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New NS_2 and $S'S_2$ ligands derivatives of pyridine and thiophene incorporating icosahedral carboranes

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Abstract

New ligands incorporating carboranyl units in organic fragments NS_2 (pyridine-dithia) or $S'S_2$ (thiophene-dithia) have been synthesized. The *closo* species of these ligands were obtained by the reaction of sodium thiolate-*o*-carborane with the corresponding difunctional electrophile derivatives of pyridine or thiophene. Partial degradation of the *closo* species derivatives of pyridine was successfully achieved with KOH in ethanol at r.t. All these compounds have been characterized by chemical analyses and NMR techniques. The ^{1}H-NMR spectrum of the *nido* species shows that these *nido* molecules are produced in stoichiometric purity but not in isomeric purity. The crystal structure of 2,6-bis(((1-methyl-1,2-dicarba-*closo*-dodecaboranyl)thio)methyl)pyridine is reported and confirms that the carborane cages are *closo* and connected to both sulfur atoms. These, through methylene bridges, are connected to the pyridine at the 2 and 6 positions.

Keywords: Carboranes; Pyridine; Thioether; Thiophene

1. Introduction

Recent studies in our group were focused to the synthesis of new ligands incorporating NS_2 (pyridine-dithia) and $S'S_2$ (thiophene-dithia) as coordinating units. Interest in such coordinating systems stems in their potential as sensitizers in ion selective electrodes [1], as carriers in supported liquid membranes and in the interesting reactivity with metals, e.g. benzothiophene condensations promoted by Pd(II) [2] and Pt(II) [3] for the NS_2 ligands.

On the other hand carboranyl compounds have found applications as electrolytes for non-aqueous solvents or in solvent extraction of radionuclides [4]. A well known carboranyl fragment is $[C_2B_9H_{12}]^-$ whose negative charge is delocalized through the cluster. This fact is responsible for the high solubility of this anion in low dielectric constant organic solvents. The incorporation of such anionic carboranyl units in organic fragments containing the coordinating cores NS_2 or $S'S_2$ should permit to produce versatile ligands good candidates for organic membrane carriers. This would eliminate the necessity to add anionic lipophilic additives because the incorporated carboranyl clusters would perform this function.

Our objective in the present work was the synthesis of new NS_2 and $S'S_2$ ligands derivatives of pyridine and thiophene heterocycles which incorporate *closo* icosahedral carboranes and their partial degradation to the corresponding *nido* compounds.

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2. Results and discussion

This work deals with the synthesis of pyridine and thiophene derivatives incorporating respectively at the 2,6- and 2,5-positions a series of carboranyl thio methyl-groups. The general structure is indicated in Fig. 1. Since the fragment $-SCH_2-$, bonded to one cluster carbon atom, is common in all of them it will not be explicited in the abbreviation utilized. The letter 'c' (*closo*) will indicate through the paper the fragment '1,2-$C_2B_{10}H_{10}$' while 'n' (*nido*) will stand for the anionic fragment '7,8-$C_2B_9H_{10}^-$'. Next to the letters 'c' or 'n', the substituent on the second cluster carbon atom will be made explicit. Thus [(py)*c*-H] will correspond to the *closo* compound in Fig. 2a and [(py)*n*-Me]$^{2-}$ will correspond to the one indicated in Fig. 2b. Derivatives of 3-chloro-pyridine, abbreviated as Clpy, and 2,5-thiophene (tp) derivatives will follow the same system (see Fig. 3).

The reaction of sodium 1-thiolate-*o*-carborane with 2,6-bis (bromomethyl)pyridine in deoxygenated methanol yielded the podand ligand [(py)*c*-H] incorporating the coordinating group NS_2 (pyridine-dithia) and two carborane cages. A similar reaction starting from sodium 1-thiolate-2-methyl-*o*-carborane, under the same conditions, yields [(py)*c*-Me].

Both compounds [(py)*c*-H] and [(py)*c*-Me], have been characterized by chemical analyses and NMR techniques. The ^{11}B-NMR displays typical resonances for a C-asymmetrically substituted *o*-carborane in the range -1 to -13 ppm. The ^{1}H-NMR spectrum displays two resonances corresponding to the pyridine ring between 7.2–7.7 ppm, the higher field integrating two being a doublet and the lower field integrating one being a triplet. It is noticeable the compressing ^{11}B-NMR spectrum effect produced by the C_c-Me group when comparing the spectra of [(py)*c*-Me] and [(py)*c*-H]. Through this section special attention will be focused on the ^{1}H-NMR resonance which appears at 4.27 ppm [(py)*c*-H] and at 4.4 ppm [(py)*c*-Me]. In both cases it is a well defined singlet resonance. To confirm the structure good crystals for X-ray diffraction were obtained from a solution of [(py)*c*-Me] in methanol by slow evaporation. The structure is illustrated in Fig. 4, crystallographic data are presented in Table 1 and selected bond lengths and angles are listed in Table 2. Crystal structure analysis of [(py)*c*-Me] confirmed that carborane cages are connected to both sulfur atoms,

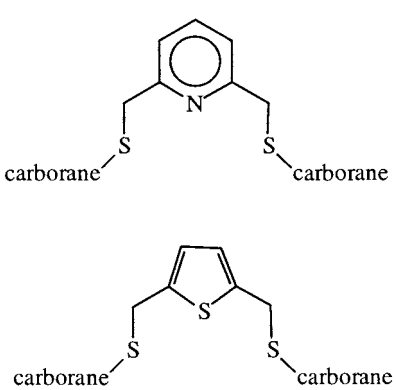


Fig. 1. General structure of [(py)*c*-R] and [(tp)*c*-R] (R = H, Me).

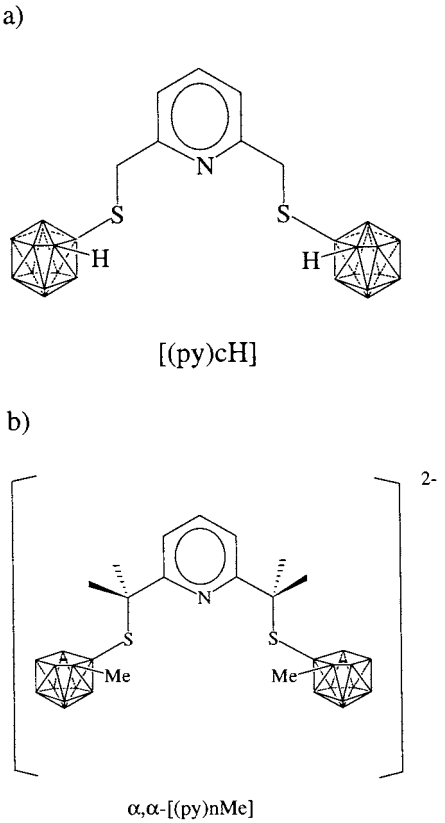


Fig. 2. Schematic drawing of (a) [(py)*c*-H] and (b) α,α-[(py)*n*-Me]$^{2-}$.

