Synthesis of Pyridine NS_2 Ligands Incorporating 1-Methoxycarbonyl-2-thio(*o*-carborane). Are They a Route to "Carboranethiophene" Compounds?

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Facilitated benzothiophene condensation has been successfully achieved in pyridinedithia(*S*-phenyl)-substituted compounds, by complexation with Pd(II). In this work, the phenyl fragment in 2,6-bis(2′-methoxycarbonylphenylthiomethyl)pyridine is replaced by *o*-carborane. This moiety is often treated as a three-dimensional aromatic system, thus it was worthwhile to see their comparative behavior toward Pd(II). To perform the reaction the new compound 2,6-bis(2′-methoxycarbonyl-1′,2′-carboranyl-1′-thiomethyl)pyridine has been synthesized. Its complexation behavior toward Pd(II), using an alcohol as a solvent, induces the cluster's partial degradation and the reduction of Pd(II) to Pd(0). The reaction of the partially degraded ligand, [2,6-bis(7′-methoxycarbonyl-7′,8′-carboranyl-7′-thiomethyl) pyridine]$^{2-}$ with Pd(II) leads to a dinuclear species, where the ligand acts in a bidentate mode. One of the ligand's arms in the complex is uncoordinated and free. This result is supported by ME (MALDI-TOFF) and ^{1}H NMR variable-temperature studies.

Introduction

Recent studies in our group were focused to the synthesis of new ligands incorporating the NS_2 (pyridinedithia) coordinating unit. 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 appropriate NS_2 ligands, as 2,6-bis(2′-methoxycarbonylphenylthiomethyl)pyridine, represented in Figure 1. On the other hand, carboranyl compounds have found applications as electrolytes for nonaqueous 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 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 $S'S_2$ (thiophenedithia) should 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 task.

As mentioned, Pt(II) and Pd(II) induce an asymmetric non-base benzothiophene condensation in 2,6-bis(2′-cyanophenylthiomethyl)pyridine and 2,6-bis(2′-methoxycarbonylphenylthiomethyl)pyridine. Due to the geometrical, chemical, and aromatic[5] similarities attributed to the *o*-carboranyl and phenyl fragments, in the present work the phenyl moiety is replaced by *o*-carborane in the aim of comparing their respective behaviors in NS_2 ligands and, in particular, its reactivity toward Pd(II) in the absence of any base.

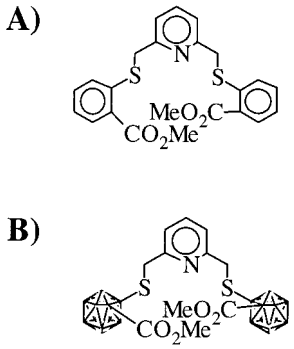

Figure 1. Schematic drawing of 2,6-bis(2′-methoxycarbonylphenylthiomethyl)pyridine (A) and **L1** (B) ligands. −S− and −CO_2Me are bonded to the carbon atoms at the carborane cluster $C_2B_{10}H_{10}$.

Experimental Section

Materials. Commercial methyl propiolate, decaborane, and a 1.6 M solution of *n*-buthyllithium in hexane were used as purchased. 1-Methoxycarbonyl-*o*-carborane[6] and 2,6-bis(bromomethyl)pyridine[7] were synthesized as reported. Degassed diethyl ether was stored over sodium benzophenone before use. All organic and inorganic salts were

