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Synthesis and Structure of Half-Sandwich Pyridine-2-thiolato Cobalt(III) and Rhodium(III) Complexes and Their Reactivity toward Monodentate or Bidentate 1,2-Dicarba-*closo*-dodecaborane Thiolate Ligands

Shu Liu, Hui Wang, Peng-Cheng Zhang, Lin-Hong Weng, and Xiu-Feng Hou*

Department of Chemistry, Fudan University, Shanghai 200433, People's Republic of China

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The half-sandwich cobalt(III) and rhodium(III) complexes with pyridine-2-thiolato ligands Cp*Co(PyS)I (**3**) and Cp*Rh(PyS)Cl (**4**) [Cp* = pentamethylcyclopentadienyl, PyS = pyridine-2-thiolate] were obtained by reactions of lithium pyridine-2-thiolate (PySLi) with Cp*Co(CO)I_2 (**1**) and [Cp*RhCl_2]$_2$ (**2**), respectively, in high yield. Complexes **3** and **4** reacted with monodentate Li$SC_2(H)B_{10}H_{10}$ to give Cp*Co(PyS)[$SC_2(H)B_{10}H_{10}$] (**5**) and Cp*Rh(PyS)[$SC_2(H)B_{10}H_{10}$] (**6**), respectively. Reactions of **3** and **4** with $Li_2S_2C_2B_{10}H_{10}$ resulted in C−H activation of a methyl group of the Cp* of the cobalt complex to give [($C_5Me_4CH_2SC_5H_4N$)Co($S_2C_2B_{10}H_{10}$)] (**7**). No such activation of a methyl group of the Cp* of the rhodium complex occurred, and Cp*Rh[Py(H)S]($S_2C_2B_{10}H_{10}$) (**8**) was the product.

Introduction

In recent years, transition metal complexes containing thiolato derivatives of the carboranes [dicarba-*closo*-dodecaboranes(12)] were shown to have potential applications[1] such as boron neutron capture therapy (BNCT),[2] photophysical properties,[3] and polymers for high temperature.[4] The rigid backbone of the *ortho*-$C_2B_{10}H_{12}$ and the relative ease of derivatization at the carbon vertices make them excellent candidates for crystal engineering,[5] which allows the synthesis of complexes that have unusual structures. With the bidentate, chelating 1,2-dicarba-*closo*-dodecaborane (12)-1,2-dithiolate ligand $[S_2C_2(B_{10}H_{10})]^{2-}$, a series of mononuclear 16-electron Cp* half-sandwich complexes of Co, Rh, and Ir have been prepared.[6]These complexes exhibit rich coordination chemistry due to both the unsaturation at the metal atom and the bridging or chelating properties of the sulfur atoms.[7] Based on these 16-electron half-sandwich metal complexes, which contain a "*pseudo-aromatic*" metalladichalcogenolene five-membered ring, many heterometallic clusters[8]and discrete supramolecular assemblies[9] have been prepared. However, with the monodentate 1,2-dicarba-*closo*-dodecaborane (12)-1-thiolate ligand $[SC_2(H)B_{10}H_{10}]^-$, only a few group 8 transition metal complexes have been reported.[3,10]

Pyridine-2-thiolate has been used as supporting ligand for transition metal complexes because of the versatility in their coordination modes.[1] Since the cyclopentadienyl (Cp) and

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* Corresponding author. Tel: +86-21-55664007. Fax: +86-21-65641740. E-mail: xfhou@fudan.edu.cn.

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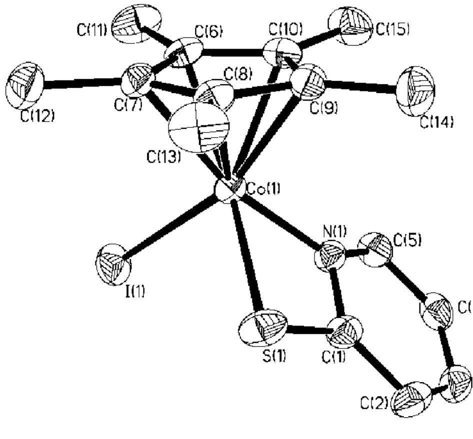


