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Synthesis and Characterization of the First Cyclic Monothioether Derivative of 1,2-*o*-Carborane and Its Reactivity toward Phosphine Transition Metal Complexes

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The first cyclic monothioether derivative of $[C_2B_9H_{12}]^-$ has been synthesized from 1-(SH)-1,2-$C_2B_{10}H_{11}$. Reaction of the latter with ^nBuLi and 1,3-dibromopropane leads to 1,2-μ-($S(CH_2)_3$)-1,2-$C_2B_{10}H_{10}$. Partial degradation leads to $[7,8\text{-}\mu\text{-}(S(CH_2)_3)\text{-}7,8\text{-}C_2B_9H_{10}]^-$. Reaction of $[7,8\text{-}\mu\text{-}(S(CH_2)_3)\text{-}7,8\text{-}C_2B_9H_{10}]^-$ with $[PdCl_2(PRR'_2)_2]$ leads to different sets of compounds depending on the nature of R and R′. If R = R′ = ^tBu, a *closo* compound with one vertex occupied by "$[Pd(P^tBu_3)_2]$" is obtained. When aryl groups are present in the starting phosphine complex, the zwitterionic non-metal-containing compounds are obtained. The crystal structure of one of them has been determined, and the compound has been proven to be 7,8-μ-($S(CH_2)_3$)-11-PPh_3-7,8-$C_2B_9H_9$. The reaction of $[7,8\text{-}\mu\text{-}(S(CH_2)_3)\text{-}7,8\text{-}C_2B_9H_{10}]^-$ with $[RhCl(PPh_3)_3]$ leads to $[Rh(7,8\text{-}\mu\text{-}(S(CH_2)_3)\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$. An agostic $B-H \rightharpoonup Rh$ interaction has been produced, identified by a $^1H\{^{11}B\}$ NMR resonance at −4.78 ppm. In this instance the cluster is connected to "Rh" via the thioether and B(11)−H. The reaction of $[7,8\text{-}\mu\text{-}(S(CH_2)_3)\text{-}7,8\text{-}C_2B_9H_{10}]^-$ with $[RuCl_2(PPh_3)_3]$ leads to a compound with two $B-H \rightharpoonup Ru$ interactions. Contrarily to its noncyclic analogues, it seems that only one isomer has been obtained.

Introduction

Thioethers are weak ligands; however, the coordinating capacity of polythioethers[1] is improved due to a higher number of participating thio groups.[2] Dithioethers, having only two thio groups, display very weak bonding capacity, although this can be dramatically improved if the fragment 7,8-dicarba-*nido*-undecaborate is adequately incorporated in the molecule.[3] This is interpreted as if the cluster's negative charge is released on the thioether, thus enhancing its donor capacity.[4] For this to happen it is required that the thio groups be directly bonded to the cluster carbon atoms.[5] The 7,8-dicarba-*nido*-undecaborate fragment has also enhanced the coordinating capacity of monothioethers toward transition metal ions.[6] Both monothioether and dithioether derivatives of $[C_2B_9H_{12}]^-$ display a good tendency to form $B-H \rightharpoonup M$ bonds,[6−8] although these are formed more easily with the monothioether ligands. The $B-H \rightharpoonup M$ bonds have been invoked in the catalytic hydrogenation mechanism of these compounds.[9]

The dithioether derivatives of $[C_2B_9H_{12}]^-$ have been produced both in a cyclic and in a noncyclic form. The cyclic form is represented in Figure 1a. On the contrary, monothioethers have only been produced in a noncyclic form (Figure 1b). Considering the $B-H \rightharpoonup M$ relevance in monothioether coordination and the importance of the cyclic or noncyclic nature in the coordinating behavior of dithioether compounds, it was considered necessary to synthesize the first cyclic monothioether derivative of

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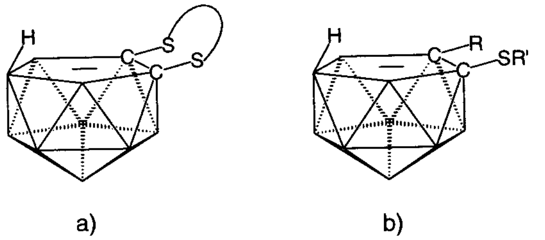

Figure 1. Schematic drawing of the dithio and monothio derivatives of 7,8-dicarba-*nido*-undecaborate(1−).

[C$_2$B$_9$H$_{12}$]$^-$, as this could bring out more information on the peculiar coordination habit of these compounds. Here we report its synthesis and preliminary complexation toward transition metal complexes containing both Cl$^-$ and PR$_3$ ligands.

Experimental Section

Materials and Methods. The compound 1-(SH)-1,2-C$_2$B$_{10}$H$_{11}$[10] and complexes [PdCl$_2$(PPh$_3$)$_2$],[11] [PdCl$_2$(PMePh$_2$)$_2$],[12] [PdCl$_2$(P^{t}Bu$_3$)$_2$],[12] [RhCl(PPh$_3$)$_3$],[13] and [RuCl$_2$(PPh$_3$)$_3$][14] were synthesized by published procedures. THF was dried with sodium and distilled under a dinitrogen atmosphere. Ethanol, dichloromethane, hexane, and ethyl acetate were of reagent quality. Inorganic salts, ^{n}BuLi, and 1,3-dibromopropane were used as purchased from Aldrich. All reactions were carried out under a dinitrogen atmosphere employing Schlenk techniques. Microanalyses were performed by using a Perkin-Elmer 240B microanalyzer. IR spectra (KBr disk) were measured on a Nicolet 710-FT spectrophotometer. The ^{1}H{^{11}B} and ^{13}C{^{1}H} NMR spectra were referenced to an internal standard of SiMe$_4$ in deuterated solvents, and the ^{31}P{^{1}H} and ^{11}B{^{1}H} NMR spectra were referenced to external standards of H$_3$PO$_4$ and BF$_3$·(Et$_2$O), respectively, and were recorded on a Bruker ARX-300 instrument.

