sensitive starting solutions. Our new design of the airtight IR OTTLE cell will be reported elsewhere.[28]

Registry No. THF, 109-99-9; $[Mn(CO)_3(DBCat)]^-$, 125665-75-0; $[Mn(CO)_3(DBCat)]^{2-}$, 125665-79-4; $[Mn(CO)_3(DBSQ)]$, 126388-40-7; $[Mn(CO)_3(DBQ)]^+$, 134109-78-7; $[Mn(CO)_3(THF)(DBQ)]^+$, 134078-40-3; $[Mn(CO)_3(PPh_3)(DBQ)]^+$, 134078-41-4; $[Mn(CO)_4(DBQ)]^+$, 134078-42-5; $[Mn(CO)_3(THF)(DBSQ)]$, 83951-62-6; $[Mn(CO)_3(PPh_3)(DBSQ)]$, 83970-81-4; $[Mn(CO)_4(DBSQ)]$, 83970-82-5; $[Mn(CO)_3(THF)(DBCat)]^-$, 134078-43-6; $[Mn(CO)_3(PPh_3)(DBCat)]^-$, 134078-44-7; $[Mn(CO)_4(DBCat)]^-$, 134078-45-8; $Bu_4N[Mn(CO)_3(DBCat)]$, 125665-77-2; PPh_3, 603-35-0; CO, 630-08-0; CH_2Cl_2, 75-09-2; Au, 7440-57-5; Pt, 7440-06-4; Hg, 7439-97-6.

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(38) Gaš, B.; Klíma, J.; Záliš, S.; Vlček, A. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *222*, 161.

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Macrocycles Incorporating Sulfur and *nido*-Carborane Cages: Reactivity toward Nickel(II) and Palladium(II). Molecular Structures of $Pd\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}_2$ and $Pd\{P(C_6H_5)_3\}Cl\{7,8\text{-}\mu\text{-}(SCH_2CH_2S)C_2B_9H_{10}\}$

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The reactions of *exo*-dithio-7,8-dicarba-*nido*-undecaborate derivatives with Ni(II) and Pd(II) chlorides and phosphine chloride complexes are presented and discussed. Three different stoichiometries have been observed, $[MLCl_2]^-$, $[M_2L_2Cl_2]$, and $[ML_2]$. The capacity of these ligands to act as tricoordinating agents through the two sulfur atoms and a $B(3)\text{-}H\rightarrow M$ bond is introduced and discussed. A regularity in the value of the dihedral angle ω (planes defined by S–M–S and $S\text{-}C_c\text{-}C_c\text{-}S$) and the length of the exo-cluster chain has been observed. The shorter the exo-cluster chain is, the smaller the ω angle. The molecular structures of $Pd\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}_2$ and $Pd\{P(C_6H_5)_3\}Cl\{7,8\text{-}\mu\text{-}(SCH_2CH_2S)C_2B_9H_{10}\}$ have been determined. The former crystallizes in space group $P2_1/c$ with 2 formula units per cell. The cell dimensions are $a = 8.140$ (2) Å, $b = 20.083$ (8) Å, $c = 11.953$ (3) Å, and $\beta = 104.09$ (2)°. The latter orystallizes in space group $P2_1/n$ with 4 formula units per cell. The cell dimensions are $a = 13.424$ (2) Å, $b = 10.315$ (2) Å, $c = 20.008$ (4) Å, and $\beta = 90.83$ (1)°.

Introduction

Thioethers are usually considered to be fairly poor ligands, not strongly bound to metals, and easily displaced by other ligands.[1] In their complexes, the "normal" coordination number of the metal ion is usually maintained, and metal–halogen coordination is dominant over metal–thioether.[2,3] Due to these characteristics most of the work about thioethers has been restricted to obtaining labile complexes, to studying pyramidal inversion at sulfur,[4-7] and searching for models for what they may reveal about structural changes accompanying oxidation and reduction of copper in metalloenzymes.[8,9] The poor ligand capacity of dithioethers has stimulated the study of all-sulfur multidentate ligands, mainly macrocycles. The polythioethers 1,4,7-trithiacyclononane (9S3),[10-13] 1,4,7,10,13,16-hexathiacyclooctadecane (18S6),[14-16] and their expanded homologues 12S3[17] and 24S6[18] have received considerable attention these last few years.

As opposed to normal dithioethers, here we wish to report on the high ligand capacity of another type of these compounds. These are derivatives of the 7,8-dicarba-*nido*-undecaborate anion, and their reactivity toward Ni(II) and Pd(II) metal ions is reported here altogether with the molecular structures of $Pd\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}_2$ and $Pd\{P(C_6H_5)_3\}Cl\{7,8\text{-}\mu\text{-}(SCH_2CH_2S)C_2B_9H_{10}\}$. In these complexes metal–thioether coordination is dominant over metal–halogen coordination as opposed to normal dithioethers and some of them have been obtained by the diplacement of PPh_3 ligands, which is very uncommon in thioether chemistry. The exaltation of the ligand capacity has to be attributed to the carborane cage near the sulfur coordinating elements. Also, the capacity of these ligands to act as tricoordinating agents through the two sulfur atoms and a $B\text{-}H\rightarrow M$ bond is introduced. This type of bond has already been previously observed[19-23] but never with the boron

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(1) Ainscough, E. W.; Brodie, A. M.; Palmer, K. C. *J. Chem. Soc., Dalton Trans.* **1976**, 2375.
(2) Lewason, W.; McAuliffe, C. A.; Murray, S. G. *J. Chem. Soc., Dalton Trans.* **1975**, 1566.
(3) Hartley, F. R.; Murray, S. G.; Levason, W.; Soutter, H. E.; McAuliffe, C. A. *Inorg. Chim. Acta* **1979**, *35*, 265.
(4) Abel, E. W.; Bhargava, S. K.; Kite, K.; Orell, K. G.; Sil, V.; Williams, B. L. *Polyhedron* **1982**, *3*, 289.
(5) Abel, E. W.; Orell, K. G.; Platt, A. W. G. *J. Chem. Soc., Dalton Trans.* **1983**, 2345.
(6) Boeré, R. T.; Willis, C. J. *Inorg. Chem.* **1985**, *24*, 1059.
(7) Gulliver, D. J.; Hale, A. L.; Levason, W.; Murray, S. G. *Inorg. Chim. Acta* **1983**, *69*, 25.
(8) Baker, E. N.; Norris, G. E. *J. Chem. Soc., Dalton Trans.* **1977**, 877.
(9) Olmstead, M. M.; Musker, W. K.; Kessler, R. M. *Inorg. Chem.* **1981**, *20*, 151.
(10) Bell, M. N.; Blake, A. J.; Schröder, M.; Küppers, H. J.; Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 250.
(11) Rawle, S. C.; Admans, G. A.; Cooper, S. R. *J. Chem. Soc., Dalton Trans.* **1988**, 93.
(12) Hüppers, H. J.; Wieghardt, K.; Yi-Hung, T.; Krüger, C.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 575.
(13) Wieghardt, K.; Küppers, H. J.; Raabe, E.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1101.
(14) Blake, A. J.; Gould, R. O.; Lavery, A. J.; Schröder, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 274.
(15) Hartman, J. A. R.; Hintsa, E. J.; Cooper, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 1208.
(16) Hartman, J. A. R.; Cooper, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 1202.
(17) Rawle, S. C.; Sewell, T. J.; Cooper, S. R. *Inorg. Chem.* **1987**, *26*, 3769.
(18) Rawle, S. C.; Hartman, J. A. R.; Watkin, D. J.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1986**, 1083.
(19) Green, M.; Howard, J. A. K.; James, A. P.; Jelfs, A. P.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1985**, 1778.
(20) Green, M.; Howard, J. A. K.; Jelfs, A. N. M.; Johnson, O.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 73.
(21) Green, M.; Howard, J. A. K.; James, A. P.; Jelfs, A. N. M.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 81.