Figure 1. Molecular structure of **3**, with ellipsoids at the 30% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Co(1)−N(1) 1.949(3), Co(1)−C(9) 2.041(4), Co(1)−C(8) 2.068(3), Co(1)−C(7) 2.068(4), Co(1)−C(10) 2.076(4), Co(1)−C(6) 2.098(4), Co(1)−S(1) 2.303(1), Co(1)−I(1) 2.5791(7), N(1)−C(5) 1.344(4), N(1)−C(1) 1.350(5), S(1)−C(1) 1.721(4); N(1)−Co(1)−S(1) 71.73(9), N(1)−Co(1)−I(1) 90.88(9), S(1)−Co(1)−I(1) 95.30(4), N(1)−C(1)−S(1) 108.9(3).

functionalized cyclopentadienyl groups form inert bonds to metals and stabilize metal complexes in both high and low oxidation states, the chemical properties of the organometallic complex containing those ligands often change dramatically due to electronic and steric effects. Few half-sandwich cobalt, rhodium, and iridium complexes with the pyridine-2-thiolate ligand are known. A pentamethylcyclopentadienylrhodium(III) complex bearing two pyridine-2-thiolate ligands [Cp*Rh(PyS)$_2$] was reported,[12] in which one PyS ligand bonds to the rhodium ion in a S-monodentate mode, while the other is chelated to the metal atom in a N,S-bidentate mode. Pentamethylcyclopentadienyliridium(III) [Cp*Ir(PyS)N$_3$][13] was reported. Photolysis of the Cp*Ir complex [Cp*Ir(PyS)N$_3$] gave a pyridine-1-imido-2-thiolato complex, in which one of the nitrogen atoms of the azido ligand has been inserted into the iridium−N(Py) bond. Here we describe the synthesis and structure of Cp*Co and Cp*Rh complexes with pyridine-2-thiolate [Cp*M(PyS)X] (M = Co, Rh; X = I, Cl) and examine the reaction of half-sandwich cobalt(III) and rhodium(III) complexes containing the pyridine-2-thiolato ligands with the 1,2-dicarba-*closo*-dodecaborane (12)-1-thiolate ligand and 1,2-dicarba-*closo*-dodecaborane (12)-1,2-dithiolato ligand. In particular, the unusual reaction and stereochemistry of those organometallic compounds are described.

Results and Discussion

Synthesis and Structures of Cp*Co(PyS)I (3) and Cp*Rh(PyS)Cl (4). These complexes, [Cp*Co(PyS)I (**3**) and Cp*Rh(PyS)Cl (**4**)], were prepared as shown in eq 1. A detailed analysis of the spectroscopic data (^{1}H NMR, ^{13}C NMR, and IR spectra) showed that the pyridine-2-thiolato ligand was coordinated to the metal center through the sulfur and nitrogen atoms.

The molecular structure of **3** (Figure 1) shows that the complex possesses a Cp*−Co^{III} half-sandwich tripod structure, in which two of the three “legs” are the S and N atoms of the pyridine-2-thiolato ligand, and the third one is an iodine atom.

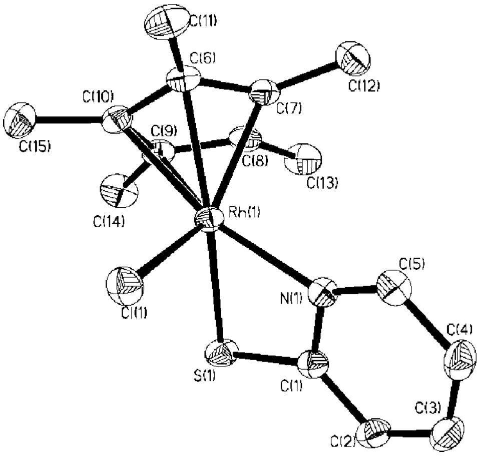
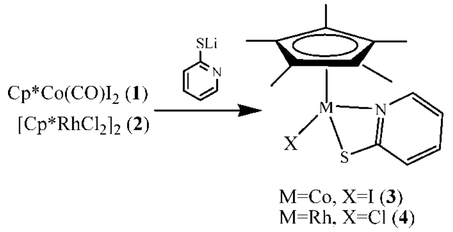


Figure 2. Structure of **4**, with ellipsoids at the 30% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh(1)−N(1) 2.102(2), Rh(1)−C(8) 2.126(3), Rh(1)−C(9) 2.141(3), Rh(1)−C(10) 2.154(3), Rh(1)−C(7) 2.158(3), Rh(1)−C(6) 2.173(3), Rh(1)−Cl(1) 2.405(1), Rh(1)−S(1) 2.4163(9), S(1)−C(1) 1.727(3), N(1)−C(1) 1.344(4), N(1)−Rh(1)−Cl(1) 86.68(7), N(1)−Rh(1)−S(1) 67.51(7), Cl(1)−Rh(1)−S(1) 92.88(4), N(1)−C(1)−S(1) 109.9(2).