Synthesis of 1,2-*μ*-(S(CH$_2$)$_3$)-1,2-C$_2$B$_{10}$H$_{10}$. A three-necked round-bottom flask (500 mL) fitted with a condenser tube and a pressure-equalizing funnel was filled with 1-(SH)-1,2-C$_2$B$_{10}$H$_{11}$ (500 mg, 2.84 mmol) in deoxygenated dry THF (100 mL). The solution was cooled (ice−water), and ^{n}BuLi (3.7 mL, 5.6 mmol, 1.5 M) was added. The mixture was stirred for 30 min at 0 °C and at room temperature for 30 min and was taken to reflux. To this solution was added 1,3-dibromopropane (0.3 mL, 2.8 mmol) in deoxygenated dry THF (50 mL) dropwise, and the mixture was stirred at reflux for 3 h. A solid which separated upon cooling of the mixture to room temperature was filtered off, and the solvent was evaporated off. The residue was purified by column chromatography (silica gel, ethyl acetate as eluent). Yield: 340 mg (55%). Anal. Calcd for C$_5$H$_{16}$B$_{10}$S: C, 27.76; H, 7.45; S, 14.82. Found: C, 28.01; H, 7.30; S, 14.49. FTIR (KBr): ν (cm^{-1}) 2586 (B−H). ^{1}H{^{11}B} NMR (CDCl$_3$): $\delta = 2.1$ (m, 1H, C**H**$_2$), 2.7 (m, 1H, Cc−C**H**$_2$), 2.9 (m, 1H, S−C**H**$_2$). ^{11}B{^{1}H} NMR (CDCl$_3$): $\delta = -3.1$ (1**B**), −5.3 (2**B**), −8.4 (6**B**), −11.3 (1**B**). ^{13}C{^{1}H} NMR (CDCl$_3$): $\delta = 21.3$ (**C**H$_2$), 26.1 (Cc−**C**H$_2$), 32.9 (S−**C**H$_2$), 67.8 (**C**c), 72.2 (S−**C**c).

Synthesis of [NMe$_4$][7,8-*μ*-(S(CH$_2$)$_3$)-7,8-C$_2$B$_9$H$_{10}$]. Partial degradation of 1,2-*μ*-(S(CH$_2$)$_3$)-1,2-C$_2$B$_{10}$H$_{10}$ was achieved following the general procedure described in the literature.[15] Yield: 250 mg (95%). Anal. Calcd for C$_9$H$_{28}$NB$_9$S: C, 38.65; H, 10.09; N, 5.01; S, 11.46. Found: C, 38.35; H, 9.71; N, 4.77; S, 11.14. FTIR (KBr): ν (cm^{-1}) 2517 (B−H), 1482, 946 (NMe$_4$). ^{1}H{^{11}B} NMR ((CD$_3$)$_2$CO): $\delta = -2.5$ (b, 1H, B−**H**−B), 1.8 (m, 2H, C**H**$_2$), 2.7 (m, 4H, Cc−C**H**$_2$ and S−C**H**$_2$), 3.4 (s, 12H, [N**Me**$_4$]$^+$). ^{11}B{^{1}H} NMR ((CD$_3$)$_2$CO): $\delta = -6.6$ (1**B**), −8.1 (1**B**), −9.1 (1**B**), −10.2 (1**B**), −17.5 (1**B**), −18.5 (2**B**), −30.0 (1**B**), −36.4 (1**B**). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO): $\delta = 32.6$ (**C**H$_2$), 42.6 (Cc−**C**H$_2$), 45,5 (S−**C**H$_2$), 54.2 ([N**Me**$_4$]$^+$).

Synthesis of 7,8-*μ*-(S(CH$_2$)$_3$)-11-PPh$_3$-7,8-C$_2$B$_9$H$_9$ (1). To deoxygenated boiling ethanol (60 mL) containing [PdCl$_2$(PPh$_3$)$_2$] (300 mg, 4.29 mmol) was added [NMe$_4$][7,8-*μ*-(S(CH$_2$)$_3$)-7,8-C$_2$B$_9$H$_{10}$] (120 mg, 4.29 mmol), and the mixture was refluxed for 4 h. After cooling to room temperature, the solid was filtered off and discarded. The solution was evaporated, and the residue was purified by column chromatography (silica gel, 1:1 dichloromethane/hexane as eluent). The solution was evaporated to yield an analytically pure white solid. Yield: 125 mg (55%). Anal. Calcd for C$_{23}$H$_{30}$B$_9$PS: C, 59.18; H, 6.48; S, 6.87. Found: C, 59.32; H, 6.11; S, 6.59. FTIR (KBr): ν (cm^{-1}) 2535 (B−H). ^{1}H{^{11}B} NMR ((CD$_3$)$_2$CO): $\delta = -2.5$ (b, 1H, B−**H**−B), 1.9 (m, 2H, C**H**$_2$), 2.2 (m, 2H, Cc−C**H**$_2$), 2.4 (m, 2H, S−C**H**$_2$), 7.5 (m, 15H, **C**$_{\mathbf{aryl}}$). ^{11}B{^{1}H} NMR ((CD$_3$)$_2$CO): $\delta = -4.8$ (2**B**), −12.3 (d, ^1J(B,P) = 153 Hz, 1**B**), −14.6 (1**B**), −18.4 (1**B**), −25.4 (2**B**), −33.9 (2**B**). ^{31}P{^{1}H} NMR ((CD$_3$)$_2$CO): 5.6 (4-line, ^1J(B,P) = 153 Hz). A white crystal suitable for X-ray analysis was grown from acetone by slow evaporation of the solvent at 4 °C.