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atom connected to both carborane carbons (B3) as is the case presented here.

Experimental Section

General Methods. *o*-Carborane-1,2-dithiol was synthesized from *o*-carborane (Dexsil Chemical Corp.).[24] The *exo*-dithio-7,8-dicarba-*nido*-undecaborate derivatives were synthesized as described elsewhere.[25-30]

All organic and inorganic salts were Fluka or Aldrich analytical reagent grade and were used as given.

All reactions were carried out under a dinitrogen atmosphere employing Schlenk techniques. Microanalyses (C, H, N) were performed in our analytical laboratory by using a Perkin-Elmer 240B microanalyzer. Infrared spectra (KBr pellets) were recorded in the region 4000–400 cm^{-1} by using a Perkin-Elmer 240 FT spectrophotometer. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM 400WB spectrometer.

Preparation of $[N(CH_3)_4]NiLCl_2$ (L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}$ and $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2N(Ts)CH_2CH_2)S)C_2B_9H_{10}\}$). To deoxygenated ethanol (30 cm^3) containing $[N(CH_3)_4[\{7,8\text{-}\mu\text{-}(S(CH_2CH_2N(Ts)CH_2CH_2)S)C_2B_9H_{10}\}$ (100 mg, 0.202 mmol) was added $NiCl_2{\cdot}6H_2O$ (49 mg, 0.202 mmol). Under a N_2 atmosphere the mixture was refluxed for 4 h. The resulting dark red solution was concentrated to a final volume of ca. 10 cm^3 and cooled (0 °C). A dark red solid separated, which was filtered out, washed with ethanol and hexane, and dried under vacuum overnight to afford a 70-mg yield (55.4%). Anal. Calc for $C_{17}H_{37}B_9Cl_2N_2NiO_2S_3$: C, 32.69; H, 5.97; N, 4.49. Found: C, 33.03; H, 6.17; N, 4.18. IR (cm^{-1}): ν(B–H) 2538.

The procedure and workup was as in the former case when $[N(CH_3)_4]\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}$ (100 mg, 0.336 mmol) was allowed to react with $NiCl_2{\cdot}6H_2O$ (81 mg, 0.336 mmol) to yield 110 mg of a brown solid (76%). Anal. Calcd for $C_8H_{26}B_9Cl_2NNiS_2$: C, 22.49; H, 6.13; N, 3.28. Found: C, 22.8; H, 6.2; N, 3.2. IR (cm^{-1}): ν(B–H) 2530. ^1H NMR (ppm, acetone-d_6): 3.44 ($N(CH_3)_4$), 2.83 (CH_2).

Preparation of $Ni_2L_2Cl_2$ (L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$ and $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2SCH_2CH_2SCH_2CH_2SCH_2CH_2)S)C_2B_9H_{10}\}$). The procedure and workup was as before; $Na\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$ (100 mg, 0.264 mmol) and $NiCl_2{\cdot}6H_2O$ (63 mg, 0.264 mmol) were mixed. Yield: 40 mg of a green product (16.6%). Anal. Calc for $C_{20}H_{52}B_{18}Cl_2Ni_2O_6S_4$: C, 26.70; H, 5.83. Found: C, 26.35; H, 5.48. IR (cm^{-1}): ν(B–H) 2539.

A compound with this same stoichiometry was obtained when $[N(CH_3)_4]\{7,8\text{-}\mu\text{-}(S(CH_2CH_2SCH_2CH_2SCH_2CH_2SCH_2CH_2)S)C_2B_9H_{10}\}$ (100 mg, 0.209 mmol) was allowed to react with $NiCl_2{\cdot}6H_2O$ (50 mg, 0.209 mmol) to yield 50 mg of a green product (24%). Anal. Calc for $C_{20}H_{52}B_{18}Cl_2Ni_2S_{10}$: C, 24.12; H, 5.26. Found: C, 24.85; H, 5.34. IR (cm^{-1}): ν(B–H) 2548.

Preparation of NiL_2 (L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$). This compound was obtained by following the same reported procedure when $[N(CH_3)_4]\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$ (100 mg, 0.32 mmol) was allowed to react with $NiCl_2{\cdot}6H_2O$ (77 mg, 0.32 mmol) to yield 25 mg (23%) of a brown solid. Anal. Calc for $C_{16}H_{44}B_{18}NiO_4S_4$: C, 28.18; H, 6.50. Found: C, 28.34; H, 6.80. IR (cm^{-1}): ν(B–H) 2544.

Preparation of PdL_2 (L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}$ and $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$). Under a dinitrogen atmosphere, $PdCl_2$ (59 mg, 0.336 mmol) was dissolved in a hot aqueous solution (20 cm^3) of KCl (50 mg, 0.672 mmol). To this warm stirred solution, $[N(CH_3)_4]\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}$ (100 mg, 0.336 mmol) in acetone (20 cm^3) was added. Upon mixing of the solutions, a solid separated immediately, which was filtered out and chromatographed over silica (acetone/methylene chloride) to yield an orange solid (80 mg, 86%). Anal. Calc for $C_8H_{28}B_{18}PdS_4$: C, 17.36; H, 5.10. Found: C, 17.25; H, 4.83. IR (cm^{-1}): ν(B–H) 2551, 2501. ^{11}B NMR ($BF_3{\cdot}Et_2O$, ppm, CH_3CN): −7.0 (1), −11.3 (4), (−17.0, −18.5, −19.7) (9), −30.6 (1), −33.7 (1), −36.6 (2).

Table I. Crystal Data and Details of Data Collection for $C_{20}H_{52}B_{18}O_6PdS_4$

chem formula	$C_{20}H_{52}B_{18}O_6PdS_4$	Z	2
fw	817.9	D_c/g cm^{-3}	1.433
a/Å	8.140 (2)	space group	$P2_1/c$
b/Å	20.083 (8)	radiation (λ/Å)	Mo Kα (0.71069)
c/Å	11.953 (3)		
β/deg	104.09 (2)	abs coeff/cm^{-1}	7.29
V/Å^3	1895.2 (1)	R	0.075
		R_w	0.056

In a similar reaction $Na\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$ (100 mg, 0.264 mmol) and K_2PdCl_4 (from 47 mg of $PdCl_2$, 0.264 mmol) were mixed. All work up was as before. Yield: 82 mg of an orange solid (76%). Anal. Calc for $C_{20}H_{52}B_{18}O_6PdS_4$: C, 29.37; H, 6.41. Found: C, 28.89; H, 6.31. IR (cm^{-1}): ν(B–H) 2529, 2553.