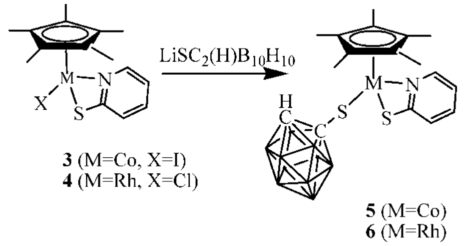
As depicted in Figure 2, the molecular structure of **4** is similar to that of the cobalt complex **3**.



(1)

Reactions of 3 and 4 with Monodentate Ligand LiSC$_2$(H)B$_{10}$H$_{10}$. Complex **3** reacted at room temperature with an equivalent amount of LiSC$_2$(H)B$_{10}$H$_{10}$ in THF to give yellow crystals of **5** in 38% yield (eq 2).

Single crystals of **5** were obtained by slow diffusion of hexane into a saturated solution of complex **5** in dichloromethane. However, single crystals of slightly differing color were isolated. So, the structures of both kinds were fully established by X-ray diffraction. Unexpectedly, they (**5a** and **5b**) are polymorphs, in which the cobalt atom is surrounded by a pentamethylcyclopentadienyl, a monodentate carboranethiolato ligand, and a bidentate pyridine-2-thiolato ligand with pseudotetrahedral geometry. As depicted in Figure 3, **5a** has similar bond lengths and angles to **5b**; however, **5a** crystallizes in the orthorhombic space group *Pbca*, whereas **5b** crystallizes in monoclinic space group *P*2(1)/*c*.



(2)

The molecular structure of complex **6** (Figure 4) is similar to that of the cobalt complex **5**.

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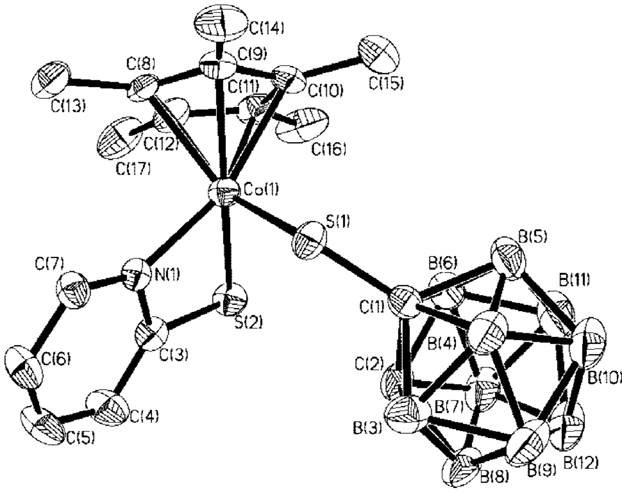


Figure 3. Molecular structure of **5**, with ellipsoids at the 30% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Co(1)−N(1) 1.943(3), Co(1)−C(12) 2.054(4), Co(1)−C(11) 2.069(5), Co(1)−C(10) 2.074(5), Co(1)−C(9) 2.077(4), Co(1)−C(8) 2.083(4), Co(1)−S(1) 2.270(1), Co(1)−S(2) 2.311(1), S(1)−C(1) 1.761(4), S(2)−C(3) 1.729(5), N(1)−C(7) 1.346(5), N(1)−C(3) 1.354(5), C(1)−C(2) 1.675(6), N(1)−Co(1)−S(1) 88.14(9), N(1)−Co(1)−S(2) 71.7(1), S(1)−Co(1)−S(2) 102.50(5), C(1)−S(1)−Co(1) 118.9(2), C(3)−S(2)−Co(1) 78.1(2), C(3)−N(1)−Co(1) 101.8(3), N(1)−C(3)−S(2) 108.3(3).