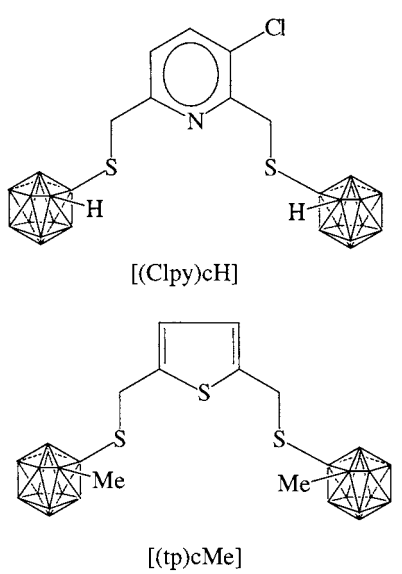


Fig. 3. Schematic drawing of [(Clpy)*c*-H] and [(tp)*c*-Me].

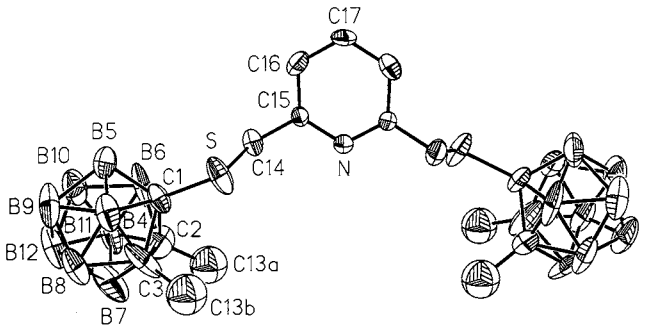


Fig. 4. A view of [(py)*c*-Me], showing 20% displacement ellipsoids. C(2) and C(3) refer to atom positions partially occupied by carbon and boron atoms, and C(13a) and C(13b) indicate disordered methyl carbon.

but the methyl groups as well as the relevant host boron atoms are disordered each occupying two positions. The molecule assumes 2-fold symmetry with the symmetry axis going through the atoms N and C(17). As indicated by the N–C(15)–C(14)–S torsion angle value of 85.2(5)° the sulfur atoms are oriented to opposite sites of the pyridine ring and thus the conformation observed in the solid state is not suitable for tridentate NS_2 coordination to a metal.

Partial degradation, or the removal of B(3) or B(6), was successfully achieved by dissolving either [(py)*c*-H] or [(py)*c*-Me] in ethanol containing KOH. Contrary to the normal procedure [5] no refluxing conditions were required and the degradation took place smoothly under r.t. conditions. Characterization was done by elemental analyses and NMR techniques. The partially degraded nature of the carborane cage was evident from the ^{11}B-NMR spectra. Resonances in the range -8 to -36 ppm, as expected, were obtained. The ^{1}H-NMR did not display significant differences in the aromatic pyridine region with regard to ligands [(py)*c*-H] or [(py)*c*-Me]. However, new resonances were ob-

Table 1
Crystallographic data and structure refinement for [(py)*c*-Me]

Empirical formula	$C_{13}H_{33}B_{20}NS_2$
Formula weight	483.72
Temperature (°C)	21
Wavelength (Å)	0.71069
Space group	Orthorhombic Iba2 (no. 45)
Unit cell dimensions	
a (Å)	16.207(3)
b (Å)	14.686(4)
c (Å)	12.452(7)
V (Å^3)	2964(2)
Z	4
$D_{calc.}$ (g cm^{-1})	1.084
μ mm^{-1}	0.187
$^{a}R_1$ [$I>2\sigma(I)$]	0.2124
wR_2 ^{b}[$I>2\sigma(I)$]	0.2535

$^{a}R_1 = \Sigma\|F_o|-|F_c\|/\Sigma|F_o|$ and $^{b}wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$.

Table 2
Selected bond lengths (Å) and angles (°) for [(py)*c*-Me]

S–C(14)	1.780(5)
S–C(1)	1.790(5)
N–C(15)	1.321(5)
N–C(15)	1.321(5)
C(1)–C(3)	1.628(10)
C(1)–B(5)	1.643(10)
C(1)–B(4)	1.645(8)
C(1)–B(6)	1.666(8)
C(1)–C(2)	1.681(10)
C(2)–C(13A)	1.551(12)
C(2)–C(3)	1.607(10)
C(2)–B(6)	1.619(12)
C(2)–B(7)	1.641(12)
C(2)–B(11)	1.646(11)
C(3)–C(13B)	1.574(9)
C(3)–B(8)	1.661(10)
C(3)–B(4)	1.662(11)
C(3)–B(7)	1.745(12)
B(4)–B(5)	1.709(11)
B(4)–B(8)	1.727(12)
B(4)–B(9)	1.739(11)
B(5)–B(10)	1.742(13)
B(5)–B(9)	1.749(13)
B(5)–B(6)	1.801(11)
B(6)–B(11)	1.652(14)
B(6)–B(10)	1.747(10)
B(7)–B(11)	1.674(13)
B(7)–B(8)	1.714(13)
B(7)–B(12)	1.739(14)
B(8)–B(9)	1.67(2)
B(8)–B(12)	1.704(12)
B(9)–B(12)	1.70(2)
B(9)–B(10)	1.795(11)
B(10)–B(12)	1.66(2)
B(10)–B(11)	1.68(2)
B(11)–B(12)	1.791(12)
C(14)–C(15)	1.471(6)
C(15)–C(16)	1.385(7)
C(16)–C(17)	1.371(6)
C(17)–C(16)	1.371(6)
C(14)–S–C(1)	105.9(2)
C(15)^{a}–N–C(15)	119.4(5)
C(3)–C(1)–B(5)	110.2(5)
C(3)–C(1)–B(4)	61.0(4)
B(5)–C(1)–B(4)	62.6(4)
C(3)–C(1)–B(6)	107.4(5)
B(5)–C(1)–B(6)	65.9(4)
B(4)–C(1)–B(6)	115.7(4)
C(3)–C(1)–C(2)	58.1(4)
B(5)–C(1)–C(2)	110.1(5)
B(4)–C(1)–C(2)	109.1(5)
B(6)–C(1)–C(2)	57.8(4)
C(3)–C(1)–S	115.4(4)
B(5)–C(1)–S	123.4(5)
B(4)–C(1)–S	114.7(4)
B(6)–C(1)–S	124.9(4)
C(2)–C(1)–S	121.6(4)
C(13A)–C(2)–C(3)	117.2(8)
C(13A)–C(2)–B(6)	123.1(8)
C(3)–C(2)–B(6)	110.8(6)
C(13A)–C(2)–B(7)	114.7(8)
C(3)–C(2)–B(7)	65.0(5)
B(6)–C(2)–B(7)	112.0(6)
C(13A)–C(2)–B(11)	119.8(9)