Preparation of $Pd_2L_2Cl_2$ (L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2SCH_2CH_2SCH_2CH_2SCH_2CH_2)S)C_2B_9H_{10}\}$ and $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2N(Ts)CH_2CH_2)S)C_2B_9H_{10}\}$). A compound with this stoichiometry was obtained by following the same reported procedure when $Cs\{7,8\text{-}\mu\text{-}(S(CH_2CH_2SCH_2CH_2SCH_2CH_2SCH_2CH_2)S)C_2B_9H_{10}\}$ (100 mg, 0.186 mmol) was allowed to react with K_2PdCl_4 (from 33 mg of $PdCl_2$, 0.186 mmol). The resulting solid was chromatographed over silica (acetone/methylene chloride) to yield 88 mg of a brown solid (86.7%). Anal. Calc for $C_{20}H_{52}B_{18}Cl_2Pd_2S_{10}$: C, 22.01; H, 4.80. Found: C, 21.66; H, 4.80. IR (cm^{-1}): ν(B–H) 2529. ^1H NMR (ppm, acetone-d_6): 2.07 (S-CH_2).

When $[N(CH_3)_4]\{7,8\text{-}\mu\text{-}(S(CH_2CH_2N(Ts)CH_2CH_2)S)C_2B_9H_{10}\}$ (100 mg, 0.202 mmol) and K_2PdCl_4 (from 36 mg of $PdCl_2$, 0.202 mmol) were allowed to react, a brown solid was obtained, which was chromatographed over silica (acetone/methylene chloride) to yield a brown compound (90 mg, 79.2%). Anal. Calc for $C_{26}H_{50}B_{18}Cl_2O_4N_2Pd_2S_6$: C, 27.75; H, 4.48; N, 2.49. Found: C, 27.89; H, 5.03; N, 2.76. IR (cm^{-1}): ν(B–H) 2539.

Reaction of $[N(CH_3)_4]\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$ with $Pd(COD)Cl_2$ under Basic Conditions. Synthesis of $Pd\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}_2$. To a round-bottom flask containing benzene-washed NaH (14 mg, 0.336 mmol) in thf (20 cm^3) was added $[N(CH_3)_4]\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$ (50 mg, 0.146 mmol). The mixture was stirred at room temperature for 1 h and the remaining solid eliminated by filtration. $Pd(COD)Cl_2$ (42 mg, 0,.146 mmol) was added, yielding a light brown solid, which was filtered out, washed with hexane, and dried in vacuo. Anal. Calc for $C_{12}H_{36}B_{18}O_2PdS_4$: C, 22.46; H, 5.65. Found: C, 22.63; H, 5.32. IR (cm^{-1}): ν(B–H) 2553.

Preparation of $Pd\{P(C_6H_5)_3\}ClL$ (L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}$, $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$, $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2SCH_2CH_2SCH_2CH_2SCH_2CH_2)S)C_2B_9H_{10}\}$, and $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2N(Ts)CH_2CH_2)S)C_2B_9H_{10}\}$). Under a dinitrogen atmosphere, $Pd\{P(C_6H_5)_3\}_2Cl_2$[31] (247 mg, 0.352 mmol) was added to a refluxing solution of $[N(CH_3)_3H]\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}$ (100 mg, 0.352 mmol) in ethanol (40 cm^3), separating in few minutes a yellow solid, which was filtered out, washed with ethanol (10 cm^3), and dried in vacuo (150 mg, 68%). Anal. Calc for $C_{22}H_{29}B_9ClPPdS_2$: C, 42.1; H, 4.66. Found: C, 39.6; H, 5.06. IR (cm^{-1}): ν(B–H) 2547. ^1H NMR (ppm, $CHCl_3$-d): 7.8–7.6 (Ar C–*H*); 3.63, 3.24, 2.79 (m).

Upon recrystallization in acetone good quality yellow crystals of $C_{22}H_{29}B_9ClPPdS_2$ were obtained.

A similar reaction was carried out with $Pd\{P(C_6H_5)_3\}_2Cl_2$ (185 mg, 0.264 mmol) and $Na\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$ (100 mg, 0.264 mmol) in ethanol (40 cm^3). After 2 h of refluxing, a small amount of solid remained, which was filtered out and discarded. The resulting solution was concentrated under vacuum (approximate final volume 5–10 cm^3) to yield an orange solid, which was filtered out, washed with diethyl ether, and vacuum-dried (120 mg, 59.8%). Anal. Calc for $C_{28}H_{41}B_9ClO_3PPdS_2$: C, 44.26; H, 5.44. Found: C, 45.0; H, 5.40. IR (cm^{-1}): ν(B–H) 2548. ^1H NMR (ppm, acetone-d_6): 7.5–7.8 (Ar *H*), 3.6–4.1 (CH_2).

The reaction of $Pd\{P(C_6H_5)_3\}_2Cl_2$ (147 mg, 0.209 mmol) with $Cs\{7,8\text{-}\mu\text{-}(S(CH_2CH_2SCH_2CH_2SCH_2CH_2SCH_2CH_2)S)C_2B_9H_{10}\}$ (100 mg, 0.209 mmol) or $Cs\{7,8\text{-}\mu\text{-}(S(CH_2CH_2N(Ts)CH_2CH_2)S)C_2B_9H_{10}\}$ (100 mg, 0.180 mmol) with $Pd\{P(C_6H_5)_3\}_2Cl_2$ (126 mg, 0.180 mmol) in butanol (40 cm^3) under refluxing conditions (4–6 h) yielded impure solids (orange and pale red), which were purified by treating them with acetone. The insoluble materials were discarded, and the filtrates were concentrated (approximate final volume 5 cm^3) and cooled to yield solids of the

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(22) Howard, J. A. K.; James, A. P.; Jelfs, A. P.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 1221.

(23) Baumann, F.; Howard, J. A. K.; Johnson, O.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 2917.

(24) Smith, H. D.; Oberland, C. O.; Papetti, S. *Inorg. Chem.* **1966**, *5*, 1013.

(25) Teixidor, F.; Rudolph, R. W. *J. Organomet. Chem.* **1983**, *241*, 301.

(26) Viñas, C.; Butler, W. M.; Teixidor, F.; Rudolph, R. W. *Organometallics* **1984**, *3*, 503.

(27) Viñas, C.; Butler, W. M.; Teixidor, F.; Rudolph, R. W. *Inorg. Chem.* **1986**, *25*, 4369.

(28) Teixidor, F.; Romerosa, A. M.; Rius, J.; Miravitlles, C.; Casabó, J.; Viñas, C.; Sanchez, E. *Inorg. Chim. Acta* **1990**, *176*, 287.

(29) Teixidor, F.; Romerosa, A. M.; Rius, J.; Miravitlles, C.; Casabó, J.; Viñas, C.; Sánchez, E. *J. Chem. Soc., Dalton Trans.* **1990**, 525.

(30) Teixidor, F.; Viñas, C.; Rius, J.; Miravitlles, C.; Casabó, J. *Inorg. Chem.* **1990**, *29*, 149.

(31) Livingstone, S. E. *Comprehensive Inorganic Chemistry*; Pergamon: Oxford, England, 1973; Vol. 3, Chapter 43.