(1) Casabó, J.; Escriche, Ll.; Alegret, S.; Jaime, C.; Pérez-Jiménez, C.; Mestres, L.; Rius, J.; Molins, E.; Miravitlles, C.; Teixidor, F. *Inorg. Chem.* **1991**, *30*, 1893.
(2) Teixidor, F.; Sánchez, G.; Lucena, N.; Escriche, Ll.; Kivekäs, R.; Casabó, J. *J. Chem. Soc., Chem. Commun.* **1992**, 163.
(3) Teixidor, F.; Viñas, C.; Anglès, P.; Kivekäs, R.; Sillanpää, R. *Inorg. Chem.* **1999**, *38*, 1642.
(4) (a) Plešek, J. *Chem. Rev.* **1992**, *92*, 269. (b) Viñas, C.; Gomez, S.; Bertran, J.; Teixidor, F.; Dozol, J. F.; Rouquette, H. *Chem. Commun.* **1998**, 191. (c) Viñas, C.; Gomez, S.; Bertran, J.; Teixidor, F.; Dozol, J. F.; Rouquette, H. *Inorg. Chem.* **1998**, *37*, 14, 3640. (d) Viñas, C.; Bertran, J.; Gomez, S.; Teixidor, F.; Dozol, J. F.; Rouquette, H.; Kivekäs, R.; Sillanpää, R. *Dalton* **1998**, 2849.
(5) (a) *Boron Compounds, Gmelin Handbook of Inorganic Chemistry*; Springer-Verlag: West Berlin, 1981; 1st supplement, Vol. 3, and earlier volumes. (b) Grimes, R. N. *Carboranes*; Academic: New York, 1970. (c) Grimes, R. N. *Metal Interactions with Boron Clusters*; Plenum: New York, 1982. (d) Olah, G. A.; Prakash; G. K. S.; Williams, R. E.; Field, L. E.; Wade, K. *Hypercarbon Chemistry*; Wiley: New York, 1987. (e) Bregadze, V. I. *Chem. Rev.* **1992**, *92*, 177.
(6) Heying, T. L.; Ager, J. W.; Clark, S. L.; Mangold, D. J.; Goldstein, H. L.; Hillman, M.; Polak, R. J.; Szymanski, J. W. *Inorg. Chem.* **1963**, *2*, 1089.
(7) Baker, W.; Buggle, K. M.; McOmie, J. F. W.; Watkins, D. A. *J. Chem. Soc.* **1958**, 3594.

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analytical reagent grade and were used as received. Solvents were reagent grade.

Physical Measurements. Microanalyses were performed by using a Perkin-Elmer 240B microanalyzer. IR spectra were obtained as KBr pellets on a Nicolet 710-FT spectrophotometer. The ^{1}H NMR (300.13 MHz), ^{11}B NMR (96.29 MHz), and ^{13}C{^{1}H} NMR (75.47 MHz) spectra were recorded on a Bruker ARX 300 spectrometer; NMR chemical shifts of are given in ppm. Chemical shift values for ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were referenced to an internal standard of $SiMe_4$. Chemical shift values for ^{11}B NMR spectra were referenced relative to external $BF_3{\cdot}OEt_2$. Unless otherwise specified all operations were carried out using Schlenk techniques.

Synthesis of 1-Mercapto-2-methoxycarbonyl-*o*-carborane [1-SH-2-CO$_2$Me-1,2-C$_2$B$_{10}$H$_{10}$]. To a solution of 1-methoxycarbonyl-*o*-carborane (1.86 g, 9.20 mmol) in diethyl ether (60 mL) at 0 °C was added slowly *n*-butyllithium (7.7 mL, 11.5 mmol). The solution was stirred at this temperature for 1 h, then maintained to room temperature for 30 min, and then cooled again to 0 °C. At this point sulfur powder (0.38 g, 12.00 mmol) was slowly added over a period of 30 min. Once the addition was finished the reaction was warmed to room temperature, treated with aqueous HCl, and extracted with diethyl ether (2 × 50 mL). After the solvent was dried over magnesium sulfate, it was evaporated under reduced pressure. Purification by column chromatography (silica-G, hexane/ethyl acetate (10/1)) yielded the analytically pure compound (R_f = 0.03). Yield: 0.59 g (27%). FTIR: ν (C−H) 2959 cm^{-1}, (B−H) 2608 and 2587 cm^{-1}, (C═O) 1750 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 3.93 (s, 3H, COOC*H*$_3$), 4.04 (b s, 1H, −S*H*). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 55.22 (s, −COO*C*H$_3$), 73.27 (s, C_c), 159.02 (s, −*C*OOCH$_3$). ^{11}B NMR ($CDCL_3$) δ: −0.08 (d, ^1J(B,H) = 152.0 Hz, 1B), −4.41 (d, ^1J(B,H) = 150.8 Hz, 1B), −7.49 (2B), −8.76(4B), −9.87 (2B). MS *m*/*z*: calcd for $C_4H_{14}B_{10}O_2S$ 234.31 found 234.05.