Synthesis of 7,8-*μ*-(S(CH$_2$)$_3$)-11-PMePh$_2$-7,8-C$_2$B$_9$H$_9$ (2). A procedure similar to that of **1** was utilized for 250 mg (0.43 mmol) of [PdCl$_2$(PMePh$_2$)$_2$]. Purification was done by column chromatography (silica gel, 1:1 dichloromethane/hexane as eluent). Yield: 105 mg (60%). Anal. Calcd for C$_{18}$H$_{28}$B$_9$PS: C, 53.28; H, 7.28; S, 7.90. Found: C, 53.54; H, 7.24; S, 7.63. FTIR (KBr): ν (cm^{-1}) 2537 (B−H). ^{1}H{^{11}B} NMR ((CD$_3$)$_2$CO): $\delta = -2.6$ (b, 1H, B−**H**−B), 1.6 (m, 3H, P−**Me**), 1.9 (m, 2H, C**H**$_2$), 2.2 (m, 2H, Cc−C**H**$_2$), 2.4 (m, 2H, S−C**H**$_2$), 7.7 (m, 10H, **C**$_{\mathbf{aryl}}$). ^{11}B{^{1}H} NMR ((CD$_3$)$_2$CO): $\delta = -5.4$ (1**B**), −9.5 (1**B**), −11.3 (d, ^1J(B,P) = 160 Hz, 1**B**), −15.2 (1**B**), −17.1(1**B**), −19.2 (1**B**), −25.1 (1**B**), −27.1 (1**B**), −35.0 (1**B**). ^{31}P{^{1}H} NMR ((CD$_3$)$_2$CO): −0.6 (4-line, ^1J(B,P) = 160 Hz).

Synthesis of [Pd(7,8-*μ*-(S(CH$_2$)$_3$)-7,8-C$_2$B$_9$H$_{10}$)(P^{t}Bu$_3$)$_2$] (3). An identical procedure as for **1** and **2** was utilized for a quantity of 225 mg (0.38 mmol) of [PdCl$_2$(P^{t}Bu$_3$)$_2$]. The product was purified by column chromatography (silica gel, 1:1 dichloromethane/hexane as eluent). Yield: 193 mg (71%). Anal. Calcd for C$_{29}$H$_{69}$B$_9$P$_2$PdS: C, 48.68; H, 9.72; S, 4.48. Found: C, 48.88; H, 9.44; S, 4.14. FTIR (KBr): ν (cm^{-1}) 2586 (B−H). ^{1}H{^{11}B} NMR ((CD$_3$)$_2$CO): $\delta = 1.1$ (m, 9H, $^{\mathbf{t}}$**Bu**), 1.9 (m, 2H, C**H**$_2$), 2.2 (m, 2H, Cc−C**H**$_2$) 2.4 (m, 2H, S−C**H**$_2$). ^{11}B{^{1}H} NMR ((CD$_3$)$_2$CO): $\delta = -2.9$ (2**B**), −8.5 (1**B**), −9.4 (1**B**), −11.5 (2**B**), −13.4 (2**B**), −14.2 (1**B**). ^{31}P{^{1}H} NMR ((CD$_3$)$_2$CO): 31.2 (d, ^2J(P,P) = 12 Hz), 27.2 (d, ^2J(P,P) = 12 Hz).

Synthesis of [Rh(7,8-*μ*-(S(CH$_2$)$_3$)-7,8-C$_2$B$_9$H$_{10}$)(PPh$_3$)$_2$] (4). To 20 mL of deoxygenated boiling ethanol containing [NMe$_4$][7,8-*μ*-(S(CH$_2$)$_3$)-7,8-C$_2$B$_9$H$_{10}$] (22 mg, 0.15 mmol) was added [RhCl(PPh$_3$)$_3$] (140 mg, 0.15 mmol), and the mixture was refluxed for 4 h. A yellow solid precipitated. This was filtered off while warm, washed with ethanol, and dried under vacuum. Yield: 112 mg (89%). Anal. Calcd for C$_{41}$H$_{46}$B$_9$P$_2$RhS: C, 59.11; H, 5.56; S, 3.84. Found: C, 58.79; H, 5.27; S, 3.69. FTIR (KBr): ν (cm^{-1}) 2535 (B−H). ^{1}H{^{11}B} NMR (CD$_2$Cl$_2$): $\delta = -4.8$ (b, 1H, B−**H**⇀Rh), −2.5 (b, 1H, B−**H**−B), 1.7 (m, 2H, C**H**$_2$), 1.9 (m, 2H, Cc−C**H**$_2$), 2.2 (m, 2H, S−C**H**$_2$), 7.5 (m, 30H, **C**$_{\mathbf{aryl}}$). ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$): $\delta = -8.1$ (1**B**), −10.5 (1**B**), −12.3 (1**B**), −14.1 (1**B**), −17.2 (1**B**), −23.8 (2**B**), −27.4 (1**B**), −37.3 (1**B**). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 42.4 (br d, ^1J(B,P) = 170 Hz).