Table II. Crystal Data and Details of Data Collection for $C_{22}H_{29}B_9ClPPdS_2$

chem formula	$C_{22}H_{29}B_9ClPPdS_2$	Z	4
fw	627.7	D_c/g cm^{-3}	1.50
a/Å	13.424 (2)	space group	$P2_1/n$
b/Å	10.315 (2)	radiation (λ/Å)	Mo Kα (0.71069)
c/Å	20.008 (4)		
β/deg	90.83 (1)	abs coeff/cm^{-1}	9.7
V/Å^3	2770.4 (9)	R	0.061
		R_w	0.048

colors indicated, which were filtered out, washed with diethyl ether, and vacuum-dried. Yield: 60 mg (40%) and 80 mg (54%), respectively. Anal. Calc for $C_{28}H_{41}B_9ClPPdS_5$: C, 41.59; H, 5.07. Found: C, 41.6; H, 5.03 IR (cm^{-1}): ν(B–H) 2539. Anal. Calc for $C_{31}H_{40}B_9ClNO_2PPdS_3$: C, 45.13; H, 4.89; N, 1.7. Found: C, 46.2; H, 5.27; N, 1.8. IR (cm^{-1}): ν(B–H) 2537.

X-ray Crystallographic Study

$C_{20}H_{52}B_{18}O_6PdS_4$. The unit cell parameters were determined by least-squares refinement from 25 carefully centered reflections (16° < 2θ < 28°) measured at ambient temperature on a Syntex P2$_1$ diffractometer. The compound crystallizes in the monoclinic crystal system and systematic absences indicated space group $P2_1/c$. Crystal data and details of data collection are presented in Table I. The data were corrected for Lorentz and polarization effects but not for extinction or absorption.

Intensity variation of three standard reflections was negligible during the data collection. A total of 3704 reflections were collected, giving 3340 unique reflections (R_{int} = 0.076). Of those 1880 were considered as observed according to the criteria $|F| > 4\sigma(F)$.

The structure was solved by direct methods by using the SHELXS86[32] program and subsequent Fourier synthesis. Least-squares refinements were performed by using the XTAL2.2 program system,[33] which minimized the function $(|F_o| - |F_c|)^2$, where $w = \sigma_F^{-2}$. After refinement of all non-hydrogen atoms with anisotropic temperature factors, the approximate positions of eight hydrogen atoms of the carborane cage could be picked from a subsequent difference Fourier map. The hydrogen atoms bonded to carbon atoms were placed in calculated positions (C–H = 0.95 Å). Inclusion of all atoms, except two hydrogens, with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms (U = 0.05 Å^2) in fixed positions reduced the R value to 0.075 (R_w = 0.056). The greatest residual maximum in the final difference Fourier map was 1.22 e Å^{-3} in the vicinity of Pd.

$C_{22}H_{29}B_9ClPPdS_2$. The unit cell parameters were determined by least-squares refinement of 20 carefully centered reflections (15° < 2θ < 24°) measured at ambient temperature on a Nicolet P3F diffractometer. The compound crystallizes in the monoclinic crystal system, and systematic absences indicated space group $P2_1/n$. Crystal data and details of data collection are presented in Table II. The data were corrected for Lorentz and polarization effects but not for extinction or absorption.

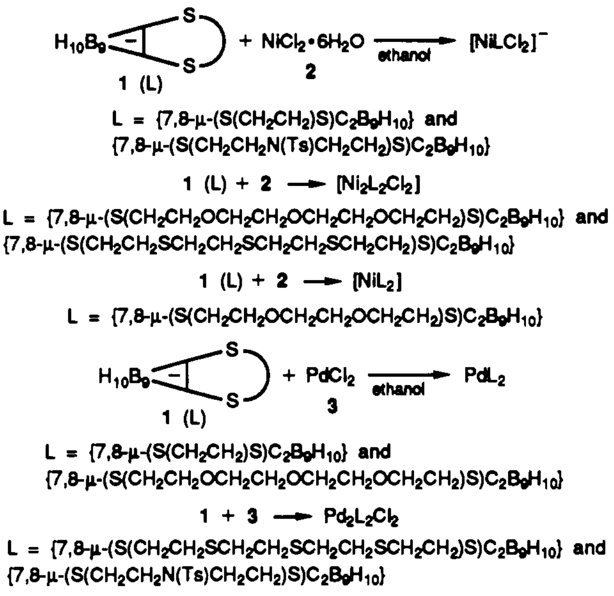
Intensity variation of three standard reflections was negligible during the data collection. A total of 5733 unique reflections were collected, giving 3397 observed reflections according to the criteria $|F| > 4\sigma(F)$.

The structure was solved by direct methods by using the SHELXS86[32] program and subsequent Fourier synthesis. Least-squares refinements were performed by using the XTAL2.2 program system,[33] which minimized the function $(|F_o| - |F_c|)^2$, where $w = \sigma_F^{-2}$. After anisotropic refinements of all non-hydrogen atoms, approximate positions of the hydrogen atoms of the carborane cage could be picked from subsequent difference Fourier map and the hydrogen atoms bonded to carbon atoms were placed in calculated positions (C–H = 0.95 Å). Inclusion of all atoms, with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms in fixed positions, reduced the R value to 0.061 (R_w = 0.048). The greatest residual maximum of 1.19 e Å^{-3} was in the vicinity of Cl.

Results

The reaction of *exo*-dithio-7,8-dicarba-*nido*-undecaborate derivatives with nickel and palladium chlorides yields complexes in which a partial or total substitution of the chlorine atoms by the carborane ligands has taken place. Scheme I exemplifies these reactions.

Scheme I



$+ NiCl_2 \cdot 6H_2O \xrightarrow[\text{ethanol}]{} [NiLCl_2]^-$

L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}$ and $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2N(Ts)CH_2CH_2)S)C_2B_9H_{10}\}$

$1\ (L) + 2 \longrightarrow [Ni_2L_2Cl_2]$

L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$ and $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2SCH_2CH_2SCH_2CH_2SCH_2CH_2)S)C_2B_9H_{10}\}$

$1\ (L) + 2 \longrightarrow [NiL_2]$

L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$

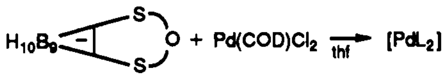
$+ PdCl_2 \xrightarrow[\text{ethanol}]{} PdL_2$

L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}$ and $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$

$1 + 3 \longrightarrow Pd_2L_2Cl_2$

L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2SCH_2CH_2SCH_2CH_2SCH_2CH_2)S)C_2B_9H_{10}\}$ and $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2N(Ts)CH_2CH_2)S)C_2B_9H_{10}\}$

Scheme II



$+ Pd(COD)Cl_2 \xrightarrow[\text{thf}]{} [PdL_2]$

All reactions have been carried out by using the same ligand to metal molar ratio (1:1); however, as is apparent in Scheme I, three different stoichiometries are found: $[MLCl_2]^-$, $[M_2L_2Cl_2]$, and $[ML_2]$.

When $[N(CH_3)_4]\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$ was allowed to react with $Pd(COD)Cl_2$ (1:1) in the presence of an excess of NaH, a compound with the stoichiometry ML_2 was, again, obtained. See Scheme II.

Discussion

The coordination chemistry of the anion 7,8-dicarba-*nido*-undecaborate and its alkyl derivatives has been thoroughly studied, expecially by Hawthorne and colleagues.[34-37] These carborane compounds either present a η^5-(C_2B_3) coordination to metal as in $(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$[38] or exo–nido coordination as in *exo-nido*-$[(PPh_3)_2Rh][7,8\text{-}\mu\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]$.[39] However, the way in which this C_2B_3 open face would behave when two electron-rich elements such as sulfur were directly connected to the carborane carbons was unknown. This is important in order to know whether or not the existence of exo-cluster elements would disturb the coordinating ability of the C_2B_3 open face. Up to now all our results have indicated that C_2B_3 coordination fails when two sulfur atoms are directly connected to the carborane cage; neither η^5 nor exo–nido coordination takes place in favor of sulfur coordination.