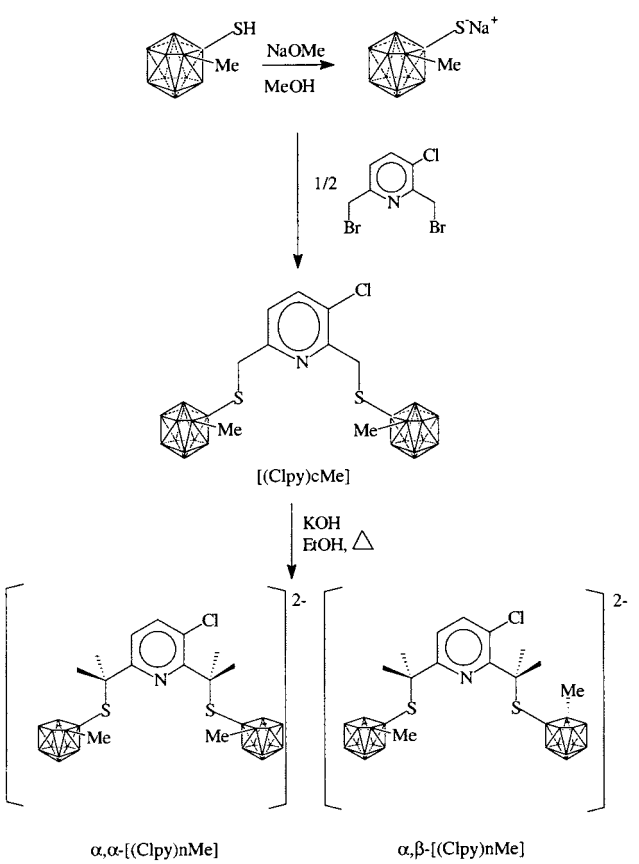
Table 2 (Continued)

C(3)–C(2)–B(11)	112.9(6)
B(6)–C(2)–B(11)	60.8(6)
B(7)–C(2)–B(11)	61.3(5)
C(13A)–C(2)–C(1)	123.9(8)
C(3)–C(2)–C(1)	59.3(4)
B(6)–C(2)–C(1)	60.6(4)
B(7)–C(2)–C(1)	111.7(6)
B(11)–C(2)–C(1)	109.1(6)
C(13B)–C(3)–C(2)	116.5(6)
C(13B)–C(3)–C(1)	114.7(5)
C(2)–C(3)–C(1)	62.6(4)
C(13B)–C(3)–B(8)	128.2(6)
C(2)–C(3)–B(8)	107.7(6)
C(1)–C(3)–B(8)	108.6(6)
C(13B)–C(3)–B(4)	118.4(6)
C(2)–C(3)–B(4)	112.0(6)
C(1)–C(3)–B(4)	60.0(4)
B(8)–C(3)–B(4)	62.6(5)
C(13B)–C(3)–B(7)	124.5(7)
C(2)–C(3)–B(7)	58.5(5)
C(1)–C(3)–B(7)	109.1(6)
B(8)–C(3)–B(7)	60.4(5)
B(4)–C(3)–B(7)	112.2(6)
C(1)–B(4)–C(3)	59.0(4)
C(1)–B(4)–B(5)	58.6(4)
C(3)–B(4)–B(5)	105.5(6)
C(1)–B(4)–B(8)	104.8(5)
C(3)–B(4)–B(8)	58.7(5)
B(5)–B(4)–B(8)	105.1(6)
C(1)–B(4)–B(9)	106.9(5)
C(3)–B(4)–B(9)	105.5(6)
B(5)–B(4)–B(9)	61.0(5)
B(8)–B(4)–B(9)	57.6(5)

[a] Equivalent position $-x, -y, -z$.

served due to the $[P(CH_3)(C_6H_5)_3]^+$ cation. The most significant difference with regard to the *closo* species was observed at the methylene resonance region. Compound $[(py)n\text{-}H]^{2-}$ showed resonances in the ^{1}H-NMR spectrum at 3.89, 3.92, 4.12 and 4.13 ppm all of equal relative intensity, each one being split into a doublet. In addition, a broad singlet at -2.48 ppm from the B–H–B bridge was noticed. Relative areas of the distinct regions of the ^{1}H-NMR spectrum indicated the stoichiometric purity of the compound, but not necessarily the isomeric purity although the equal intensity of the four $-CH-$ resonances could lead to this conclusion.

Reaction of the pyridine asymmetrically substituted 3-chloro-2,6-bis(bromomethyl)pyridine with sodium 1-thiolato-*o*-carborane or 1-thiolato-2-methyl-*o*-carborane using similar conditions as before led to [(Clpy)*c*-H] and [(Clpy)*c*-Me]. These compounds were characterized as before. The chlorine atom, which occupies a non symmetric position on the aromatic ring, is responsible for the higher complexity of the ^{1}H-NMR spectra, with regard to the [(py)*c*-H] and [(py)*c*-Me] analogues. Two singlets from the methylene group in the ^{1}H-NMR spectra were observed at 4.24 and 4.43 ppm for [Cl(py)*c*-H] and at 4.20 and 4.38 ppm for [Cl(py)*c*-Me]. This is in agreement with the existence of two non-equivalent arms in these molecules. Partial degradation was achieved by dissolving [(Clpy)*c*-H] and [(Clpy)*c*-Me] in a solution of KOH in ethanol at r.t. in the case of [(Clpy)*c*-H] and refluxing conditions in the case of [(Clpy)*c*-Me]. The chemical analyses proved the stoichiometric purity of the compound and the NMR spectra confirmed the partial degradation process. However, inspection of the ^{1}H-NMR spectra at the methylene region indicated greater complexity of the system in solution than for $[(py)n\text{-}H]^{2-}$ or $[(py)n\text{-}Me]^{2-}$ ones. The system may be accounted for by considering two diastereomers with a fast inversion at the sulfur center at r.t. The possible diastereomers are α,α and α,β. Each has its optical enantiomer. The BHB resonances at the ^{1}H-NMR are in agreement with the existence of two diastereomers. Four BHB resonances are found in $[(Clpy)n\text{-}Me]^{2-}$ at -2.44, -2.43, -2.18 and -2.12 ppm and four methyl resonances are found at 1.12, 1.22, 1.26 and 1.35 ppm. The reactions leading to these compounds are illustrated in Scheme 1.



Scheme 1.

The reaction of sodium 1-thiolate-*o*-carborane and 2,5-bis(chloromethyl)thiophene yields a ligand [(tp)*c*-H] incorporating the $S'S_2$ (thiophene-dithia) coordinating group. A similar reaction utilizing sodium 1-thiolate-2-methyl-*o*-carborane, under the same conditions yields [(tp)*c*-Me]. The NMR spectra are in agreement with the proposed stoichiometry and the interpretation is the same as the one described for the pyridine compounds [(py)*c*-H] and [(py)*c*-Me]. The methylene region displays only one resonance at 4.29 ppm for [(tp)*c*-H] and at 4.26 ppm for [(tp)*c*-Me], which is very comparable to the chemical shift found for the pyridine compound.