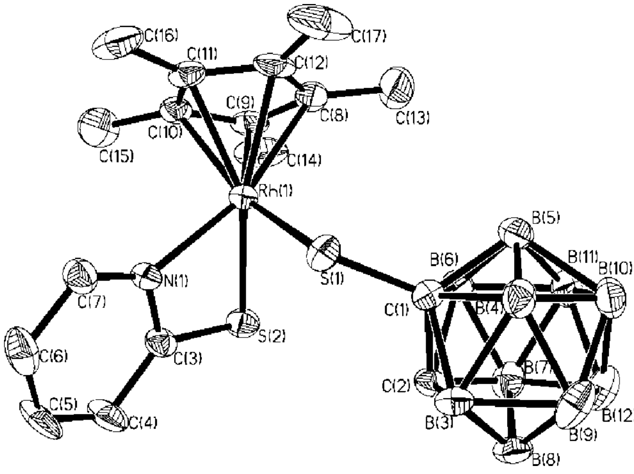


Figure 4. Molecular structure of **6**, with ellipsoids at the 30% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh(1)−N(1) 2.085(5), Rh(1)−C(11) 2.162(6), Rh(1)−C(9) 2.169(6), Rh(1)−C(10) 2.172(5), Rh(1)−C(12) 2.175(6), Rh(1)−C(8) 2.194(6), Rh(1)−S(1) 2.379(2), Rh(1)−S(2) 2.416(2), S(1)−C(1) 1.781(5), S(2)−C(3) 1.723(6), N(1)−C(3) 1.351(7), C(1)−C(2) 1.691(7), N(1)−Rh(1)−S(1) 84.1(1), N(1)−Rh(1)−S(2) 68.1(1), S(1)−Rh(1)−S(2) 93.87(6), N(1)−C(3)−S(2) 110.5(4).

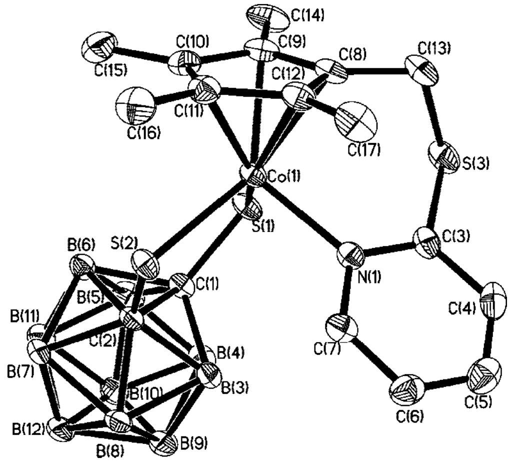
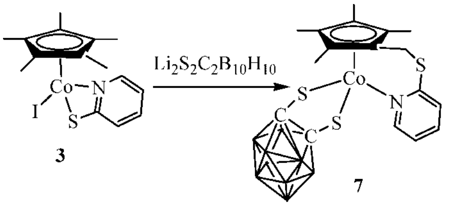


Figure 5. Molecular structure of complex **7**, with ellipsoids at the 30% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Co(1)−N(1) 2.025(3), Co(1)−C(8) 2.057(3), Co(1)−C(10) 2.077(4), Co(1)−C(12) 2.078(3), Co(1)−C(11) 2.091(4), Co(1)−C(9) 2.097(4), Co(1)−S(2) 2.244(1), Co(1)−S(1) 2.266(1), N(1)−C(3) 1.350(5), S(1)−C(1) 1.782(4), S(2)−C(2) 1.770(4), S(3)−C(3) 1.763(4), S(3)−C(13) 1.814(4), C(1)−C(2) 1.648(5). N(1)−Co(1)−S(2) 97.34(9), N(1)−Co(1)−S(1) 93.39(9), S(2)−Co(1)−S(1) 92.20(4), C(3)−N(1)−Co(1) 122.6(3), C(3)−S(3)−C(13) 100.8(2), N(1)−C(3)−S(3) 121.4(3), C(8)−C(13)−S(3) 113.0(3).