Synthesis of [RuCl(7,8-*μ*-(S(CH$_2$)$_3$)-7,8-C$_2$B$_9$H$_{10}$)(PPh$_3$)$_2$] (5). To 15 mL of deoxygenated boiling ethanol containing [NMe$_4$][7,8-*μ*-(S(CH$_2$)$_3$)-7,8-C$_2$B$_9$H$_{10}$] (29 mg, 0.1 mmol) was added [RuCl$_2$(PPh$_3$)$_3$] (100 mg, 0.10 mmol), and the mixture was refluxed for 4 h. A deep blue solid precipitated. The solid was filtered off while warm, washed with deoxygenated warm ethanol and diethyl ether, and dried under vacuum. Yield: 62 mg (71%). Anal. Calcd for C$_{41}$H$_{46}$ClB$_9$P$_2$RuS: C, 56.82; H, 5.35; S, 3.70. Found: C, 56.54; H, 5.47; S, 3.41. FTIR (KBr): ν (cm^{-1}) 2538 (B−H). ^{1}H{^{11}B} NMR (CD$_2$Cl$_2$): $\delta = -11.9$ (s, 1H, B−**H**⇀Ru), −3.7 (s, 1H, B−**H**⇀Ru), −1.9 (b, 1H, B−**H**−B), 1.7 (m, 2H, C**H**$_2$), 2.4 (m, 2H, Cc−C**H**$_2$), 2.8 (m, 2H, S−C**H**$_2$), 7.3 (m, 30H, **C**$_{\mathbf{aryl}}$). ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$): $\delta = -6.3$ (1**B**), −11.2 (1**B**), −16.9 (2**B**), −22.1 (1**B**), −26.5 (2**B**), −36.1 (2**B**). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 75.8 (d, ^2J(P,P) = 33 Hz), 37.3 (d, ^2J(P,P) = 33 Hz).

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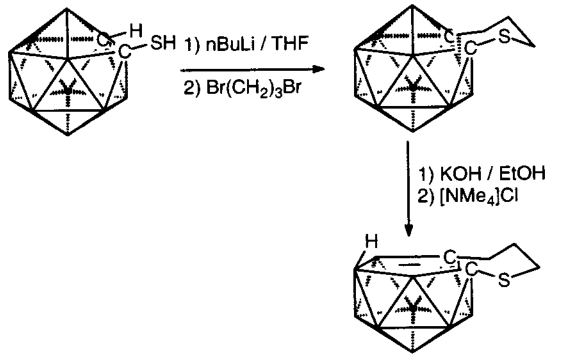

Figure 2. Synthesis of 1,2-μ-(S(CH$_2$)$_3$)-1,2-$C_2B_{10}H_{10}$ and [7,8-μ-(S(CH$_2$)$_3$)-7,8-$C_2B_9H_{10}$]$^-$.

X-ray Structure Determination of 7,8-μ-(S(CH$_2$)$_3$)-11-PPh$_3$-7,8-$C_2B_9H_9$ (1). Single-crystal data collection was performed at room temperature on a Rigaku AFC5S diffractometer using graphite-monochromatized Mo Kα radiation. The unit cell parameters were determined by least-squares refinement of 25 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 9368 reflections were collected by an $\omega/2\theta$ scan mode ($2\theta_{\max} = 50°$). Of those reflections, 8919 were independent ($R_{\text{int}} = 0.0172$).

The structure was solved by direct methods using the SHELXS program,[16] and least-squares refinements were performed using the SHELXL-93 program.[17] For both molecules the non-hydrogen atoms were refined 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.

Results and Discussion

The straightforward method to produce monothioether derivatives of *o*-carborane is based on utilizing C-alkyl or C-aryl monosubstituted *o*-carboranes. The synthesis of 1-SH-1,2-$C_2B_{10}H_{11}$ requires much more controlled reaction conditions due to the monolithiation/dilithiation/*o*-carborane equilibrium process indicated in eq 1.[18]

$$2\ 1\text{-Li-}1,2\text{-}C_2B_{10}H_{11} \leftrightarrow 1,2\text{-Li}_2\text{-}1,2\text{-}C_2B_{10}H_{10} + 1,2\text{-H}_2\text{-}1,2\text{-}C_2B_{10}H_{10} \quad (1)$$

This equilibrium can be shifted to the monolithiated *o*-carborane if a chelating ether is utilized, which has permitted us to isolate 1-SH-1,2-$C_2B_{10}H_{11}$ in good yield.[10]