Synthesis of 2,6-Bis(2′-methoxycarbonyl-1′,2′-carboranyl-1′-thiomethyl)pyridine (L1). To a solution of 1-mercapto-2-methoxycarbonyl-*o*-carborane (0.52 g, 2.20 mmol) in diethyl ether (100 mL) at 0 °C were added potassium carbonate (0.49 g, 3.60 mmol) and water (64 μL, 3.6 mmol). The solution was stirred at this temperature for 30 min and then maintained at room temperature during 30 min more. To this suspension, 2,6-bis(bromomethyl)pyridine (0.29 g, 1.10 mmol) was added. The mixture was stirred for 2 h at room temperature. A white precipitate appeared (KBr) and was filtered. The filtrate was evaporated under reduced pressure. The compound was obtained in 90% yield. Purification by chromatography on silica-G using hexane/ethyl acetate (3/1) as the mobile phase (R_f = 0.18). FTIR: ν (C_{aryl}-H) 3065 cm^{-1}, (C_{alkyl}-H) 2966 cm^{-1}, (B−H) 2594 cm^{-1}, (C═O) 1750 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 0.91 (m, −CH$_3$ hexane), 1.28 (bs, −CH$_2$− hexane), 3.91 (s, 6H, −COOCH$_3$), 4.35 (s, 4H, py-C*H*$_2$−S), 7.30 (d, ^3J(H,H) = 7.6 Hz, 2H, H_{3py}), 7.72 (t, ^3J(H,H) = 7.6 Hz, 1H, H_{4py}). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 29.67 (s, hexane), 42.66 (s, py−*C*H$_2$−S), 55.18 (s, −COO*C*H$_3$), 79.98 (s, C_c-S), 81.91 (s, C_c-COOCH$_3$), 122.71 (s, C_{3py}), 138.19 (s, C_{4py}), 154.33 (s, C_{2py}), 159.00 (s, −*C*OOCH$_3$). ^{11}B NMR ($CDCl_3$) δ: −0.71 (d, ^1J(B,H) = 152.6 Hz, 2B), −3.50 (d, ^1J(B,H) = 148.4 Hz, 2B), −9.02 to −10.25 (m, 16B). Anal. Calcd for $C_{15}H_{33}B_{20}NO_4S_2$ + 10% hexane: C, 32.29; H, 5.97; N, 2.41; S, 11.05. Found: C, 32.86; H, 5.84; N, 2.17; S, 10.51.