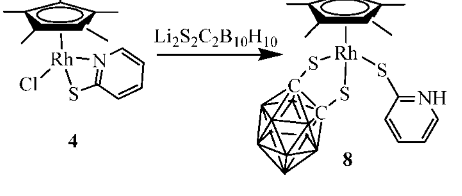
Reaction of 3 and 4 with Bidentate Ligand $Li_2S_2C_2B_{10}H_{10}$. Reactions of complexes **3** and **4** with $Li_2S_2C_2B_{10}H_{10}$ also were of interest. Unexpectedly, each complex gave a different result. When Cp*Co(PyS)I (**3**) reacted with 1 equiv of $Li_2S_2C_2B_{10}H_{10}$ in THF at −78 °C for 24 h, lithiation of a methyl group of the Cp* ligand occurred to give the red product **7** in 37% yield (eq 3) and, as a byproduct, the mononuclear 16-electron dithio-*ortho*-carboranylcobalt(III) complex ($Cp^*CoS_2C_2B_{10}H_{10}$) in 30% yield. The ^1H NMR spectrum of **7** showed two signals for the different types of ring-methyl groups (δ 2.15 and 1.80) and one signal for the substituted methylene (δ 3.72). The ^{13}C NMR spectrum of **7** showed three signals for C_5Me_4 (δ 94.53, 92.05, 92.03), two signals for $C_5\mathit{Me}_4$ (δ 10.40, 9.53), and a signal for $C_5Me_4\mathit{CH}_2$ (δ 25.89).

An X-ray diffraction study showed that complex **7** contains a pyridine-functionalized cyclopentadienyl ligand [$C_5Me_4CH_2$-SC_5H_4N], a 1,2-dicarba-*closo*-dodecaborate cluster, and a cobalt atom (Figure 5). The Co^{III} center is coordinated by the nitrogen atom in the pyridine, and the nearly planar pyridine builds an interplanar angle of 142.1° to the Cp ring. Thus a six-membered Co-N-C-S-C-C ring is formed. The five-membered metallacycle CoS_2C_2 has a distorted envelop conformation (the dihedral angle along the S_1−S_2 vector is 170.3°), which shows structural effects resulting from its steric requirements.



(3)

When Cp*Rh(PyS)I (**4**) was reacted with 1 equiv of $Li_2S_2C_2B_{10}H_{10}$ under the same reaction conditions, the expected complex with activation of a Cp* methyl group did not occur; rather complex **8** was obtained in moderate yield (eq 4). The ^1H NMR spectrum of **8** displayed four signals at δ 7.68, 7.58, 7.40, and 6.91 ppm due to the pyridine-2-thiolato unit, and one singlet at 7.27 ppm was assigned as the N-H proton of Py(H)S.



(4)

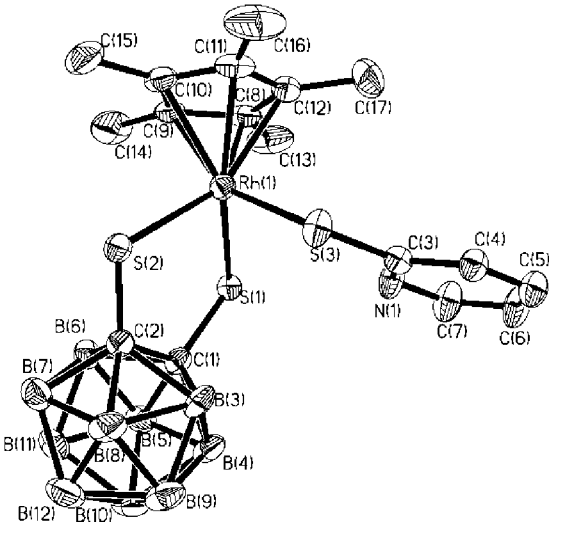


Figure 6. Molecular structure of **8**, with ellipsoids at the 30% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh(1)−C(9) 2.177(6), Rh(1)−C(8) 2.182(6), Rh(1)−C(11) 2.185(6), Rh(1)−C(12) 2.192(6), Rh(1)−C(10) 2.203(6), Rh(1)−S(2) 2.375(2), Rh(1)−S(1) 2.387(2), Rh(1)−S(3) 2.418(2), S(1)−C(1) 1.794(6), S(2)−C(2) 1.775(6), S(3)−C(3) 1.714(6), N(1)−C(3) 1.339(7), C(1)−C(2) 1.673(7), S(2)−Rh(1)−S(1) 89.17(6), S(2)−Rh(1)−S(3) 91.86(6), S(1)−Rh(1)−S(3) 98.97(6), N(1)−C(3)−S(3) 121.1(4).