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(32) Sheldrick, G. M. SHELXS86. Program for Crystal Structure Solution. University of Göttingen, FRG, 1986.

(33) Hall, S. R., Stewart, J. M., Eds. XTAL2.2 User's Manual. Universities of Western Australia and Maryland, March 1987.

(34) Rees, W. S., Jr.; Schubert, D. M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 5367 and references therein.

(35) Hewew, J. D.; Kreimendahl, C. W.; Marder, T. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 1757.

(36) Long, J. A.; Marder, T. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 3004.

(37) Walker, J. A.; Zheng, L.; Knobler, C. B.; Soto, J.; Hawthorne, M. F. *Inorg. Chem.* **1987**, *26*, 1608.

(38) (a) Behnken, P. E.; Belmont, J. A.; Busby, D. C.; Delaney, M. S.; King, R. E., III; Kreimendahl, C. W.; Marder, T. B.; Wilczynski, J. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 3011. (b) Baker, R. T.; Delaney, M. S.; King, R. E., III; Knobler, C. B.; Long, J. A.; Marder, T. B.; Paxson, T. E.; Teller, R. G.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 2965.

(39) (a) Long, J. A.; Marder, T. B.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 1979. (b) Knobler, C. B.; Marder, T. B.; Mizusawa, E. A.; Teller, R. G.; Long, J. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 2990.

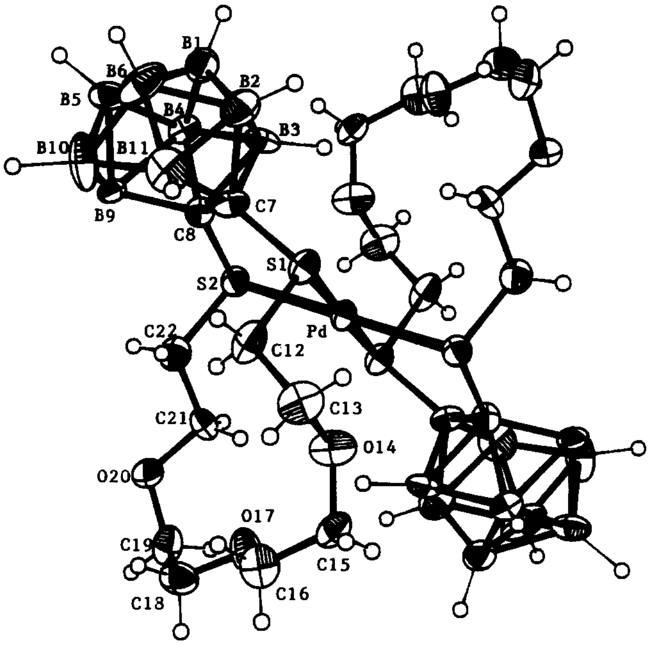

Figure 1. Molecular structure of $Pd\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}_2$.

One of the most intriguing features about the reactivity of these dithioether ligands derivatives of the 7,8-dicarba-*nido*-undecaborate anion is the variety of observed stoichiometries. All ligands have identical coordinating elements placed in the same position with respect to the carborane cage. It is interesting to notice that, by considering steric effects alone, some of these stoichiometries can be predicted. Considering the ligand $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2N(Ts)CH_2CH_2)S)C_2B_9H_{10}\}$, which has a bulky $CH_3C_6H_4SO_2$ (Ts) group on the tertiary nitrogen, a compound with an L:Ni ratio of 1:1 could be expected. In a 2:1 ratio high steric hindrances would be expected either in a tetrahedral or square-planar arrangement. Medium-sized nonbranched chains such as L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$ yield NiL_2. With a longer chain L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$ and $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2SCH_2CH_2SCH_2CH_2SCH_2CH_2)S)C_2B_9H_{10}\}$, the 2:1 (L:Ni) ratio is unfavorable and the 1:1 product is found. These last two ligands are so large that a tetrahedral environment (green compounds, 575 nm, $\epsilon = 100$) is preferred by nickel to minimize steric repulsions, instead of adopting the square-planar arrangement observed in the soichiometries $NiLCl_2^-$ and NiL_2 (red or brown compounds, 555 nm, $\epsilon = 60$). The shorter ligand L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}$ apparently is an exception, since a 1:1 (L:Ni) ratio is found, when a 2:1 ratio would have been expected if only steric effects were considered. The 2:1 stoichiometry is found with this ligand when Pd is the metal ion used. We will go back to this later in this paper. The larger size of the Pd ion should permit more relaxed structures, and ligands that yielded 1:1 ratios with Ni could now yield 1:1 or 2:1 ratios. Consequently, the compounds with stoichiometry PdL_2 (L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}$, $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$, and $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2S)C_2B_9H_{10}\}$) and with stoichiometry $Pd_2L_2Cl_2$ (L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2SCH_2CH_2SCH_2CH_2SCH_2CH_2S)C_2B_9H_{10}\}$ and $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2N(Ts)CH_2CH_2)_2S)C_2B_9H_{10}\}$) follow this hypothesis well.

To enhance the reactivity of the open face, the reaction of $Pd(COD)Cl_2$ with $[N(CH_3)_4]\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$ was carried on under basic conditions; however, even in this situation sulfur coordination took place. Consequently, the behavior of these dithioether ligands (derivatives of the 7,8-dicarba-*nido*-undecaborate anion) did not parallel that of the "normal" dithioethers. To further prove this hypothesis, the reaction of these *exo*-dithio-7,8-dicarba-*nido*-undecaborate derivatives with $Pd\{P(C_6H_5)_3\}_2Cl_2$ in a 1:1 (L:M) molar ratio was carried out. Normal dithioethers should remove neither the halogen nor the PPh_3; however, in all cases, complexes with the stoichiometry $Pd\{P(C_6H_5)_3\}ClL$ were obtained.

Table III. Final Positional Parameters ($\times 10^4$) with Esd's in Parentheses and Equivalent Temperature Coefficients ($Å^2 \times 10^3$) for the Non-Hydrogen Atoms of $C_{20}H_{52}B_{18}O_6PdS_4$

atom	x	y	z	U_{eq}
Pd	5000	5000	5000	33
S1	2191 (4)	4667 (1)	4538 (2)	38
S2	5734 (3)	3928 (1)	4587 (3)	38
B1	1950 (18)	3488 (7)	1509 (11)	56
B2	814 (15)	3966 (6)	2280 (10)	36
B3	3058 (16)	4074 (7)	2497 (10)	43
B4	3950 (18)	3298 (7)	2355 (12)	60
B5	2331 (20)	2700 (7)	2183 (13)	75
B6	366 (18)	3089 (7)	2105 (11)	51
C7	2114 (12)	3956 (5)	3659 (8)	35
C8	3843 (12)	3595 (5)	3699 (8)	36
B9	3641 (18)	2788 (6)	3499 (13)	59
B10	1440 (19)	2640 (6)	3361 (15)	74
B11	499 (17)	3432 (6)	3482 (10)	46
C12	1893 (13)	4293 (5)	5832 (9)	48
C13	2506 (13)	4700 (5)	6877 (9)	52
O14	1917 (9)	4406 (4)	7765 (6)	58
C15	2783 (14)	4591 (5)	8881 (10)	58
C16	4312 (14)	4196 (5)	9398 (9)	55
O17	5617 (9)	4372 (3)	8879 (7)	58
C18	7003 (14)	3944 (5)	9108 (10)	59
C19	8215 (13)	4172 (5)	8467 (9)	49
O20	7544 (9)	4166 (3)	7260 (6)	59
C21	7589 (14)	3544 (5)	6725 (10)	59
C22	5980 (13)	3413 (5)	5876 (10)	57