Synthesis of Tetramethylammonium 2,6-Bis(8′-methoxycarbonyl-7′,8′-dicarba-*nido*-undecaborate-7′-thiomethyl)pyridine. [H][NMe$_4$]-[L2]. Compound **L1** (0.22 g, 0.40 mmol) was dissolved in methanol (50 mL). The solution was allowed to stir overnight at room temperature. After evaporation of the solvent under reduced pressure, slightly acidified water (30 mL) was added to the residue and the solution was filtered through Zelite. To the resulting clear solution was added an excess of tetramethylammonium chloride in water (5 mL), while N_2 was bubbled; a white solid precipitated. The solid was collected by filtration under N_2 atmosphere, washed with water (2 × 5 mL), and dried under vacuum to get a white solid. Yield: 0.21 g (83%). FTIR: ν (C_{aryl}-H) 3044 cm^{-1}, (C_{alkyl}-H) 2959 cm^{-1}, (B−H) 2538 cm^{-1}, (C═O) 1715 cm^{-1}, (C═O···H) 1680 cm^{-1}, (N(CH$_3$)$_4$) 1490 cm^{-1}. ^{1}H NMR ((CD$_3$)$_2$CO) δ: −2.56 (b s, 2H, B*H*B), 3.47 (b s, 12H, N(C*H*$_3$)$_4$), 3.62 (s, 3H, −(COOC*H*$_3$)$_A$), 3.63 (s, 3H, −(COOC*H*$_3$)$_B$), 4.58 (m, 4H, py−C*H*$_2$−S), 8.00 (m, 2H, H_{3py}), 8.48 (m, 1H, H_{4py}). ^{13}C{^{1}H}, NMR ((CD$_3$)$_2$CO) δ: 37.41 (s, py−*C*H$_2$−S), 51.65 (s, −(COO*C*H$_3$)$_A$), 55.13 (s, N(*C*H$_3$)$_4$), 55.18 (s, −(COO*C*H$_3$)$_B$), 126.43 (s, C_{3py}), 146.66 (s, C_{4py}), 154.81 (s, C_{2py}), 170.08 (s, −*C*OOCH$_3$). ^{11}B NMR ((CD$_3$)$_2$CO) δ: −7.81 (d, ^1J(B,H) = 150.2 Hz, 2B), −12.42 (1B), −14.97 (1B), −16.71 (2B), −19.93 (1B), −32.29 (d, ^1J(B,H) = 134.1 Hz, 1B), −35.58 (d, ^1J(B,H) = 135.9 Hz, 1B). Anal. Calcd. for $C_{19}H_{46}B_{18}N_2O_4S_2$: C, 36.50; H, 7.42; N, 4.48; S, 10.25. Found: C, 36.27; H, 7.58; N, 4.44; S, 9.67.

Synthesis of [NMe$_4$]$_2$[Pd$_2$Cl$_2${L2}$_2$]. A solution of compound [H]-[NMe$_4$][**L2**] (50 mg, 7.2 × 10^{-5} mmol) and [PdCl$_2$(CH$_3$CN)$_2$] (19 mg, 7.2 × 10^{-5} mmol) in 10 mL of *t*-BuOH/CH_2Cl_2 (1/1) was refluxed for 3 h. After cooling, the yellow precipitate obtained was washed with water (2 × 3 mL) and ether (3 × 5 mL) and vacuum-dried. Yield: 39 mg (36%). FTIR: ν (C_{aryl}-H) 3044 cm^{-1}, (C_{alkyl}-H) 2952 cm^{-1}, (B−H) 2545 cm^{-1}, (C═O) 1715 cm^{-1}, (N(CH$_3$)$_4$) 1483 cm^{-1}. ^{1}H{^{11}B} NMR (CD_3CN) δ: −2.40 (b s, 1H, (B*H*B)$_A$), −2.60 (b s, 1H, (B*H*B)$_B$), 3.10 (s, 24H, N(C*H*$_3$)$_4$), 3.70 (s, 12H, −COOC*H*$_3$), 4.60−4.90 (bb, 4H, (py−C*H*$_2$−S)$_{free}$), 4.89 (d, ^2J(H,H) = 18.4 Hz, 2H, (py−C*H*$_a$H$_b$−S)$_{fixed}$), 5.07 (d, ^2J(H,H) = 18.4 Hz, 2H, (py−CH$_a$*H*$_b$−S)$_{fixed}$), 7.62 (bd, 2H, H_{3py}), 7.68 (d, ^3J(H,H) = 8.1 Hz, 2H, H_{5py}), 8.05 (m, 2H, H_{4py}). ^{11}B NMR (CD_3CN) δ: −4.53 to −20.22 (7B), −31.72 (d, ^1J(B,H) = 117.3 Hz, 1B), −34.99 (d, ^1J(B,H) = 135.8 Hz, 1B). Anal. Calcd. for $C_{38}H_{90}B_{36}Cl_2N_4O_8Pd_2S_4$: C, 29.79; H, 5.92; N, 3.66; S, 8.37. Found: C, 29.84; H, 5.66; N, 3.44; S, 7.49. MS (MALDI-TOF) *m*/*z*: 692 [$^1/_2$(Pd$_2$Cl$_2$-{(**L2**)}$_2$)$^{2-}$] and 656 [$^1/_2$(Pd$_2${(**L2**)}$_2$)$^{2-}$].