The reaction of 1-SH-1,2-$C_2B_{10}H_{11}$ with ^{n}BuLi at 0 °C in THF produced the dilithiated salt 1-SLi-2-Li-1,2-$C_2B_{10}H_{10}$. High dilution conditions were used when adding 1,3-dibromopropane to minimize the synthesis of undesired compounds. The result was the *closo* cyclic monothioether 1,2-μ-(S(CH$_2$)$_3$)-1,2-$C_2B_{10}H_{10}$, (Figure 2). When no high-dilution conditions were used, compound 1,2-μ-(S(CH$_2$)$_3$)-1,2-$C_2B_{10}H_{10}$ was obtained in very low yield. Equivalent six-members cyclic dithioether derivatives of the *o*-carborane are synthesized with no need of high dilution.[5] This different behavior can be accounted for by considering the different nucleophilicity of Cc$^-$ and Cc$-$S$^-$ present in the same molecule, while the nucleophilicity is the same for the homodisubstituted [1,2-S$_2$-1,2-$C_2B_{10}H_{10}$]$^{2-}$ compound. A ν(B$-$H) stretching frequency at 2586 cm^{-1}, typical for a *closo* compound, was found. The resonances of the ^{11}B{^{1}H} NMR integrating 1:2:6:1 in the range $-3/-11$ ppm also support the *closo* nature of the cluster. The ^{1}H{^{11}B} and ^{13}C{^{1}H} NMR and elemental analysis were in agreement with the proposed formula.

The reaction of 1,2-μ-(S(CH$_2$)$_3$)-1,2-$C_2B_{10}H_{10}$ with KOH in boiling ethanol produced, after the addition of [NMe$_4$]Cl, the monothioether *nido* derivative [NMe$_4$][7,8-μ-(S(CH$_2$)$_3$)-7,8-$C_2B_9H_{10}$]. The reaction is indicated in Figure 2. This *nido* ligand was characterized by elemental analysis and ^{1}H{^{11}B}, ^{13}C{^{1}H}, and ^{11}B{^{1}H} NMR. The partial degradation was clearly proven by the appearance of a ^{1}H{^{11}B} resonance at -2.5 ppm attributed to the endohedral open face hydrogen. A ν(B$-$H) stretching frequency at 2517 cm^{-1} is a clear indication of the *nido* formation. The 1:1:1:1:1:2:1:1 pattern in the ^{11}B{^{1}H} NMR in the range $-6/-37$ ppm is consistent with the partial degradation. The ^{1}H{^{11}B} NMR spectrum of [NMe$_4$][7,8-μ-(S(CH$_2$)$_3$)-7,8-$C_2B_9H_{10}$] displayed, in addition to the tetramethylammonium protons, three sets of resonances in a ratio of 1:1:1 attributed to the methylene hydrogens. The number and positions of the carbon signals are in agreement with the proposed formula.

Ligand [7,8-μ-(S(CH$_2$)$_3$)-7,8-$C_2B_9H_{10}$]$^-$ is unique in the sense that in contrast to its noncyclic monothioether analogues it has one thioether group with restricted mobility. According to previous data, based on other [7,8-$C_2B_9H_{12}$]$^-$ derivatives, ligand [7,8-μ-(S(CH$_2$)$_3$)-7,8-$C_2B_9H_{10}$]$^-$ can produce η^5 coordination via the C_2B_3 open face,[19] *exo-nido* coordination via B$-$H$\rightharpoonup$M,[20] or *exo-nido* coordination via the thioether group supported by one or two B$-$H$\rightharpoonup$M bonds.[6,7] To explore the coordination capacity of this cyclic monothioether ligand, complexation reactions with Pd(II), Rh(I), and Ru(II) were performed. These are well established with noncyclic monothioether compounds and shall permit us to access the influence of the cycle on coordination.

The reaction of [7,8-μ-(S(CH$_2$)$_3$)-7,8-$C_2B_9H_{10}$]$^-$ with [PdCl$_2$(PPh$_3$)$_2$] in ethanol produced a white product, 7,8-μ-(S(CH$_2$)$_3$)-11-PPh$_3$-7,8-$C_2B_9H_9$ (**1**). The lack of color suggested the absence of Pd in the compound. The absorption at -2.5 ppm in the ^{1}H{^{11}B} NMR spectrum indicates the presence of the B$-$H$-$B interaction. The ^{11}B{^{1}H} NMR pattern, 2:1:1:1:2:2 in the range $-1/-34$ ppm is consistent with a *nido* cluster. The ^{11}B{^{1}H} NMR absorption at -12.3 ppm was split in two, in the same way as was the ^{11}B NMR, indicating that a B$-$P bond had been formed (^1J(B,P) = 153 Hz). Similar ligand transfer has been previously reported in (phosphino)metallacarboranes of Ru,[21] Rh,[22] Ni,[23] and Pt.[24] In these examples a metal-bonded PPh$_3$ unit migrates and forms a B$-$PPh$_3$ bond with B(10). The 4-line resonance in the ^{31}P{^{1}H} NMR spectrum at 5.6 ppm is also fully consistent with the B$-$P bond. The point was to discern which boron was bonded to PPh$_3$. According to the literature[25] the B(10) position, the one further apart from the two cluster

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Table 1. Crystallographic Data for 7,8-μ-(S(CH$_2$)$_3$)-11-PPh$_3$-7,8-C$_2$B$_9$H$_9$ (1)

empirical formula	$C_{23}H_{30}B_9PS$
fw	466.79
a, Å	12.443(2)
b, Å	22.7021(14)
c, Å	9.5418(7)
α, deg	97.717(6)
β, deg	108.751(9)
γ, deg	89.670(10)
V, Å^3	2527.2(5)
Z	4
space group	$P\bar{1}$ (No. 2)
T, °C	21
λ, Å	0.71069
D_{calcd}, g cm^{-3}	1.227
μ, cm^{-1}	2.03
R1^a [$I > 2\sigma(I)$]	0.0520
wR2^b [$I > 2\sigma(I)$]	0.1292

