 - iv V. Slaviček, B. Grüner, R. Vespalec, *J. Chromatogr. A*, 2003, 984, 121.
 - v F. Foret, L. Křivánková, P. Boček, *Capillary Zone Electrophoresis*, VCH, Weinheim, 1993.
 - vi B. Chankvetadze, *Capillary Electrophoresis in Chiral Analysis*, Wiley, Chichester (1997).
 - vii R. Vespalec, B. Boček, *Chem. Rev.* 2000, 100, 3715.
 - viii R. Coult, M. A. Fox, W. R. Gill, P. L. Herbertson, J. A. H. Macbride, K. Wade, *J. Organometal. Chem.*, **1993**, 19.