Results and Discussion

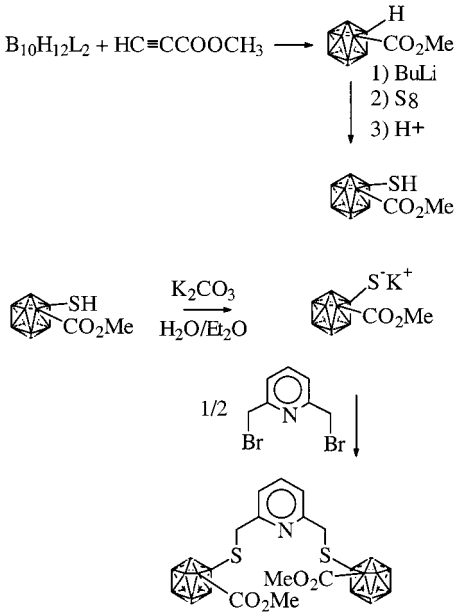
This work deals with the synthesis of 2,6-bis(2′-methoxycarbonyl-1′,2′-carboranyl-1′-thiomethyl)pyridine (**L1**), the carboranyl analogous of 2,6-bis(2′-methoxycarbonylphenyl thiomethyl)pyridine where the phenyl fragment is replaced by the carboranyl cluster. Both ligands contain the −CO_2Me substituent in ortho position (see Figure 1). To perform its synthesis, the 1-mercapto-2-methoxycarbonyl-*o*-carborane (1-SH-2-CO$_2$Me-1,2-C$_2$B$_{10}$H$_{10}$) was considered the most adequate starting material. Attempts to produce it from 1-CO$_2$Me-1,2-C$_2$B$_{10}$H$_{11}$ and bases such as NaH or ^{t}BuOK failed. The C−CO_2Me bond was broken, and *o*-carborane was recovered. Surprisingly a strong base such as BuLi was able to deprotonate the cluster's C−H moiety leaving unaltered the −CO_2Me group. The monolithiated salt reacts with sulfur, and after protonation, 1-SH-2-CO$_2$Me-1,2-C$_2$B$_{10}$H$_{10}$ was obtained in 27% yield. The synthesis of **L1** was attempted following the method previously described[8] for 2,6-bis((*R*)-phenylthiomethyl)pyridine which is based on NaOMe using methanol as a solvent. This procedure, however, did not produce **L1**. Most probably 1-SH-2-CO$_2$Me-1,2-C$_2$B$_{10}$H$_{10}$ suffers easy partial degradation under these conditions. Better results were obtained when diethyl ether and potassium carbonate were used instead of methanol and NaOMe. To enhance the solubilization of K_2CO_3, water in molar ratio 1:1 with respect to K_2CO_3, was added to the ether solution. The global synthesis of **L1** is shown in Scheme 1.

Compound **L1** has been characterized by elemental analysis, IR, NMR, and mass spectroscopies. The IR spectrum shows the expected ν(C_{aryl}−H) absorption at 3065 cm^{-1}, the ν(B−H) at 2594 cm^{-1}, and the ν(C═O) at 1750 cm^{-1} which prove the existence of the aromatic ring, the *closo*-C$_2$B$_{10}$H$_{10}$ cluster, and the ester group in the molecule. The ^{11}B NMR spectrum presents a 2:2:8:8 pattern in the range of −0.71 to −10.25 ppm which proves the closo nature of the carborane cluster. The ^{13}C{^{1}H} NMR spectrum shows the cluster carbon atoms resonances at 79.98 and 81.91 ppm, respectively.