Ligands incorporating both a coordinating moiety, either NS_2 (pyridine-dithia) or $S'S_2$ (thiophene-dithia), and carborane fragments (*closo* or *nido*) has been successfully achieved. It is the result of combining the bis(thiomethyl)pyridine or bis(thiomethyl)thiophene moieties with the 1,2-dicarba-*closo*-dodecaborane or 7,8-dicarba-*nido*-undecaborate(-1) clusters. For the pyridine compounds two sets of molecules have been produced, one is based on the 2,6-disubstituted pyridine and the second is based on the 2,3,6-trisubstituted pyridine. The two are similar but the last one incorporates a Cl– substituent on the aromatic ring at the 3-position which aims at introducing extra asymmetry to the molecule and to differentiate the coordinating capacity of both arms. For the thiophene compounds the molecules are based on the 2,5-disubstituted thiophene. In the *closo* species, pyridine and thiophene derivatives, fast inversion with regard to NMR time scale takes place on the sulfur atoms at r.t., thus preventing the existence of large number of invertomers (according to the terminology used by Abel et al.[6]). Fast inversion on S is proven by studying the methylene or the methyl region in the ^{1}H-NMR spectra of the *closo* compounds: [(py)*c*-Me], etc. Only one sharp resonance is observed in the spectrum either for $-CH_2-$ or $-CH_3$. If slow inversion was present a larger number of resonances should be found depending on the relative ratio of the distinct invertomers present. The pyridine *closo* species can be viewed similar to the organic molecules represented in Fig. 5 which have produced a rich NS_2 chemistry although it is expected that the bulky nature of the cluster shall induce changes. One striking point of the aryl NS_2 compounds has been their tendency to modify themselves upon coordination to metal to produce anionic ligands. In this process the original NS_2 coordinating moiety was considerably altered, e.g. reverting from NS_2 to NSO^2 or $NS(NH)^3$ anionic fragments.

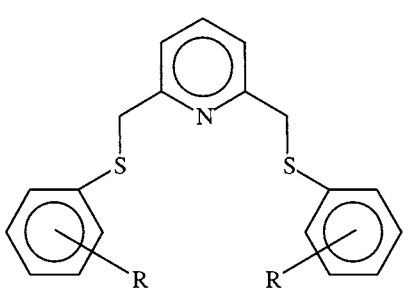


Fig. 5. Schematic drawing of [(py)PhR].

The carboranyl NS_2 *closo* compounds presented here would have an easy pathway to become anionic ligands maintaining the original NS_2 coordinating moiety. This would consist on the deboronation reaction of the *closo* species, [(py)*c*-H], [(py)*c*-Me], [(Clpy)*c*-H] and [(Clpy)*c*-Me] to produce the *nido* ones, $[(py)n\text{-}H]^{2-}$, $[(py)n\text{-}Me]^{2-}$, $[(Clpy)n\text{-}H]^{2-}$ and $[(Clpy)n\text{-}Me]^{2-}$. This process is presented in this paper without the participation of metal. From the spectroscopic data it seems that these *nido* molecules are produced in stoichiometric purity but not in isomeric one. Two diastereomers (along with their enantiomers) are produced in each case, except for the species α,α-$[(py)n\text{-}R]^{2-}$ (being R=H or Me), which have no enantiomer. The species α,α-$[(py)n\text{-}Me]^{2-}$, α,β-$[(py)n\text{-}Me]^{2-}$ and its enantiomer are represented in Fig. 6. No attempts have been made to separate the diastereomers.

An interesting characteristic of these ligands is their possibility to coordinate to metal, having extra vacant sites to be filled while internally compensating the metal's charge. If attention is focused on α,α-$[(py)n\text{-}Me]^{2-}$, to mention just one of the *nido* compounds, two independent coordination motifs are found which have shown definite coordinating capacity: the *nido*-carborane thioether fragment and the NS_2 (pyridine-dithia) fragment. The combination of the two, or which one will prevail on the second coordinating capacity is something to be studied in the future. Work is now under way to study the metal coordination behavior of these ligands.

3. Experimental section

3.1. General methods

Commercial *o*-carborane was sublimed under high vacuum at 0.01 mmHg prior to use. 1-Thiol-*o*-carborane [7], 1-methyl-2-thiol-*o*-carborane [8], 2,6-bis(bromomethyl)pyridine [9], 2,6-dimethyl-3-chloropyridine [10] and 2,5-bis(chloromethyl)thiophene [11] were synthesized according to the literature. Solvents were placed under vacuum to eliminate dissolved oxygen. All organic and inorganic salts were analytical reagent grade and were used as received. All reactions were carried out under a dinitrogen atmosphere employing Schlenk techniques. Microanalyses were performed by using a Perkin–Elmer 240 B microanalyser. IR spectra were obtained as KBr pellets on a Nicolet 710-FT spectrophotometer. The ^{1}H-NMR (300.0 MHz),

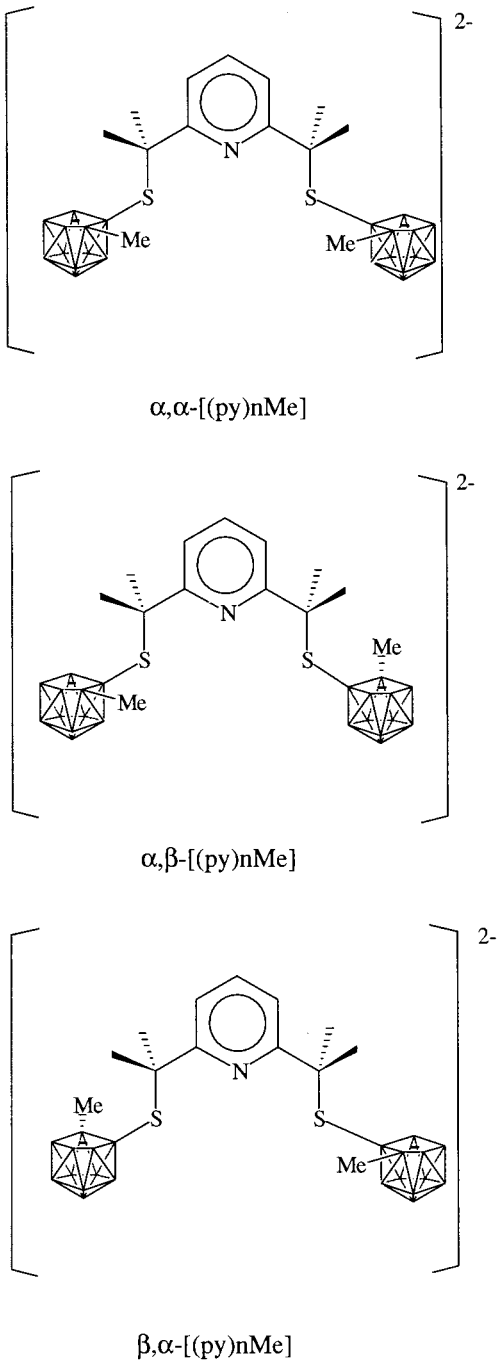


Fig. 6. Schematic drawing of α,α-[(py)n-Me]$^{2-}$, α,β-[((py)n-Me]$^{2-}$ and β,α-[((py)n-Me]$^{2-}$.