Table IV. Bond Lenghts (Å) with Esd's in Parentheses for $C_{20}H_{52}B_{18}O_6PdS_4$

S1–Pd	2.317 (3)	B6–B5	1.76 (2)
S2–Pd	2.320 (3)	B9–B5	1.68 (2)
C7–S1	1.767 (10)	B10–B5	1.74 (3)
C12–S1	1.789 (12)	B10–B6	1.79 (2)
C8–S2	1.774 (9)	B11–B6	1.76 (2)
C22–S2	1.827 (11)	C8–C7	1.573 (14)
B2–B1	1.74 (2)	B11–C7	1.66 (2)
B3–B1	1.75 (2)	B9–C8	1.642 (15)
B4–B1	1.74 (2)	B10–B9	1.78 (2)
B5–B1	1.77 (2)	B11–B10	1.79 (2)
B6–B1	1.81 (2)	C13–C12	1.474 (15)
B3–B2	1.79 (2)	O14–C13	1.397 (14)
B6–B2	1.80 (2)	C15–O14	1.399 (13)
C7–B2	1.729 (14)	C16–C15	1.479 (15)
B11–B2	1.86 (2)	O17–C16	1.400 (15)
B4–B3	1.74 (2)	C18–O17	1.392 (13)
C7–B3	1.76 (2)	C19–C18	1.46 (2)
C8–B3	1.717 (15)	O20–C19	1.413 (12)
B5–B4	1.76 (2)	C21–O20	1.408 (13)
C8–B4	1.74 (2)	C22–C21	1.472 (14)
B9–B4	1.78 (2)		

Due to the low solubility of these complexes in common NMR solvents, which precluded a better structural characterization, it was necessary to study them by X-ray diffraction analysis whenever it was possible. Unfortunately, we were unsuccessful in growing crystals of the Ni series. Good quality crystals of $Pd\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}_2$ and $Pd(PPh_3)Cl\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}$ were obtained.

The solid-state structure of $Pd\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2S)C_2B_9H_{10}\}_2$ is illustrated in Figure 1. Listings of atomic positional parameters, bond lengths, and bond angles appear in Tables III–V. The molecular structure consists of discrete molecules formed by two $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2S)C_2B_9H_{10}\}$ moieties linked to a central Pd(II) through the sulfur atoms. The Pd(II) ion displays a perfect square-planar arrangement due to a center of inversion placed on the Pd. The most significant structural feature is that the Pd ion occupies an anti position versus the open face C_2B_3. It implies that the two sulfur lone pairs occupy the

Table V. Selected Bond Angles (deg) with Esd's in Parentheses for $C_{20}H_{52}B_{18}O_6PdS_4$

S2–Pd–S1	88.40 (10)	C7–C8–S2	119.0 (7)
C7–S1–Pd	105.4 (3)	B9–C8–S2	120.1 (7)
C12–S1–Pd	104.4 (3)	C13–C12–S1	114.2 (8)
C12–S1–C7	100.5 (5)	O14–C13–C12	107.5 (9)
C8–S2–Pd	104.2 (3)	C15–O14–C13	115.2 (8)
C22–S2–Pd	109.1 (4)	C16–C15–O14	115.7 (9)
C22–S2–C8	101.1 (5)	O17–C16–C15	109.3 (9)
B2–C7–S1	118.8 (7)	C18–O17–C16	115.0 (8)
B3–C7–S1	113.7 (7)	C19–C18–O17	108.8 (9)
C8–C7–S1	116.9 (6)	O20–C19–C18	113.0 (8)
B11–C7–S1	120.1 (8)	C21–O20–C19	115.2 (8)
B3–C8–S2	112.4 (7)	C22–C21–O20	110.8 (9)
B4–C8–S2	116.8 (8)	C21–C22–S2	112.1 (8)

Table VI. Final Positional Parameters (×10^4) with Esd's in Parentheses and Equivalent Temperature Coefficients (Å^2 × 10^3) for the Non-Hydrogen Atoms of $C_{22}H_{29}B_9ClPPdS_2$

atom	x	y	z	U_{eq}
Pd	5632.2 (5)	5180.1 (6)	1227.4 (3)	37
Cl	5778.1 (13)	3329 (2)	572.8 (9)	32
S1	3920.0 (15)	4767 (3)	1440.2 (11)	49
S2	5221.7 (15)	6961 (2)	1854.2 (11)	40
P	7227.6 (15)	5873 (2)	1050.6 (11)	36
C1	3461 (6)	6362 (10)	1156 (4)	62
C2	4163 (6)	7460 (9)	1352 (4)	56
B1	4533 (8)	4618 (10)	3571 (5)	52
B2	3816 (7)	3938 (10)	2930 (5)	48
B3	4959 (7)	4719 (10)	2772 (5)	44
B4	5053 (7)	6074 (10)	3307 (5)	47
B5	3970 (8)	6118 (11)	3784 (5)	51
B6	3204 (7)	4793 (11)	3546 (5)	53
C7	3884 (5)	5090 (8)	2312 (4)	42
C8	4558 (5)	6248 (8)	2527 (4)	38
B9	4078 (8)	7144 (10)	3091 (5)	52
B10	2906 (8)	6400 (12)	3292 (6)	60
B11	2842 (6)	5047 (11)	2712 (5)	49
C10	7942 (5)	5025 (8)	428 (4)	39
C11	8202 (6)	3729 (8)	529 (4)	49
C12	8781 (6)	3100 (8)	69 (5)	55
C13	9077 (6)	3711 (9)	−503 (4)	55
C14	8819 (6)	4982 (10)	−607 (4)	56
C15	8251 (6)	5638 (8)	−142 (4)	47
C20	8027 (5)	5919 (8)	1794 (4)	39
C21	8983 (7)	5518 (11)	1803 (5)	79
C22	9572 (7)	5642 (11)	2362 (5)	87
C23	9229 (7)	6150 (11)	2914 (5)	77
C24	8297 (8)	6559 (17)	2921 (5)	132
C25	7688 (7)	6452 (15)	2360 (5)	108
C30	7119 (6)	7526 (8)	750 (4)	39
C31	6389 (6)	7810 (9)	283 (4)	54
C32	6260 (7)	9035 (9)	35 (5)	66
C33	6891 (8)	9990 (9)	240 (5)	78
C34	7620 (9)	9715 (10)	691 (6)	100
C35	7760 (7)	8498 (9)	961 (5)	75