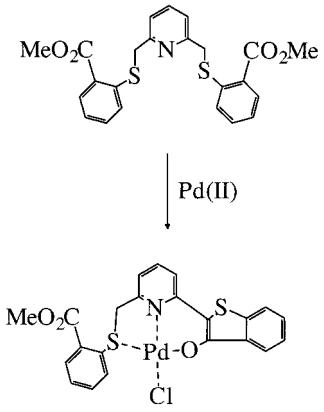
Ligand **L1** is geometrically (see Figure 1) and chemically similar to 2,6-bis(2′-methoxycarbonylphenylthiomethyl)pyridine. This last had proceeded to a benzothiophene condensation upon

(8) Teixidor, F.; Sánchez-Castelló, G.; Lucena, N.; Escriche, Ll.; Kivekäs, R.; Sundberg, M.; Casabó, J. *Inorg. Chem.* **1991**, *30*, 4931.

Scheme 1. Synthetic Process for **L1**



Scheme 2. Benzothiophene Condensation Induced by Pd(II) in 2,6-Bis(2′- Methoxycarbonylphenylthiomethyl)pyridine



reaction with $[PdCl_2(CH_3CN)_2]$ in ethanol. The *o*−CO_2Me substituent is necessary to produce the five-membered thiophene ring. Any other position does not permit the benzothiophene condensation shown in Scheme 2. To ascertain the chemical similarity of the two structurally alike ligands **L1** and 2,6-bis-(2′-methoxycarbonylphenylthiomethyl)pyridine, the reaction of **L1** with $[PdCl_2(CH_3CN)_2]$ was also performed. This was attempted in different solvents {ethanol, CH_3CN/ethanol (1/1), and methanol/CCl_4 (1/1)} but in all cases a large quantity of Pd(0) (black powder) and a mixture of partially degraded cluster compounds was obtained. In no case there was any evidence that the closo cluster had been retained. On the contrary, a nido cluster containing species was produced.

This simple reaction illustrates some points of resemblance between **L1** and 2,6-bis(2′-methoxycarbonylphenylthiomethyl)-pyridine and also stresses the singularities of both compounds as a result of the phenyl and *o*-carborane fragments. A common point in both compounds is their tendency to become anionic upon reaction to Pd(II). The aromatic and neutral 2,6-bis(2′-methoxycarbonylphenylthiomethyl)pyridine reverted to the monoanionic asymmetric ligand upon a benzothiophene condensation (Scheme 2). The Pd(II) in ethanol was responsible of the condensation process in absence of any base. Also the *o*-carboranyl containing and neutral **L1** ligand changed to an anionic species, but this was not the carboranyl analogous to the benzothiophene. The new anionic species was due to the closo to nido transformation of the cluster cage. Due to the electron-withdrawing capacity of the two cluster carbon substituents, the closo to nido transformation could be due either to a spontaneous partial degradation caused by the ethanol or, contrarily, to the Pd(II) in solution.

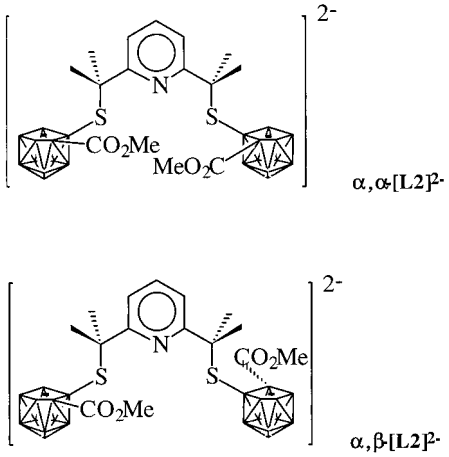


Figure 2. Schematic drawing of α,α- and α,*β*-[**L2**]$^{2-}$ isomers.