The crystal structure of **8** (Figure 6) shows that the rhodium center adopts a three-legged piano-stool conformation and that all "three legs" are Rh−S bonds. The five-membered metallacycle RhS_2C_2 has a distorted envelop conformation similar to the $RhSe_2C_2$ ring found in $Cp^*Rh(PMe_3)(Se_2C_2B_{10}H_{10})$ and the RhS_2C_2 ring in $Cp^{tt}Rh(CNtBu)(S_2C_2B_{10}H_{10})$.[6d,e]

Experimental Section

General Procedures. All manipulations of the reactions were carried out using standard Schlenk techniques under a nitrogen atmosphere. Solvents were dried and deoxygenated by an M. Braun solvent purification system (4464) and collected just before use. $Li_2S_2C_2B_{10}H_{10}$,[17] $LiSC_2(H)B_{10}H_{10}$,[10a,18] $Cp^*Co(CO)I_2$,[19] and $[Cp^*RhCl_2]_2$[20] were synthesized according to the procedures described in the literature. 2-Mercaptopyridine was used as purchased without further purifications. Separation of product mixtures and purification of the components were accomplished by column chromatography. The silica gel had been activated at 200 °C overnight and kept under nitrogen before use. The element analyses were performed on an Elementar III Vario EI analyzer. Infrared spectra were recorded on a Nicolet AVATAR-360IR spectrometer. ^1H NMR (500 MHz), ^{13}C NMR (125 MHz), and ^{11}B NMR (160 MHz) spectra were obtained using a Bruker DMX-500 spectrophotometer in $CDCl_3$, respectively. Chemical shifts (downfield from TMS (^1H and ^{13}C) and $BF_3 \cdot OEt_2$ (^{11}B)) and coupling constants are reported in ppm and in Hz, respectively.

Preparation of Cp*Co(PyS)I (3). A solution of n-BuLi (1.6 M, 0.70 mL, 1.12 mmol) in hexane was added dropwise to a solution of 2-mercaptopyridine (124 mg, 1.12 mmol) in 15 mL of THF at 0 °C . The suspension was kept at room temperature and stirred for another 1 h. The resulting solution was slowly added to a solution of $Cp^*Co(CO)I_2$ (**1**) (530 mg, 1.12 mmol) in THF (15 mL) at −78 °C . After it had been stirred for 1 day, the solvent was removed under reduced pressure and the product was extracted with CH_2Cl_2. The clear green solution was precipitated in hexane to give green solid **3** (450 mg, 93%). Anal. Calcd for $C_{15}H_{19}CoINS$: C 41.78; H 4.44; N 3.25; S 7.43. Found: C 41.80; H 4.48; N 3.20; S 7.45. ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 8.31(d, 1H, PyS, $J_{H\text{-}H} = 6.44$ Hz); 7.23(t, 1H, PyS, $J_{H\text{-}H} = 7.36$ Hz); 6.71(t, 1H, PyS, $J_{H\text{-}H} = 7.32$ Hz); 6.44(d, 1H, PyS, $J_{H\text{-}H} = 8.24$ Hz); 1.71(s, 15H, Cp*). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 176.53, 149.56, 135.51, 126.10, 117.13 (PyS), 90.70, 10.64 (Cp*). IR (KBr disk): ν 3069, 2977, 2952, 2905, 1575, 1548, 1440, 1419, 1376, 1253, 1148, 1135, 1084, 1020, 760, 734 cm^{-1}.

Preparation of Cp*Rh(PyS)Cl (4). Following the procedure described for **3**, using n-BuLi (1.6 M, 1.0 mL, 1.62 mmol), 2-mercaptopyridine (178 mg, 1.62 mmol), and $[Cp^*RhCl_2]_2$ (**1**) (500 mg, 0.81 mmol) gave red crystals of **4** (447 mg, 72%). Anal. Calcd for $C_{15}H_{19}RhClNS$: C 47.00; H 5.00; N 3.66; S 8.35. Found: C 46.95; H 4.42; N 3.69; S 8.32. ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 7.97(d, 1H, PyS); 7.30(t, 1H, PyS); 6.78(t, 1H, PyS); 6.74(d, 1H, PyS); 1.82(s, 15H, Cp*). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 178.47, 145.67, 135.58, 127.44, 116.67 (PyS), 93.87, 9.35 (Cp∗). IR (KBr disk): ν 3094, 3052, 2957, 2913, 1712, 1575, 1544, 1480, 1439, 1418, 1373, 1250, 1139, 1087, 1018, 771, 732, 423 cm^{-1}.