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 7,8-μ-(S(CH$_2$)$_3$)-11-PPh$_3$-7,8-C$_2$B$_9$H$_9$ (1)

	molecule **A**	molecule **B**
S(1)−C(7)	1.798(4)	1.794(4)
S(1)−C(12)	1.816(5)	1.822(5)
P(1)−B(11)	1.931(4)	1.934(4)
P(1)−C(15)	1.820(3)	1.817(3)
P(1)−C(21)	1.824(3)	1.822(3)
P(1)−C(27)	1.814(3)	1.821(2)
C(7)−C(8)	1.563(5)	1.567(5)
C(7)−B(11)	1.618(5)	1.621(5)
C(8)−C(14)	1.522(5)	1.527(6)
C(7)−S(1)−C(12)	101.2(2)	101.7(2)
C(15)−P(1)−B(11)	110.1(2)	109.0(2)
C(21)−P(1)−B(11)	112.4(2)	112.9(2)
C(27)−P(1)−B(11)	114.9(2)	115.6(2)
B(2)−C(7)−S(1)	117.4(2)	117.9(2)
B(3)−C(7)−S(1A)	110.4(2)	110.4(2)
C(8)−C(7)−S(1)	113.5(2)	113.9(3)
B(11)−C(7)−S(1)	123.8(2)	124.1(2)
C(14)−C(8)−B(3)	118.4(3)	118.5(3)
C(14)−C(8)−B(4)	124.8(3)	125.4(3)
C(14)−C(8)−C(7)	116.2(3)	115.6(3)
C(14)−C(8)−B(9)	119.2(4)	119.1(4)
B(2)−B(11)−P(1)	118.0(2)	119.0(3)
B(6)−B(11)−P(1)	123.6(2)	124.1(3)
C(7)−B(11)−P(1)	122.1(2)	121.5(3)
B(10)−B(11)−P(1)	123.0(2)	122.4(2)

carbon atoms, seemed to be preferred. However, the reaction of noncyclic monothioether [7-SMe-8-Me-7,8-C$_2$B$_9$H$_{10}$]$^-$ with [PdCl$_2$(PPh$_3$)$_2$] produced [PdCl(7-SMe-8-Me-11-PPh$_2$-7,8-C$_2$B$_9$H$_{10}$)(PPh$_3$)],[25] where the B(11) position contains the B−PPh$_2$ moiety. This undoubtedly had taken place induced by the thioether coordination to the metal. If a similar process had taken place with [7,8-μ-(S(CH$_2$)$_3$)-7,8-C$_2$B$_9$H$_{10}$]$^-$, B−H substitution by PPh$_3$ may have occurred at B(11). To unambiguously determine the structure of **1**, good-quality crystals were grown in acetone. The asymmetric unit of the structure consists of two crystallographically nonequivalent but geometrically very similar zwitterionic molecules, labeled **A** and **B**. Crystallographic data are presented in Table 1, selected bond lengths and angles are listed in Table 2, and a view of molecule **A** is illustrated in Figure 3. In each molecule the 7,8-dicarba-*nido*-undecaborate moiety is linked to the *exo* cluster chain which forms a six-membered cycle containing the S−C−C unit. The cluster's negative charge is compensated by the triphenylphosphonium ion bonded at the cluster 11 position.

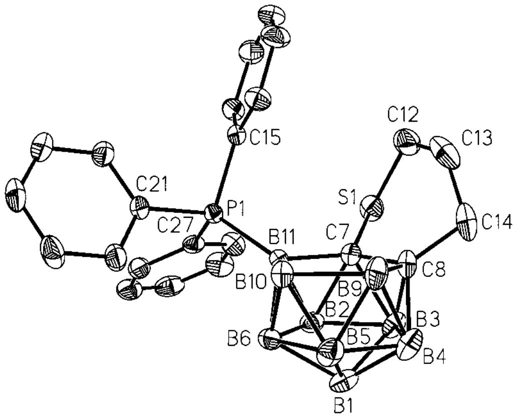

Figure 3. A view of molecule **A** of 7,8-μ-(S(CH$_2$)$_3$)-11-PPh$_3$-7,8-C$_2$B$_9$H$_9$ (**1**) showing 30% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

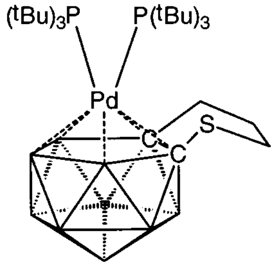

Figure 4. Proposed structure of [Pd(7,8-μ-(S(CH$_2$)$_3$)-7,8-C$_2$B$_9$H$_{10}$)-(P^{t}Bu$_3$)$_2$] (**3**).

Almost all bond lengths and angles for **A** and **B** are equal, and even orientations of the PPh$_3$ groups are very similar. The largest difference between the molecules is in the deviation of the phosphorus atom from the plane through the C$_2$B$_3$ open face. In molecule **A** the phosphorus atom deviates by 0.873(6) Å from the mean plane while in molecule **B** the corresponding value is 0.920(6) Å. Consequently, the S(1)−C(7)−C(8)−P(1) torsion angles are slightly different, being 0.5(4)° for **A** and −1.5(4)° for **B**. Deviation of the S(1)−C(7)−C(8)−C(14) unit from planarity [torsion angle values of 9.6(4)° and 10.0(5)° for **A** and **B**, respectively] can be considered as a result of ring strain.