To ascertain it, compound **L1** was allowed to stir in methanol overnight in absence of Pd(II) at room temperature. After evaporation and solubilization in acetone-d_6, the appearance of a signal corresponding to the B−H−B bridge in the ^{1}H NMR spectrum at approximately −2.56 ppm, and the 2:1:1:2:1:1:1 ^{11}B−NMR spectrum pattern in the range of −7.81 to −35.58 ppm indicates that the closo cluster structure was not stable in methanol and that partial degradation had taken place. The partial degradation of **L1** was accomplished neither with the concourse of any conventional base nor with Pd(II). The partial degradation of **L1** agrees with recent results in our group which indicate that the C−S−R thioether moiety behaves as an electron-withdrawing group.[9] Since the remaining cluster carbon is also bonded to a second electron-withdrawing group (CO_2Me), the combination of both substituents makes the B(3) and B(6) ready for a nucleophilic attack. Thus, soft nucleophiles such as alcohols could remove B(3) or B(6) to produce anionic partially degraded clusters. The ^{1}H NMR spectrum of the free ligand [2,6-bis(7′-methoxycarbonyl-7′,8′-carboranyl-7′-thiomethyl)-pyridine]$^{2-}$, [**L2**]$^{2-}$, shows the diastereotopic CH_2 protons as a broad singulet centered at 4.5 ppm. The possible diastereomers are α,α-[**L2**]$^{2-}$ and α,*β*-[**L2**]$^{2-}$, the last one having its optical enantiomer. They are represented in Figure 2, and no attempts have been made to obtain their separation.

It has been proven that a carboranethiophene fragment cannot be produced by reaction of **L1** with Pd(II) in alcohols. Since polar solvents are required and **L1** no longer exist in these solvents, it seems that the carboranethiophene condensation reaction has no chance of occurring.

The reaction of partially degraded ligand, [**L2**]$^{2-}$, with $[PdCl_2(CH_3CN)_2]$ in the molar ratio 1:1 was conducted in a mixture of CH_2Cl_2/^{t}BuOH. A solid did separate which permitted its characterization by spectroscopic techniques. In the complex, the ligand's structure has not been modified, although the shape and position of their resonances in the ^{1}H and ^{11}B NMR spectra have changed considerably. The ^{1}H NMR spectrum of the complex shows at room temperature two well-defined reso-

(9) Viñas, C.; Pedrajas, J.; Bertran, J.; Teixidor, F.; Kivekäs, R.; Sillanpää, R. *Inorg. Chem.* **1997**, *36*, 2482.

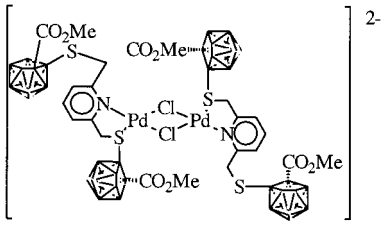


Figure 3. Proposed structure for $[NMe_4]_2[Pd_2Cl_2\{\mathbf{L2}\}_2]$.

nances corresponding to the diastereotopic proton atoms. One is a doublet of doublets corresponding to a rigid $-CH_aH_b$ (geminal splitting), and the second corresponds to two broad bands due to diastereotopic $-CH_aH_b$. The broad bands show evidence of fast rotation through the CH_2-py bond. In addition, two B−H−B resonances at −2.40 and −2.60 ppm are observed along with three resonances at the aromatic zone corresponding to H_{3py}, H_{4py}, and H_{5py}. The ^{1}H NMR spectrum is consistent with one $[N(CH_3)_4]^+$ for every two cluster cages and fully supports the existence of two nonequivalent arms. The molecular weight of the complex was obtained by a MALDI-TOF analysis, which confirms the proposed binuclear nature of the complex. According to these data a dinuclear structure is proposed (see Figure 3). The ligand $[\mathbf{L2}]^{2-}$ would act as bidentate through N and S although it has three coordinating binding units (one N and two S). The remaining two sites of Pd would be occupied by bridging chlorides.

To ascertain the fast free rotation of one of the two arms in the pyridine derivative ligand, variable-temperature ^{1}H NMR spectra of the complex $[NMe_4]_2[Pd_2Cl_2\{\mathbf{L2}\}_2]$ were recorded in the range of 24 to −33 °C in CD_3CN solution. On cooling to −33 °C, the spectral lines sharpened to give a better resolved spectrum. The complex methylene region consists of several sets of AB doublets, two of them remaining unaltered throughout the low-temperature experiment. This doublet of doublets corresponds to the rigid $-CH_aH_b-$, while the second one corresponds to the methylene protons in the noncoordinated pyridine arm. New resonances are found at 5.7, 5.0, and 4.5 ppm, which are doublets with geminal splitting. It was not possible to distinguish the exact number of resonances that were underlying the resonance of the rigid $-CH_aH_b-$ (5.0 ppm); however, the multiple doublets obtained are consistent with different quenched conformations of this uncoordinated arm.