Preparation of $Cp^*Co(PyS)(SC_2(H)B_{10}H_{10})$ (5). To a solution of $Cp^*Co(PyS)I$ (**3**) (86 mg, 0.20 mmol) in THF (10 mL) was added a Et_2O solution (10 mL) of $LiSC_2(H)B_{10}H_{10}$ (0.20 mmol). The reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel and eluted with THF/hexane (1:1). Recrystallization of product from CH_2Cl_2/hexane afforded yellow crystals of **5** (36 mg, 38%). Anal. Calcd for $C_{17}H_{30}B_{10}CoNS_2$: C 42.58; H 6.31; N 2.92; S 13.37. Found: C 42.54; H 6.29; N 2.90; S 13.34. ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 7.90(d, 1H, PyS, $J_{H\text{-}H} = 5.48$ Hz); 7.32(t, 1H, PyS, $J_{H\text{-}H} = 8.24$ Hz); 6.77(t, 1H, PyS, $J_{H\text{-}H} = 6.40$ Hz); 6.51(d, 1H, PyS, $J_{H\text{-}H} = 8.28$ Hz); 4.01(s, 1H, carborane); 1.43(s, 15H, Cp*). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 176.06, 148.97, 135.88, 125.38, 117.82 (PyS), 92.44, 9.73 (Cp*), 82.73, 68.72 (carborane). ^{11}B NMR (160 MHz, $CDCl_3$, ppm): δ −2.10, −3.03, −8.16, −9.16, −9.97, −10.85, −11.76, −12.45. IR (KBr disk): ν 3018, 2911, 2581, 1581, 1550, 1474, 1446, 1421, 1375, 1260, 1138, 1068, 1017, 857, 742 cm^{-1}.

Preparation of $Cp^*Rh(PyS)(SC_2(H)B_{10}H_{10}$ (6). To a solution of $Cp^*Rh(PyS)Cl$ (**4**) (115 mg, 0.30 mmol) in THF (10 mL) was added a Et_2O solution (10 mL) of $LiSC_2(H)B_{10}H_{10}$ (0.30 mmol). The reaction mixture was stirred for 15 h at room temperature. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel and eluted with THF/hexane (1:1). Recrystallization of product from CH_2Cl_2/hexane afforded deep red crystals of **6** (91 mg, 58%). Anal. Calcd for $C_{17}H_{30}B_{10}RhNS_2$: C 38.84; H 5.76; N 2.67; S 12.18. Found: C 38.81; H 5.71; N 2.69; S 12.17. ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 7.78(d, 1H, PyS, $J_{H\text{-}H} = 5.04$ Hz); 7.37(t, 1H, PyS, $J_{H\text{-}H} = 7.80$

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Hz); 6.78(t, 1H, PyS, $J_{\text{H-H}} = 5.04$ Hz); 6.76(d, 1H, PyS, $J_{\text{H-H}} = 7.80$ Hz); 4.16(s, 1H, carborane); 1.73(s, 15H, Cp*). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 177.99, 146.74, 135.81, 126.93, 117.27 (PyS), 96.17, 9.48 (Cp*), 83.20, 69.67 (carborane). ^{11}B NMR (160 MHz, $CDCl_3$, ppm): δ −2.09, −3.00, −8.63, −9.91, −10.84, −12.53. IR (KBr disk): ν 3026, 2990, 2912, 2582, 1579, 1550, 1446, 1421, 1376, 1260, 1135, 1069, 1017, 856, 744 cm^{-1}.