$^{13}C\{^1H\}$-NMR (75.0 MHz) $^{11}B\{^1H\}$-NMR (96.3 MHz) and $^{31}P\{^1H\}$-NMR (121.5 MHz) spectra were recorded on a Bruker ARX 300WB spectrometer. Chemical shift values for ^{1}H-NMR and $^{13}C\{^1H\}$-NMR spectra were referenced to an internal standard of $SiMe_4$ in deuterated solvents. Chemical shift values for ^{11}B-NMR spectra were referenced relative to external $BF_3.OEt_2$. Chemical shift values for $^{31}P\{^1H\}$-NMR spectra were referenced relative to external 85% H_3PO_4.

3.2. Synthesis of 2,6-bis(bromomethyl)-3-chloropyridine

A stirred mixture of 2,6-dimethyl-3-chloropyridine (2.3 g, 0.016 mol), N-bromosuccinimide (6.94 g, 0.039 mol), azobis[isobutyronitrile] (ca. 250 mg) and benzene (100 ml), was refluxed under light (200 W, incandescent bulb) for 2 h. After this time benzene was removed under reduced pressure, the residue dissolved in diethyl ether and washed twice with a sodium carbonate aqueous solution. After, the organic phase was washed twice with distilled water, and the solvent removed under reduced pressure. The oily residue was chromatographed on silica gel, using chloroform/hexane (1:1) as mobile phase ($R_f = 0.31$). 2,6-bis(bromomethyl)-3-chloropyridine was obtained as a white solid, yield: 0.57 g, 1.9 mmol (12%). FTIR (KBr): υ (cm^{-1}) (C–Br) 581. ^{1}H-NMR ($CDCl_3$): δ (ppm) 4.53 (s, 2H, py–(CH_2)$_a$–Br), 4.68 (s, 2H, py–(CH_2)$_b$–Br), 7.4 (d, ^3J(H,H) = 8.4 Hz, 1H, H_5), 7.71 (d, ^3J(H,H) = 8.4 Hz, 1H, H_4). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ (ppm) 30.7 (py–(CH_2)$_a$–Br), 32.5 (py–(CH_2)$_b$–Br), 124.5 (C_{5py}), 131 (C_{3py}), 138.6 (C_{4py}), 153.5 (C_{6py}), 155.2 (C_{2py}). Anal. Calc. for $C_7H_6Br_2ClN$: C, 28.08; H, 2.02; N, 4.68. Found: C, 28.47; H, 2.00; N, 4.36.

3.3. Synthesis of closo species

3.3.1. 2,6-Bis(((1,2-dicarba-closo-dodecaboranyl)thio) methyl)pyridine [(py)c-H)]

To a three necked round bottom flask (15 ml) containing deoxygenated methanol (10 ml) were added sodium metal (26 mg, 1.131 mmol) and 1-thiol-o-carborane (200 mg, 1.131 mmol). After stirring for 1 h, 2,6-bis (bromomethyl)pyridine (150 mg, 0.565 mmol) was added and the mixture was allowed to stir at r.t. for 24 h. After removal of solvent in vacuum, the residue was extracted with chloroform (15 ml) and the organic layer was washed with aqueous 1M KOH (2×10 ml) and with water (2×10 ml), dried over anhydrous magnesium sulfate, and vacuum evaporated to afford a yellow oil, yield: 226 mg, 0.5 mmol (88%). FTIR (KBr): υ (cm^{-1}) (B–H) 2586. ^{1}H-NMR ($CDCl_3$): δ (ppm) 4.00 (br s, 2H, C_c–H), 4.27 (s, 4H, py–(CH_2)–S), 7.24 (d, ^1J(H,H) = 7.5 Hz, 2H, H_{3py}), 7.66 (t, ^1J(H,H) = 7.5 Hz, 1H, H_{4py}). ^{11}B-NMR ($CDCl_3$): δ (ppm) −1.2 (d, ^1J(B,H) = 144.4 Hz, 1B), −4.6 (d, ^1J(B,H) = 144.4 Hz, 1B), −8.6 (d, ^1J(B,H) = 144.4 Hz, 4B), −12.1 (d, ^1J(B, H) = 163.7 Hz, 4B). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ (ppm) 42.7 (s, py–(CH_2)–S), 74.3 (s, C_c), 122.3 (s, C_{3py}), 138.0 (s, C_{4py}), 155.0 (s, C_{2py}). Anal. Calc. for $C_{11}H_{29}B_{20}NS_2$: C, 28.99; H, 6.41; N, 3.07; S, 14.07. Found: C, 28.57; H, 6.21; N, 2.97; S, 13.02.

3.3.2. 2,6-Bis(((1-methyl-1,2-dicarba-closo-dodecaborany l)thio)methyl)pyridine [(py)c-Me)]

The procedure was analogous to that described for [(py)*c*-H] using 1-methyl-2-thiol-*o*-carborane as starting material (200 mg, 1.05 mmol) and 2,6-bis (bromomethyl)pyridine (139 mg, 0.525 mmol). The compound was purified by chromatography on silica gel using CH_2Cl_2/*n*–hexane (1:1) as mobile phase, to afford a white solid, yield: 177 mg, 0.4 mmol (70%). FTIR (KBr): υ (cm^{-1}) (B–H) 2579. ^{1}H-NMR ($CDCl_3$): δ (ppm) 2.18 (s, 6H, C_c–CH_3), 4.40 (s, 4H, py–(CH_2)–S), 7.48 (d, ^1J(H, H) = 7.7 Hz, 2H, H_{3py}), 7.84 (t, ^1J(H,H) = 7.7 Hz, 1H, H_{4py}). ^{13}C{^{1}H}-NMR: δ (ppm) 22.63 (s, C_c–CH_3), 42.53 (s, py–(CH_2)–S), 122.66 (s, C_{3py}), 138.10 (s, C_{4py}), 155.00 (s, C_{2py}). ^{11}B-NMR ($CDCl_3$): δ (ppm) −3.7 (d, ^1J(B,H) = 131.6 Hz, 1B), 5.03 (d, ^1J(B,H) = 144.2 Hz, 1B), −8.47 (d, ^1J(B,H) = 122.7 Hz, 2B), 9.61 (d, ^1J(B,H) = 148.4 Hz, 6B). Anal. Calc. for $C_{13}H_{33}B_{20}NS_2$: C, 32.28; H, 6.88; N, 2.90; S, 13.26. Found: C, 32.68; H, 6.90; N, 2.89; S, 13.06.