A reaction similar to the synthesis of **1** but with [PdCl$_2$-(PMePh$_2$)$_2$] was performed to produce also a white compound **2**, which according to spectral data is structurally similar to **1**. In compound **2** the B(11) substituent is PMePh$_2$. The more basic character of the phosphine produces a shift of the ^{31}P resonance toward higher field.

Contrarily to **1** and **2**, the reaction of [7,8-μ-(S(CH$_2$)$_3$)-7,8-C$_2$B$_9$H$_{10}$]$^-$ with [PdCl$_2$(P^{t}Bu$_3$)$_2$] in ethanol yielded, after purification, a yellow compound **3**. Absorptions in the ^{11}B{^{1}H} NMR spectra with intensities 2:1:1:2:2:1 in the range −3/−14 ppm were consistent with a *closo* nature of the compound. No absorption corresponding to B−H−B in the ^{1}H{^{11}B} NMR spectra was observed. The stretching frequency at 2586 cm^{-1} also supports a *closo* formation. The ^{31}P{^{1}H} NMR does not display any 4-line resonance. On the contrary it shows two sets of doublets at 31.2 and 27.2 ppm, both with ^2J(P,P) = 12 Hz. The analysis supports the stoichiometry [Pd(7,8-μ-(S(CH$_2$)$_3$)-7,8-C$_2$B$_9$H$_9$)(P^{t}Bu$_3$)$_2$]. On the basis of the NMR data a η^5 coordination of the C$_2$B$_3$ open face to Pd is proposed (Figure 4). The Pd(P^{t}Bu$_3$)$_2$ moiety would occupy the missing vertex of the icosahedron. The behavior of [7,8-μ-(S(CH$_2$)$_3$)-7,8-C$_2$B$_9$H$_{10}$]$^-$ toward Pd(II) does not parallel that of its noncyclic analogues.

Reaction of [7,8-μ-(S(CH$_2$)$_3$)-7,8-C$_2$B$_9$H$_{10}$]$^-$ with [RhCl-(PPh$_3$)$_3$] in boiling ethanol yielded a yellow compound **4**. The

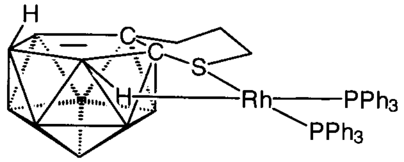

Figure 5. Proposed structure of [Rh(7,8-μ-(S(CH$_2$)$_3$)-7,8-$C_2B_9H_{10}$)-(PPh$_3$)$_2$] (**4**).

IR spectrum of **4** exhibited an intense absorption at 2535 cm^{-1} corresponding to the B−H stretching of *nido*-carboranes, along with bands associated with PPh$_3$. The ^{11}B{^{1}H} NMR spectrum of **4** contained 8 resonances in the ratio 1:1:1:1:1:2:1:1 in the range of −8/−37 ppm. The ^{1}H{^{11}B} NMR spectrum displayed a broad band at −4.78 ppm indicating the existence of B−H−Rh interactions. The resonance at −2.5 ppm was assigned to the B−H−B bridge being consistent with the *nido* nature of the cluster. A complex series of resonances centered at 7.5 ppm is present in the ^{1}H{^{11}B} NMR spectrum, which is characteristic of phenyl protons. The ratio of the areas corresponding to phenyl protons, B−H−B, and B−H⇀Rh is 30:1:1. Finally the ^{31}P-{^{1}H} NMR spectrum revealed only a relatively broad doublet centered at 42.4 ppm (^1J(Rh,P) = 170 Hz). Thus the spectroscopic data and elemental analysis are consistent with an *exo-nido*-carborane rhodium complex containing two mutually *cis* PPh$_3$ ligands with the stoichiometry [Rh(7,8-μ-(S(CH$_2$)$_3$)-7,8-$C_2B_9H_{10}$)(PPh$_3$)$_2$]. These spectroscopic results compare well to the compound [Rh(7-SPh-8-Me-7,8-$C_2B_9H_{10}$)(PPh$_3$)$_2$],[9] which also shows a broad doublet in the ^{31}P{^{1}H} NMR. This sharpens at low temperatures producing two doublets corresponding to the coupling of the two nonequivalent PPh$_3$ ancillary ligands. Thus, the PPh$_3$ ligands exchange readily on the NMR time scale at ambient temperature. The proposed structure is shown in Figure 5. The B−H−Rh most probably utilizes B(11), as has been found for [Rh(7-SPh-8-Me-7,8-$C_2B_9H_{10}$)(PPh$_3$)$_2$]. Two PPh$_3$ ligands complete the coordination sphere of the rhodium center.