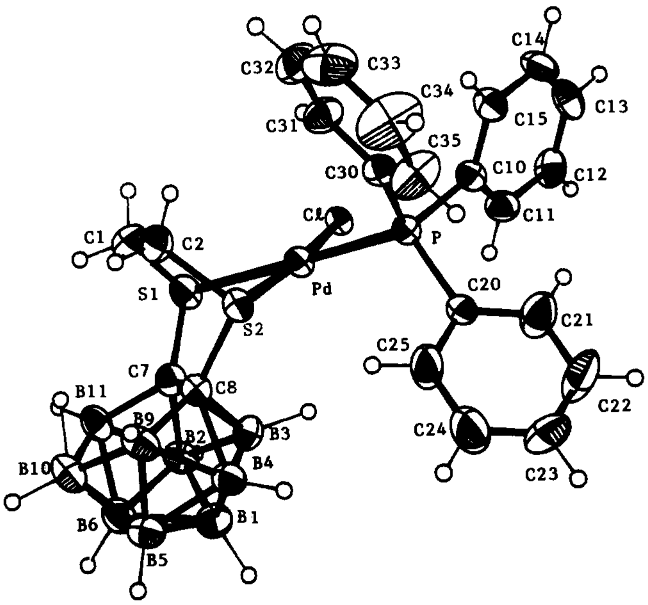

Figure 2. Molecular structure of $Pd\{P(C_6H_5)_3\}Cl\{7,8\text{-}\mu\text{-}(SCH_2CH_2S)C_2B_9H_{10}\}$.

Table VII. Bond Lengths (Å) with Esd's in Parentheses for $C_{22}H_{29}B_9ClPPdS_2$

Cl–Pd	2.325 (2)	B9–B5	1.753 (15)
S1–Pd	2.382 (2)	B10–B5	1.748 (15)
S2–Pd	2.296 (2)	B10–B6	1.78 (2)
P–Pd	2.290 (2)	B11–B6	1.752 (14)
C1–S1	1.843 (10)	C8–C7	1.555 (11)
C7–S1	1.777 (8)	B11–C7	1.622 (11)
C2–S2	1.804 (9)	B9–C8	1.602 (13)
C8–S2	1.783 (8)	B10–B9	1.801 (15)
C10–P	1.808 (8)	B11–B10	1.82 (2)
C20–P	1.822 (8)	C11–C10	1.396 (12)
C30–P	1.814 (8)	C15–C10	1.374 (11)
C2–C1	1.521 (13)	C12–C11	1.376 (12)
B2–B1	1.740 (14)	C13–C12	1.369 (13)
B3–B1	1.709 (14)	C14–C13	1.372 (13)
B4–B1	1.741 (15)	C15–C14	1.388 (12)
B5–B1	1.778 (15)	C21–C20	1.348 (12)
B6–B1	1.794 (14)	C25–C20	1.344 (13)
B3–B2	1.766 (14)	C22–C21	1.368 (14)
B6–B2	1.733 (15)	C23–C22	1.312 (15)
C7–B2	1.719 (13)	C24–C23	1.321 (15)
B11–B2	1.786 (14)	C25–C24	1.384 (14)
B4–B3	1.764 (14)	C31–C30	1.376 (11)
C7–B3	1.743 (12)	C35–C30	1.382 (12)
C8–B3	1.734 (13)	C32–C31	1.368 (13)
B5–B4	1.752 (14)	C33–C32	1.359 (14)
C8–B4	1.697 (12)	C34–C33	1.352 (15)
B9–B4	1.761 (15)	C35–C34	1.379 (14)
B6–B5	1.771 (15)		

Table VIII. Selected Angles (deg) with Esd's in Parentheses for $C_{22}H_{29}B_9ClPPdS_2$

S1–Pd–Cl	92.48 (8)	C30–P–Pd	105.9 (3)
S2–Pd–Cl	170.95 (7)	C20–P–C10	105.3 (3)
P–Pd–Cl	94.73 (7)	C30–P–C10	105.5 (4)
S2–Pd–S1	78.79 (8)	C30–P–C20	106.8 (4)
P–Pd–S1	172.06 (9)	C2–C1–S1	112.5 (6)
P–Pd–S2	93.86 (8)	C1–C2–S2	114.3 (6)
C1–S1–Pd	96.0 (3)	C8–C7–S1	113.0 (5)
C7–S1–Pd	100.5 (2)	B2–C7–S1	125.4 (6)
C7–S1–C1	97.0 (4)	B3–C7–S1	116.3 (5)
C2–S2–Pd	96.7 (3)	B11–C7–S1	121.0 (5)
C8–S2–Pd	102.0 (3)	C7–C8–S2	113.8 (5)
C8–S2–C2	98.0 (4)	B3–C8–S2	115.6 (5)
C10–P–Pd	117.5 (3)	B4–C8–S2	123.0 (5)
C20–P–Pd	115.0 (3)	B9–C8–S2	120.3 (6)

farthest positions with respect to the C_2B_3 core. This ligand's conformation is as expected for the free ligand in order to minimize electronic repulsions.

The macrocyclic fragments tend to be aligned with the hypothetical 5-fold axis of the carborane fragment.

The distances of the carbon atoms (*C*H$_2$–S) to the plane S1–C7–C8–S2[40] are 1.763 Å (C12) and 1.775 Å (C22), values comparable to those found in the sodium salt of the free ligand (1.766 Å).[30]

The solid-state structure of $Pd(PPh_3)Cl\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}$ is illustrated in Figure 2. Listings of atomic positional parameters, bond lengths, and bond angles appear in Tables VI–VIII. The molecular structure consists of discrete molecules formed by a square-planar Pd ion bonded to one $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}$ moiety, one PPh_3, and one Cl. As in the former complex, the Pd ion occupies an anti position vs the open face of the *exo*-dithiocarborane ligand.

The distances of the carbon atoms (*C*H$_2$–S) to the plane S1–C7–C8–S2[41] are −1.597 Å (C1) and −1.546 Å (C2), smaller values

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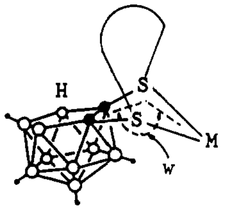
(40) The studied plane is $-0.3145x - 0.5747y + 0.7554z = -1.5629$ (the deviations of the component atoms from this plane are 0.0032 (S1), −0.0031 (S2), −0.0065 (C7), and 0.0064 Å (C8).

Table IX. ω Angle as a Function of the Chain Length



compd[a]	ring size	ω/deg	B3–M/Å	S–S/Å	ref
1		152.2			43
2	15	156.8	3.55	3.23	*b*
3	12	154.2	3.55	3.22	44
4	6	131	3.27	2.97	*b*
5	6	129.4	3.30	2.96	45
6	6	108	2.12	2.97	42

[a] Key: $[Cu(dth)_2][BF_4]$ (**1**); $Pd\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}_2]$ (**2**); $(PPh_3)_2Rh\{7,8\text{-}\mu\text{-}S(CH_2CH_2OCH_2CH_2OCH_2CH_2)S\text{-}7,8\text{-}C_2B_9H_{10}\}$ (**3**); $Pd(PPh_3)Cl\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}$ (**4**); $Rh(PPh_3)_2\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}$ (**5**); $[N(CH_3)_4][RhCl\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}\{\sigma\text{-}7,8\text{-}\mu\text{-}(S(CH_2)_2S)C_2B_9H_{10}\}]$ (**6**). [b] This work.

than those found in other ligands, due to the rigidness caused by the short exo-cluster chain.

The main apparent difference in these ligands is the chain length, which we have used here to justify some of the observed stoichiometries. However, there is another factor that we believe to be of great importance in determining the stoichiometry, especially in complexes where the metal ion is five- or six-coordinated.