3.3.3. 2,6-Bis(((1,2-dicarba-closo-dodecaboranyl)thio) methyl)-3-chloropyridine [(Clpy)c-H]

The compound was prepared analogously to the method described for [(py)*c*-H], using 2,6-bis(-bromethyl)-3-chloropyridine (133 mg, 0.5 mmol) as starting material. The compound was purified by column chromatography on silica gel, using diethyl ether/*n*–hexane (3:2) as mobile phase, yield: 147 mg, 0.3 mmol (61%). FTIR (KBr): υ (cm^{-1}) (B–H) 2599. ^{1}H-NMR ($CDCl_3$): δ (ppm) 0.91 (m, hexane), 1.28 (m, hexane), 3.93 (br s, 1H, (C_c–H)$_a$), 4.00 (br s, 1H, (C_c–H)$_b$), 4.24 (s, 2H, py–(CH_2)$_a$–S), 4.43 (s, 2H, py–(CH_2)$_b$–S), 7.24 (d, ^3J(H,H) = 8.3 Hz, 1H, H_{5py}), 7.70 (d, ^3J(H,H) = 8.3 Hz, 1H, H_{4py}). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ (ppm) 29.71 (C_{hexane}), 40.53 (s, py–(CH_2)$_a$–S), 42.04 (s, py–(CH_2)$_b$–S), 67.85 and 74.00 (s, C_c–B), 123.56 (s, C_{5py}), 138.21 (s, C_{4py}), 151.96 (s, C_{6py}), 152.97 (s, C_{2py}). ^{11}B-NMR ($CDCl_3$): δ (ppm) −1.20 (d, ^1J(B,H) = 151.4 Hz, 1B), −4.49 (d, ^1J(B,H) = 150.2 Hz, 1B), −8.50 (4B), −12.16 (d, ^1J(B,H) = 173.5 Hz, 4B). Anal. Calc. for $C_{11}H_{28}B_{20}ClNS_2 \times 1/2\ C_6H_{14}$: C, 31.53; H, 6.62; N, 2.63; S, 12.02. Found: C, 31.63; H, 6.41; N, 2.56; S, 11.53.

3.3.4. 2,6-Bis(((1-methyl-1,2-dicarba-closo-dodecabo ranyl)thio)methyl)-3-chloropyridine [(Clpy)c-Me]

The compound was prepared analogously to the method described for [(py)*c*-Me] using 2,6-bis(bromomethyl)-3-chloropyridine (133 mg, 0.5 mmol) as starting material. The compound was purified by column chromatography on silica gel, using dichloromethane/*n*–hexane (3:2) as mobile phase, yield: 154 mg, 0.3 mmol (60%). FTIR (KBr): υ (cm^{-1}) (B–H) 2587. ^{1}H-NMR ($CDCl_3$): δ (ppm) 2.12 (s, 3H, (C_c–CH_3)$_a$), 2.12 (s, 3H, (C_c–CH_3)$_b$), 4.20 (s, 2H, py–(CH_2)$_a$–S), 4.38 (s, 2H, py–(CH_2)$_b$–S), 7.30 (d, ^3J(H, H) = 8.3 Hz, 1H, H_{5py}), 7.71 (d, ^3J(H,H) = 8.3 Hz, 1H, H_{4py}). ^{11}B-NMR ($CDCl_3$): δ (ppm) −3.17 (1B), −4.80 (d, ^1J(B,H) = 152.00 Hz, 1B), −9.42 (8B). Anal. Calc. for $C_{13}H_{32}B_{20}ClNS_2$: C, 30.13; H, 6.22; N, 2.70; S, 12.37. Found: C, 31.10; H, 6.19; N, 2.85; S, 12.08.

3.3.5. 2,5-Bis(((1,2-dicarba-closo-dodecaboranyl)thio) methyl)thiophene [(tp)c-H]

To a three necked round bottom flask (15 ml) containing deoxygenated methanol (10 ml) were added sodium metal (39 mg, 1.7 mmol) and 1-thiol-*o*-carborane (300 mg, 1.7 mmol). After stirring for 1 h, 2,5-bis(chloromethyl)thiophene (155 mg, 0.9 mmol) was added and the mixture was allowed to reflux for 4 h. After cooling and removal of solvent in vacuum, the residue was extracted with chloroform (15 ml) and the organic layer was washed with water (2 × 10 ml), dried over anhydrous magnesium sulfate, and vacuum evaporated to afford a yellow oil. The compound was purified by column chromatography on silica gel, using dichloromethane/*n*–hexane (1:1) as mobile phase, yield: 180 mg, 0.4 mmol (46%). FTIR (KBr): υ (cm^{-1}) (B–H) 2593. ^{1}H-NMR ($CDCl_3$): δ (ppm) 3.77 (s, 2H, C_c–H), 4.29 (s, 4H, tp–(CH_2)–S), 6.84 (s, 2H, H_{3tp}). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ (ppm) 35.93 (s, tp–(CH_2)–S), 67.80 and 73.91 (B–C_c), 127.80 (s, C_{3tp}), 137.63 (s, C_{2tp}). ^{11}B{^{1}H}-NMR ($CDCl_3$): δ (ppm) −1.09 (1B), −4.43 (1B), −8.01(2B), −9.61 (2B), −12.15 (4B). Anal. Calc. for $C_{10}H_{28}B_{20}S_3$: C, 26.07; H, 6.13; S, 20.88. Found: C, 25.89; H, 6.36; S, 20.66.

3.3.6. 2,5-Bis(((1-methyl-1,2-dicarba-closo-dodecabo ranyl)thio)methyl)thiophene [(tp)c-Me]

This compound was prepared analogously to the method described for [(tp)*c*-H] using 1-methyl-2-thiol-*o*-carborane (200 mg, 1.1 mmol) and 2,5-bis(-chloromethyl)thiophene (95 mg, 0.5 mmol) as starting material. The compound was purified by column chromatography on silica gel, using dichloromethane/*n*–hexane (1:1) as mobile phase, yield: 168 mg, 0.3 mmol (66%). FTIR (KBr): υ (cm^{-1}) (B–H) 2593. ^{1}H-NMR ($CDCl_3$): δ (ppm) 2.11 (s, 6H, C_c–CH_3), 4.26 (s, 4H, tp–(CH_2)–S), 6.87 (s, 2H, H_{3tp}). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ (ppm) 23.31 (s, C_c–CH_3), 35.90 (s, tp–(CH_2)–S), 79.79 and 80.92 (B–C_c), 127.97 (s, C_{3tp}), 137.54 (s, C_{2tp}). ^{11}B{^{1}H}-NMR ($CDCl_3$): δ (ppm) −3.07 (1B), −4.07 (1B), −9.37 (8B). Anal. Calc. for $C_{12}H_{32}B_{20}S_3$: C, 29.49; H, 6.60; S, 19.68. Found: C, 29.89; H, 6.95; S, 19.89.