The reaction of [NMe$_4$][7,8-μ-(S(CH$_2$)$_3$)-7,8-$C_2B_9H_{10}$] with [RuCl$_2$(PPh$_3$)$_3$] in boiling ethanol yielded a deep blue compound **5**. A ν(B−H) stretching absorption at 2538 cm^{-1} in the IR spectrum indicated the *nido* nature of the carborane, along with bands associated with PPh$_3$. The ^{11}B{^{1}H} NMR spectrum of **5** displays resonances in the range of −6/−36 in the ratio 1:1:2:1:2:2. The ^{1}H{^{11}B} NMR displayed at −1.9 ppm the signal of the B−H−B bridge, and resonances at −11.9 and at −3.7 ppm are indicative of the existence of two B−H−Ru agostic bonds. Similar resonances have been found with [7-PPh$_2$-8-Me-7,8-$C_2B_9H_{10}$]$^-$ upon reaction with [RuCl$_2$(PPh$_3$)$_2$]. The dissimilar position of the B−H⇀Ru resonances is influenced mostly by the *trans* ancillary ligand as has earlier been demonstrated[26] and not so much by the location of the boron atom. The B−H⇀Ru resonance corresponding to −11.9 ppm has a larger Ru−H character while that at −3.7 ppm has a larger B−H character.[8] The one having higher B−H character is the B−H located *trans* to the PPh$_3$, while that showing highly Ru−H character is *trans* to Cl.[26] At 7.3 ppm there is a series of complex resonances characteristic of phenyl protons. The ratio of these protons, B−H−B, and B−H⇀Ru is 30:1:2. Finally, the ^{31}P-{^{1}H} NMR spectrum shows two doublets at 75.8 and 37.3 ppm with ^2J(P,P) = 33 Hz. Thus, the spectroscopic data and elemental analysis of **5** are consistent with an *exo-nido* carborane ruthenium complex containing two mutually *cis* PPh$_3$ ligands and a chloride atom with the stoichiometry [RuCl(7,8-μ-(S(CH$_2$)$_3$)-7,8-$C_2B_9H_{10}$)(PPh$_3$)$_2$]. The proposed structure is indicated in Figure 6. The carborane cage acts as a tridentate ligand, where the Ru(II) is connected to the cluster through a S−Ru and two B−H⇀Ru bonds. The ^{31}P{^{1}H} NMR of compound **5** has only two well-defined doublets, corresponding to the two PPh$_3$ ligands. The steric crowding near the *exo*-cluster chain would, most probably, stabilize a unique isomer. The simplicity of the ^{31}P{^{1}H} NMR spectra at room temperature contrasts with that of the noncyclic monothioether compounds which was interpreted as a spectrum of several isomers as a result of the different ordering of the ancillary ligands coexisting.[6]

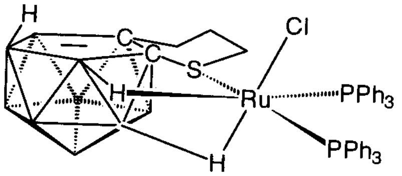

Figure 6. Proposed structure of [RuCl(7,8-μ-(S(CH$_2$)$_3$)-7,8-$C_2B_9H_{10}$)-(PPh$_3$)$_2$] (**5**).

In conclusion, a six-membered monothioether cycle incorporating the moiety "$C_2B_{10}H_{12}$" has been synthesized. Partial degradation readily takes place to produce the anionic [7,8-μ-(S(CH$_2$)$_3$)-7,8-$C_2B_9H_{10}$]$^-$ ligand. The anionic cluster enhances the donor capacity of the monothioether group, and halogens are removed from the coordination sphere of [MCl$_{(1\text{ or }2)}$(PPh$_3$)$_{(2\text{ or }3)}$] (M = Pd(II), Rh(I), Ru(II)) complexes. Ligand [7,8-μ-(S(CH$_2$)$_3$)-7,8-$C_2B_9H_{10}$]$^-$ behaves as dicoordinating or tricoordinating depending on the metal's nature, the metal's charge, and the coordination number requirement of the metal. The coordination takes place via the SR and BH groups. The B−H groups utilized in coordination are the ones surrounding the Cc−SR units. The cyclic nature of the ligand restricts the mobility of the thioether, modulating its coordination characteristics; thus no precise parallel behavior is found between cyclic and noncyclic monothioether derivatives of [$C_2B_9H_{12}$]$^-$. This rigidness or the steric crowding caused by the cycle also seems relevant to lower the number of possible complex isomers. It is noteworthy that the differing reactivity of [7,8-μ-(S(CH$_2$)$_3$)-7,8-$C_2B_9H_{10}$]$^-$ toward [PdCl$_2$(PRR'$_2$)$_2$] depends on the nature of the R groups. If aryl groups are present, B(11)−P bonds are formed, while in their absence η^5 coordination to Pd of the C_2B_3 open face is found. The explanation is ambiguous and may be due to the decreased basicity of the aryl phosphines vs alkyl phosphines or the facilitated B−P formation if aryl groups are present in the starting phosphine complexes. We do not have arguments at present to indicate the reasons for this different behavior.

More work is now underway to extend the coordination chemistry of 1,2-μ-(S(CH$_2$)$_3$)-1,2-$C_2B_{10}H_{10}$ and [7,8-μ-(S(CH$_2$)$_3$)-7,8-$C_2B_9H_{10}$]$^-$ and to elucidate the effect of the cycle in catalysis, as compared to their noncyclic analogues.

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Supporting Information Available: Tables of X-ray experimental details, atomic positional parameters, thermal parameters, and interatomic distances and angles for 7,8-μ-(S(CH$_2$)$_3$)-11-PPh$_3$-7,8-$C_2B_9H_9$ **1** (24 pages). Ordering information is given on any current masthead page.

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