Consistent with this explanation is the appearance of new resonances at the ^{1}H NMR pyridine region. The set of variable-temperature ^{1}H NMR experiments are shown in Figure 4. These confirm the existence of a dynamic process in one of the two arms of the ligand $[\mathbf{L2}]^{2-}$ while the second one remains unaltered, discarding a S,S metal switch between the two arms.[10]

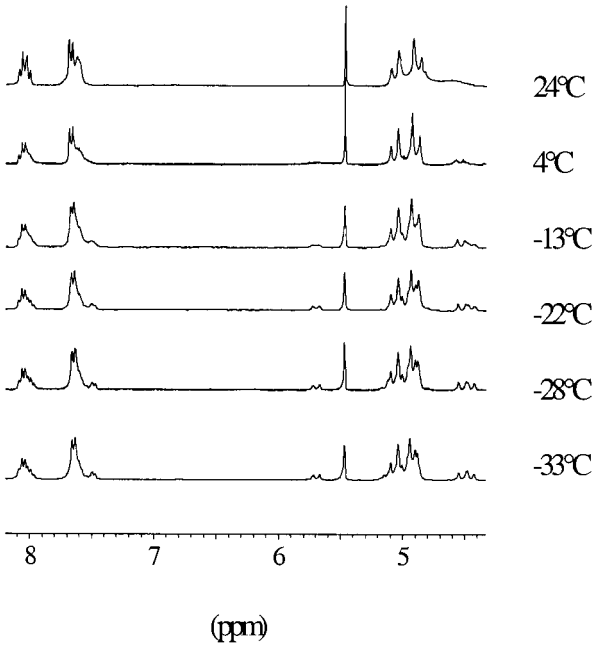


Figure 4. Variable-temperature ^{1}H NMR spectra of complex $[NMe_4]_2[Pd_2Cl_2\{\mathbf{L2}\}_2]$ in CD_3CN.

Conclusions

The new ligand 2,6-bis(2′-methoxycarbonyl-1′,2′-carboranyl-1′-thiomethyl)pyridine, **L1**, incorporating a NS_2 coordinating unit and two carborane cages, has been synthesized. Although structurally very similar to the corresponding phenyl analogues, they have a very dissimilar behavior toward Pd(II) in polar solvents. While both tend to modify themselves to become anionic, they do this in a very different manner. The carboranyl NS_2 closo compound **L1** has an easy pathway to become anionic, maintaining the original NS_2 coordinating moiety. The $-S-R$ and $-CO_2Me$ substituents at the cluster carbon atoms in **L1** are both electron-withdrawing groups, and their combination produces, in alcohols, the cluster deboronation to yield the dianionic ligand $[\mathbf{L2}]^{2-}$. **L1** becomes anionic irrespective of the presence or absence of Pd(II) or base; it only requires a smooth nucleophile. On the other hand, 2,6-bis(2′-methoxycarbonyl-phenylthiomethyl)pyridine requieres the presence of Pd(II) or a base to perform the modification to an anionic form. An interesting potential function of $[\mathbf{L2}]^{2-}$ and other structurally related carborane derivative compounds is their ability to coordinate to metal through the NS_2 moiety. In effect, the existence of inner, low coordinating, negative moieties provides for a distinct coordinating behavior of the metal. The metal ion satisfies within the molecule its need for charge compensation, permitting, on the other hand, the availability of coordinating sides for other purposes (e.g., in catalysis or in active transport in membranes). We are currently studying what effects may be produced in coordination with the existence of both moieties, the NS_2 and the *o*-carborane.

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(10) Abel, E. W.; Heard, P. J.; Orrell, K. G.; Hursthouse, M. B.; Mazid, M. A. *J. Chem. Soc., Dalton Trans.* **1993**, 3795.