3.4. Synthesis of nido species

3.4.1. Methyl triphenyl phosphonium salt of 2,6-bis(((7,8-dicarba-nido-undecaborate)-thio)methyl) pyridine (–2) [(py)n-H]$^{2-}$

To a necked round bottom flask (25 ml) containing deoxygenated ethanol (15 ml), was added KOH (588 mg, 8.9 mmol). After stirring for 15 min at r.t., 2,6-bis(((1,2-carboranyl)thio)methyl)pyridine (406 mg, 0.9 mmol) was added. The mixture was allowed to stir overnight at r.t. After removal of solvent under vacuum, the residue was dissolved in water (5 ml) and an excess of methyl triphenyl phosphonium bromide in water (10 ml) was added to afford a white solid, yield: 695 mg, 0.7 mmol (79%). FTIR (KBr): υ (cm^{-1}) (B–H) 2516. ^{1}H-NMR ($(CD_3)_2CO$): δ (ppm) −2.48 (br s, 2H, B–*H*–B), 3.19 (d, ^1J(H,P) = 14.1 Hz, 6H, $[P(CH_3)(C_6H_5)_3]^+$), 3.89/3.92/4.12/4.13 (4 d, ^1J(H,H) = 12.7 Hz, 4H, py–(CH_2)–S), 7.25–7.81 (m, 33H, H_{ar}). ^{13}C{^{1}H}-NMR ($(CD_3)_2CO$): δ (ppm) 7.63 (d, ^1J(C,P) = 57.0 Hz, P(CH_3)$(C_6H_5)_3]^+$), 43.23 (s, py–(CH_2)–S), 119.165 (s, $[P(CH_3)(C_6H_5)_3]^+$), 120.36 (s, $[P(CH_3)(C_6H_5)_3]^+$), 121.15 (s, C_{4py}), 130.43 (d, J(C,P) = 13.9 Hz, $[P(CH_3)(C_6H_5)_3]^+$), 133.28 (d, J(C,P) = 11.1 Hz, $[P(CH_3)(C_6H_5)_3]^+$), 135.49 (s, $[P(CH_3)(C_6H_5)_3]^+$), 137.02 (s, C_{3py}), 159.0 (s, C_{2py}). ^{31}P{^{1}H}-NMR ($(CD_3)_2CO$): δ (ppm) 22.85 (s, $[P(CH_3)(C_6H_5)_3]^+$). ^{11}B-NMR ($(CD_3)_2CO$): δ (ppm) −9.24 (1B), −9.88 (1B), −13.41 (1B), −14.41 (1B), −16.88 (d, ^1J(B,H) = 142.4 Hz, 2B), −22.00 (d, ^1J(B,H) = 146.0 Hz, 1B), −32.62 (d, ^1J(B,H) = 92.8 Hz, 1B), 37.48 (d, ^1J(B,H) = 135.8 Hz, 1B). Anal. Calc. for $C_{49}H_{65}B_{18}NS_2P_2 \times 1H_2O$: C, 59.52; H, 6.63; N, 1.42; S, 6.49. Found: C, 58.40; H, 6.65; N, 1.39; S, 6.35.

3.4.2. Methyl triphenyl phosphonium salt of 2,6-bis(((7-methyl-7,8-dicarba-nido-unde-caborate)thio) methyl)pyridine (–2) [(py)n-Me]$^{2-}$

The method was analogous to the preparation of [(py)*n*-H]$^{2-}$ using 2,6-bis(((1-methyl-1,2-carboranyl)-thio)methyl)pyridine (36 mg, 0.1 mmol) as starting material and (25 mg, 0.4 mmol) of KOH in 5 ml of deoxygenated ethanol to afford a white solid, yield: 30 mg, 0.03 mmol (61%). FTIR (KBr): υ (cm^{-1}) (B–H) 2516. ^{1}H-NMR ($(CD_3)_2CO$): δ (ppm) −2.40 (br s, 2H, B*H*B), 1.29/1.32 (two s, 6H, C_c–CH_3), 3.2 (d, ^1J(H,P) = 14.0 Hz, 6H, $[P(CH_3)(C_6H_5)_3]^+$), 3.84/3.90/4.09 (three d, ^1J(H,H) = 12.1 Hz, 4H, py–(CH_2)–S), 7.26–7.83 (m, 33H, H_{ar}). ^{13}C{^{1}H}-NMR ($(CD_3)_2CO$): δ (ppm) 7.59 (d, J(C,P) = 57.1 Hz, $[P(CH_3)(C_6H_5)_3]^+$), 22.66 (s, C_c–CH_3), 43.47 (s, py–(CH_2)–S), 119.22 (s, $[P(CH_3)(C_6H_5)_3]^+$), 120.39 (s, $[P(CH_3)(C_6H_5)_3]^+$), 121.28 (s, C_{3py}), 130.21 (d, J(C,P) = 12.0 Hz, $[P(CH_3)(C_6H_5)_3]^+$), 133.30 (d, J(C,P) = 11.0 Hz, $[P(CH_3)(C_6H_5)_3]^+$), 135.00 (d, J(C,P) = 4.5 Hz, $[P(CH_3)(C_6H_5)_3]^+$), 136.48 (s, C_{4py}), 159.51 (s, C_{2py}). ^{31}P{^{1}H}-NMR ($(CD_3)_2CO$): δ (ppm) 22.89 (s, $[P(CH_3)(C_6H_5)_3]^+$). ^{11}B-NMR ($(CD_3)_2CO$): δ (ppm) −8.21 (d, ^1J(B,H) = 135.8 Hz, 2B), −11.22 (1B), −16.83 (2B), −17.75 (2B), −33.92 (d, ^1J(B,H) = 51.5 Hz, 1B), −36.09 (d, ^1J(B,H) = 138.9 Hz, 1B). Anal. Calc. for $C_{51}H_{69}B_{18}NS_2P_2 \times 2CH_2Cl_2$: C, 53.83; H, 6.02; N, 1.01; S, 4.83. Found: C, 53.65; H, 6.16; N, 1.18; S, 5.19.