Preparation of [($C_5Me_4CH_2SC_5H_4N$)Co($S_2C_2B_{10}H_{10}$)] (7). To a solution of Cp*Co(PyS)I (**3**) (86 mg, 0.20 mmol) in THF (10 mL) was added a Et_2O solution (10 mL) of $Li_2S_2C_2B_{10}H_{10}$ (0.20 mmol) at −78 °C . The reaction mixture was stirred 15 h at room temperature. The color of the solution changed from deep green to red. The solvent was evaporated under reduced pressure, and the residue was chromatographed on silica gel. Elution with dichloromethane/hexane (1:1) gave a first red zone confirmed by NMR (^{1}H, ^{13}C, and ^{11}B) spectra as known complex $Cp^*CoS_2C_2B_{10}H_{10}$ (25 mg, 30% relative to **3**) and a second red zone that contained **7** (38 mg, 37% relative to **3**). Recrystallization of product **7** from CH_2Cl_2/hexane afforded deep red crystals. Anal. Calcd for $C_{17}H_{28}B_{10}CoNS_3$: C 40.07; H 5.54; N 2.75; S 18.87. Found: C 40.01; H 5.50; N 2.71; S 18.82. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.24(d, 1H, PyS, $J_{\text{H-H}} = 4.6$ Hz); 7.16(t, 1H, PyS, $J_{\text{H-H}} = 7.80$ Hz); 6.65(t, 1H, PyS, $J_{\text{H-H}} = 7.32$ Hz); 6.36(d, 1H, PyS, $J_{\text{H-H}} = 7.32$ Hz); 3.72 (s, 2H, CH_2S); 2.15(s, 6H, C_5Me_4); 1.80(s, 6H, C_5Me_4). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 159.86, 154.54, 137.40, 128.48, 122.53 (PyS), 94.53, 92.05, 92.03, 25.89, 10.40, 9.53 ($C_5Me_4CH_2S$), 94.45 (carborane). ^{11}B NMR (160 MHz, $CDCl_3$, ppm): δ −7.22, −8.20, −8.85, −9.85, −11.14. IR (KBr disk): ν 3062, 2960, 2910, 2589, 2563, 1643, 1577, 1445, 1420, 1377, 1255, 1136, 1071, 1018, 969, 866, 727 cm^{-1}.

Preparation of Cp*Rh(PySH)($S_2C_2B_{10}H_{10}$) (8). To a solution of Cp*Rh(PyS)Cl (**4**) (77 mg, 0.20 mmol) in THF (10 mL) was added a Et_2O solution (10 mL) of $Li_2S_2C_2B_{10}H_{10}$ (0.20 mmol) at −78 °C. The reaction mixture was stirred for 16 h at room temperature. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel and eluted with THF/hexane (1:1). Recrystallization of product from CH_2Cl_2/hexane afforded yellow crystals of **8** (48 mg, 37%). Anal. Calcd for $C_{18}H_{32}B_{10}RhCl_2NS_3$: C 33.69; H 5.03; N 2.18; S 14.96. Found: C 33.66; H 4.99; N 2.17; S 14.92. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.68(d, 1H, Py(H)S, $J_{\text{H-H}} = 5.36$ Hz); 7.58(d, 1H, Py(H)S, $J_{\text{H-H}} = 7.68$ Hz); 7.40(t, 1H, Py(H)S, $J_{\text{H-H}} = 8.80$ Hz); 6.91(t, 1H, Py(H)S, $J_{\text{H-H}} = 6.36$ Hz); 7.25(s, 1H, Py(H)S); 1.61(s, 15H, Cp*). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 136.68, 136.29, 132.33, 125.51, 115.19 (Py(H)S), 98.46, 8.70 (Cp*), 92.97 (carborane). ^{11}B NMR (160 MHz, $CDCl_3$, ppm): δ −4.57, −7.97, −10.18, −11.05. IR (KBr disk): ν 3197, 3074, 2959, 2910, 2583, 1609, 1572, 1494, 1445, 1372, 1265, 1126, 1096, 1021, 992, 862, 749, 726 cm^{-1}.

Crystal Structure Determination. Crystals of **3**, **4**, **5a**, **5b**, **6**, **7**, and **8** suitable for X-ray crystallography were grown by slow diffusion of hexane into CH_2Cl_2 or THF solution. The single crystals of **3**, **4**, **5a**, **5b**, **6**, **7**, and **8** for X-ray were, respectively, sealed in glass capillaries and were sequentially mounted on a CCD-Bruker Smart diffractometer. All the determinations of unit cell and intensity data were performed with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). All the data were collected at room temperature using the ω scan technique. These structures were solved by the direct methods, expanded using Fourier techniques, and refined on F^2 by a full-matrix least-squares method. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included but not refined. All the calculations were carried out with the Siemens SHELXTL PLUS program.[21] Details of crystal data for complexes **3**, **4**, **5a**, **5b**, **6**, **7**, and **8** are summarized in Tables 1 and 2.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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[21] *SHELXTL 6.10*; Bruker Analytical Instrumentation: Madison, WI, 2000.