Even though the data we have is limited, there seems to be a regularity in the value of the dihedral angle ω (planes defined by S–M–S and S–C_c–C_c–S) (Table IX) and the length of the exo-cluster chain. Table IX presents the observed ω values for several *exo*-dithiocarborane complexes and the B3–M distances. For comparison purposes the observed ω angle in $[Cu(dth)_2][BF_4]$ (dth = 2,5-dithiahexane) has been included. The ω values expand from 156.8° in $Pd\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}_2$ (a 15-member exo-cluster ring) to 129.4° in $Rh(PPh_3)_2\{7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{-}C_2B_9H_{10}\}$ (a 6-member ring). As can be observed in Table IX, the ω values observed for $Pd\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2O\text{-}CH_2CH_2OCH_2CH_2)S\text{-}C_2B_9H_{10}\}_2$ and $[Cu(dth)_2][BF_4]$ are very similar. This suggests that the chain does not cause any constraint to the former. The ω reduction implies a physical approximation of B3 and the metal ion. This forces a H(B3)–M distance reduction, 2.8 Å in $C_{22}H_{29}B_9ClPPdS_2$ vs 3.11 Å in $C_{20}H_{52}B_{18}O_6PdS_4$, while the angle Pd–H–B3 remains almost invariable, 100° vs 100.6°. If this trend is correct, within this family of macrocycles there can be potentially tridentate (through two sulfur atoms and B3–H) ligands and purely bidentate (through two sulfur atoms). Ligands with a long exo-cluster chain will be purely bidentate; however, those with shorter chains can be potentially tridentate.

There are several facts that support our hypothesis, e.g. the ^{11}B NMR spectrum of $Pd\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}_2$, which displays signals at −7.0 (1), −11.3 (4), (−17.0, −18.5, −19.7) (9), −30.6 (1), −33.7 (1), and −36.6 ppm (2). This pattern clearly indicates the existence of two nonequivalent cages, and most probably this compound should be renamed as $Pd\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}\{\sigma\text{-}7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}$. A similar pattern has been observed with Pt as the metal ion. It is important to notice that in both examples (Pd and Pt) a clear, sharp, and strong ν(B–H) signal at 2500 cm^{-1} has been found. Furthermore, the molecular structure of $[N(CH_3)_4][RhCl\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}\{\sigma\text{-}7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}]$,[42] where a B3–Rh distance of 2.12 Å (Table IX) has been found, clearly proves a B3–M interaction.

We do not know at present where the limits, in terms of chain lengths will be, and more work is being done in this area.

In conclusion it is apparent from the data we have presented in this paper that the presence of two electron-rich coordinating elements directly bonded to the carbon atoms of the carborane cage strongly disturbs the coordinating ability of the C_2B_3 open face. Complexes of these ligands present neither η^5 nor exo–nido but sulfur coordination. These ligands are not similar to normal dithioethers, since in them metal–sulfur coordination is dominant over metal–halogen. Apparently, the existence of an exo-cluster chain linking both sulfur atoms in these ligands modulates their coordinating ability. Ligands with longer chains are bidentate, but those with shorter chains can be tridentate through the two sulfur elements and B–H→M bond.

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Registry No. $[N(CH_3)_4]NiLCl_2$ (L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}$), 134152-28-6; $[N(CH_3)_4]NiLCl_2$ (L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)N(Ts)CH_2CH_2)S)C_2B_9H_{10}\}$), 134131-60-5; $[N(CH_3)_4]\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}$, 131994-73-5; $[N(CH_3)_4]\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)N(Ts)CH_2CH_2)S)C_2B_9H_{10}\}$, 134131-62-7; $NiCl_2$, 7718-54-9; $Ni_2L_2Cl_2$ (L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$), 134131-66-1; $Ni_2L_2Cl_2$ (L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2SCH_2CH_2SCH_2CH_2SCH_2CH_2)S)C_2B_9H_{10}\}$), 134152-29-7; $Na\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$, 122967-19-5; $[N(CH_3)_4]\{7,8\text{-}\mu\text{-}(S(CH_2CH_2SCH_2CH_2SCH_2CH_2SCH_2CH_2)S)C_2B_9H_{10}\}$, 134131-68-3; NiL_2 (L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$), 134131-69-4; $[N(CH_3)_4]\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$, 122924-07-6; PdL_2 (L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}$), 134131-70-7; PdL_2 (L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)OCH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$), 134131-71-8; $PdCl_2$, 7647-10-1; $Pd_2L_2Cl_2$ (L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2SCH_2CH_2SCH_2CH_2SCH_2CH_2)S)C_2B_9H_{10}\}$), 134131-72-9; $Pd_2L_2Cl_2$ (L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2N(Ts)CH_2CH_2)S)C_2B_9H_{10}\}$), 134131-73-0; $Cs\{7,8\text{-}\mu\text{-}(S(CH_2CH_2SCH_2CH_2SCH_2CH_2SCH_2CH_2)S)C_2B_9H_{10}\}$, 134131-74-1; $Pd\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}_2$, 134131-77-4; $[N(CH_3)_4]\{7,8\text{-}\mu\text{-}(S(CH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}_2$, 134131-76-3; $Pd(COD)Cl_2$, 12107-56-1; $Pd\{P(C_6H_5)_3ClL$ (L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}$), 134131-78-5; $Pd\{P(C_6H_5)_3\}ClL$ (L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)OCH_2CH_2OCH_2CH_2OCH_2CH_2)S)C_2B_9H_{10}\}$), 134131-79-6; $Pd\{P(C_6H_5)_3\}ClL$ (L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)SCH_2CH_2SCH_2CH_2SCH_2CH_2)S)C_2B_9H_{10}\}$), 134131-80-9; $Pd\{P(C_6H_5)_3\}ClL$ (L = $\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)N(Ts)CH_2CH_2)S)C_2B_9H_{10}\}$), 134131-65-0; $Pd\{P(C_6H_5)_3\}_2Cl_2$, 13965-03-2; $[N(CH_3)_3H]\{7,8\text{-}\mu\text{-}(S(CH_2CH_2)S)C_2B_9H_{10}\}$, 134131-64-9; $Cs\{7,8\text{-}\mu\text{-}(S(CH_2CH_2N(Ts)CH_2CH_2)S)C_2B_9H_{10}\}$, 127993-72-0.

Supplementary Material Available: A full table of crystal data (1 page); listings of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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(41) The studied plane is $0.7563x - 0.6349y + 0.1581z = 1.2845$ (the deviations of the component atoms from this plane are −0.0030 (S1), −0.0028 (S2), 0.0056 (C7), and −0.0053 Å (C8).

(42) Teixidor, F.; Romerosa, A.; Viñas, C.; Rius, J.; Miravitlles, C.; Casabó, J. *J. Chem. Soc., Chem. Commun.* **1991**, 192.

(43) Baker, E. N.; Norris, G. E. *J. Chem. Soc., Dalton Trans.* **1977**, 377.

(44) Teixidor, F.; Viñas, C.; Casabó, J.; Rius, J.; Miravitlles, C. To be submitted for publication.

(45) Teixidor, F.; Viñas, C.; Escriche, Ll.; Sanchez, E.; Rius, J.; Miravitlles, C.; Casabó, J. *Inorg. Chim. Acta* **1990**, *176*, 61.