3.4.3. Methyltriphenylphosphonium salt of 3-chloro-2,6-pyridil-(7-thiomethyl-7,8-di-carba-nido-und ecaborate) [(Clpy)n-H]$^{2-}$

This compound was prepared analogously to the method described for [(py)*n*-H]$^{2-}$, using [(Clpy)*c*-H] (75 mg, 0.15 mmol) as starting material, yield: 124 mg, 0.1 mmol (81%). FTIR (KBr): υ (cm^{-1}) (B–H) 2523. ^{1}H-NMR ($(CD_3)_2CO$): δ (ppm) −2.55/−2.51/−2.22/−2.20 (four br s, 2H, B–*H*–B), 3.21 (d, ^2J(P,H) = 14.1 Hz, 6H, $[P(CH_3)(C_6H_5)_3]^+$), 3.95–4.32 (m, 4H, py–CH_2–S), 7.35 (two d, 1H, ^3J(H,H) = 8.0 Hz, $^3J'$(H,H) = 8.2 Hz, H_{5py}, $H_{5py'}$), 7.67 (two d, ^3J(H,H) = 8.0 Hz, $^3J'$(H,H) = 8.2 Hz, 1H, H_{4py}, $H_{4py'}$), 7.77–8.00 (m, 30H, $[P(CH_3)(C_6H_5)_3]^+$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ (ppm) 8.00 (d, ^2J(C,P) = 57.9 Hz, $[P(CH_3)(C_6H_5)_3]^+$), 40.62/40.75/42.50/42.81 (four s, py–(CH_2)–S), 119.17 (s, $[P(CH_3)(C_6H_5)_3]^+$), 120.34 (s, $[P(CH_3)(C_6H_5)_3]^+$), 123.10 (s, C_{5py}), 123.21 (s, $C_{5py'}$), 128.01 (s, C_{3py}), 130.33 (d, J(C,P) = 12.1 Hz, $[P(CH_3)(C_6H_5)_3]^+$), 133.36 (d, J(C,P) = 11.3 Hz, $[P(CH_3)(C_6H_5)_3]^+$), 135.14 (d, J(C,P) = 3.0 Hz, $[P(CH_3)(C_6H_5)_3]^+$), 137.07 (s, C_{4py}), 155.82 (s, C_{6py}), 158.26 (s, C_{2py}), 158.45 (s, $C_{2py'}$). ^{11}B-NMR ($(CD_3)_2CO$): δ (ppm) −9.45 (d, ^1J(B,H) = 123.9 Hz, 2B), −16.80 (4B), −22.34 (d, ^1J(B,H) = 153.2 Hz, 1B), −32.63 (d, ^1J(B,H) = 124.5 Hz, 1B), −36.60 (d, ^1J(B,H) = 139.4 Hz, 1B). ^{31}P{^{1}H}-NMR ($(CD_3)_2CO$): δ (ppm) 22.91 (s, $[P(CH_3)(C_6H_5)_3]^+$). Anal. Calc. for $C_{49}H_{64}B_{18}ClNP_2S_2 \times 1H_2O$: C, 56.47; H, 6.34; N, 1.34; S, 6.15. Found: C, 56.51; H, 6.40; N, 1.29; S, 5.48.

3.4.4. Methyltriphenylphosphonium salt of 3-chloro-2,6-pyridil-(7-thiomethyl-8-methyl-7,8-dicarba-nido-undecaborate) [(Clpy)n-Me]$^{2-}$

This compound was prepared analogously to the method described for [(py)*n*-Me]$^{2-}$, using [(Clpy)*c*-Me] (40 mg, 0.1 mmol) as starting material. The reaction mixture was refluxed during 4 h, yield: 63 mg, 0.1 mmol (78%). ^{1}H-NMR ($(CD_3)_2CO$): δ (ppm) −2.44/−2.43/−2.18/−2.12 (four br s, 2H, B–*H*–B), 1.12/1.22/1.26/1.35 (four s, 6H, C_c–CH_3), 3.22 (d, ^2J(P,H) = 14.1 Hz, 6H, $[P(CH_3)(C_6H_5)_3]^+$), 3.93–4.25 (m, 4H, py–CH_2–S), 7.35 (d, ^3J(H,H) = 8.1 Hz, 1H, H_{5py}), 7.66 (d, ^3J(H,H) = 8.1 Hz, 1H, H_{4py}), 7.70–8.00 (m, 30H, $[P(CH_3)(C_6H_5)_3]^+$). ^{13}C{^{1}H}-NMR ($(CD_3)_2CO$): δ (ppm) 7.97 (d, ^1J(C,P) = 56.9 Hz, $[P(CH_3)(C_6H_5)_3]^+$), 22.41/22.76 (two br s, C_c–CH_3), 40.75/40.90/42.68

(three s, py–(CH_2)–S), 119.18 (s, $[P(CH_3)(C_6H_5)_3]^+$), 120.36 (s, $[P(CH_3)(C_6H_5)_3]^+$), 123.14 (s, C_{5py}), 123.26 (s, $C_{5py'}$), 128.30 (s, C_{3py}), 130.32 (d, J(C,P) = 12.8 Hz, $[P(CH_3)(C_6H_5)_3]^+$), 133.36 (d, J(C,P) = 11.3 Hz, $[P(CH_3)(C_6H_5)_3]^+$), 135.16 (s, $[P(CH_3)(C_6H_5)_3]^+$), 136.98 (s, C_{4py}), 137.05 (s, $C_{4py'}$), 155.19 (s, C_{6py}), 158.04 (s, $C_{2py'}$). ^{11}B-NMR ($(CD_3)_2CO$): δ (ppm) −8.31 (d, ^1J(B,H) = 129.9 Hz, 2B), −11.40 (d, ^1J(B,H) = 156.2 Hz, 1B), −17.48 (4B), −34.01 (1B), −36.17 (d, ^1J(B,H) = 147.8 Hz, 1B). ^{31}P{^{1}H}-NMR ($(CD_3)_2CO$): δ (ppm) 22.92 (s, $[P(CH_3)(C_6H_5)_3]^+$). Anal. Calc. for $C_{51}H_{68}B_{18}ClNP_2S_2$: C, 58.27; H, 6.51; N, 1.33; S, 6.10. Found: C, 58.04; H, 6.62; N, 1.32; S, 5.82.

3.5. X-ray structure determination of [(py)c-Me]

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 20 carefully centered reflections. The data obtained were corrected for Lorentz and polarization effects and for dispersion, and corrections for empirical absorption (ψ scan) were also applied. A total of 1375 independent reflections were collected by $\omega/2\theta$ scan mode ($2\theta_{max}$ = 50°).

The structure was solved by direct methods by using the MITRIL program [12], and least-squares refinements were performed using the SHELXL-93 program [13]. The molecule assumes 2-fold symmetry and it is partly disordered with the methyl group as well as the relevant host boron atom occupying two positions. The disordered carbon atom was refined with isotropic but rest of the non-hydrogen atoms with anisotropic displacement parameters. Hydrogen atoms were included in the calculations at fixed distances from their host atoms and treated as riding atoms using the SHELXL-93 default parameters.

4. Supplementary data

X-ray of experimental details, atomic positions parameters, thermal parameters, interatomic distances and angles for (Py*c*-Me) (11 pages). Ordering information is given on any current masthead page.

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