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The "Rh(PPh$_3$)$_2$" and "Rh(cod)" Fragments as Probes To Compare the Coordinating and Electronic Characteristics of C−SR and C−PPh$_2$ in Heterodisubstituted Carborane Ligands

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Comparison of the coordinating and electronic characteristics of C−SR and C−PPh$_2$ in [7-PPh$_2$-8-SR-7,8-C$_2$B$_9$H$_{10}$]$^-$ has been achieved with the fragments "Rh(PPh$_3$)$_2$" and "Rh(cod)". The C−SR moiety has a strong polarizing effect on the carborane cage, depleting C−PPh$_2$ of electronic density and shifting its position in the ^{31}P NMR downfield as compared to non-thioether-containing complexes. The resolution of the structure of [Rh(7-PPh$_2$-8-SR-7,8-C$_2$B$_9$H$_{10}$)(cod)] has evidenced a stronger σ donation capacity of the C−SR group as compared to the C−PPh$_2$ group.

Introduction

Research in our group has been focused on the synthesis of dithioether (1,2-(SR)$_2$-1,2-C$_2$B$_{10}$H$_{10}$],[1] monothioether [1-SR-2-R′-1,2-C$_2$B$_{10}$H$_{10}$],[2] diphosphino [1,2-(PR$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$], and monophosphino (1-PR$_2$-2-R′-1,2-C$_2$B$_{10}$H$_{10}$][3] carborane derivatives of 1,2-dicarba-*closo*-dodecaborane. It has been shown that both the partially degraded monothioether ([7-SR-8-R′-C$_2$B$_9$H$_{10}$]$^-$) and the monophosphino ([7-PPh$_2$-8-R′-C$_2$B$_9$H$_{10}$]$^-$) ligands behave as bidentate for square-planar-demanding transition metal ions[4] and as tridentate for octahedral-demanding transition metal ions.[2,5] The coordinating sites are provided by either −SR or −PPh$_2$ and by B−H groups, forming B−H → M agostic bonds.

The homodisubstituted ligands provide two strong coordinating elements, either −SR or −PR$_2$, while the monosubstituted ligands provide only one. As a consequence, the monosubstituted ligands require one B−H vertex more than the disubstituted ligands to attain the metal coordination demands. While the monosubstituted ligands activate B(11)−H and B(2)−H, the homodisubstituted activate B(3)−H.

This has briefly shown the major differences between monosubstituted and homodisubstituted ligands. The recent synthesis of S,P heterodisubstituted derivatives of *o*-carborane has brought the opportunity to study their coordination behavior and to compare their coordinating capacity. Similarities with the homodisubstituted ligands are expected, but due to the asymmetry of the chelating groups, some resemblances with the monosubstituted ligands are anticipated.

In this paper we disclose the difference in reactivity of the C−SR and C−PPh$_2$ groups upon adequate reactivity toward Rh(I) complexes

Experimental Section

Materials and Methods. Commercial *o*-carborane was sublimed under vacuum at 0.01 mmHg prior to use. 1-SH-*o*-carborane and 1-PPh$_2$-2-SR-*o*-carborane were synthesized according to the literature.[6] A 1.6 M solution of *n*-butyllithium in *n*-hexane was used as purchased. [RhCl(PPh$_3$)$_3$][7] and [RhCl(cod)]$_2$[8] were synthesized as described elsewhere. All organic compounds and inorganic salts were analytical reagent grade and were used as received. The solvents were reagent grade. All reactions were carried out under a dinitrogen atmosphere by using Schlenck techniques. Microanalyses were performed on a Perkin-Elmer 240B microanalyzer. IR spectra were obtained as KBr pellets on a Nicolet 710-FT spectrophotometer. The ^{1}H NMR (300.0 MHz), ^{11}B NMR (96.3 MHz), and ^{31}P{^{1}H} NMR (121.5 MHz) spectra were recorded on a Bruker

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ARX 300 spectrometer. Chemical shift values for ^{1}H NMR spectra were referenced to an internal standard of $SiMe_4$ in deuterated solvents. Chemical shift values for ^{11}B NMR spectra were referenced relative to external $BF_3{\cdot}OEt_2$. Chemical shift values for $^{31}P\{^1H\}$ NMR spectra were referenced relative to external 85% H_3PO_4.

Synthesis of [Rh(7-PPh$_2$-8-SBu-C$_2$B$_9$H$_{10}$)(PPh$_3$)$_2$] (1). [RhCl(PPh$_3$)$_3$] (110 mg, 0.12 mmol) was added to a solution of 1-PPh$_2$-2-SBu-1,2-C$_2$B$_{10}$H$_{10}$ (50 mg, 0.12 mmol) in deoxygenated ethanol (5 mL). The brown-orange slurry was refluxed for 2 h. The resulting yellow-orange solid was isolated by filtration, washed with hot ethanol (5 mL) and diethyl ether (5 mL), and dried in a vacuum to afford an orange solid, yield 88 mg (71%). Anal. Calcd for $C_{54}H_{59}B_9P_3RhS$: C, 62.77; H, 5.76; S, 3.10. Found: C, 62.85 H, 6.02; S, 3.09. FTIR (KBr): ν(B−H) 2530 cm^{-1}. ^{1}H {^{11}B} NMR (CD_2Cl_2): δ (ppm) −2.6 (bs, 1H, B*H*B), 0.9 (m, 3H, C*H*$_3$), 1.2 (m, 2H, C*H*$_2$−CH$_3$), 1.7 (m, 2H, −C*H*$_2$−CH$_2$−), 3.5 (m, 2H, −S−C*H*$_2$−), 7.0−8.2 (m, 40 H, C$_{aryl}$−*H*). ^{11}B NMR (CD_2Cl_2): δ (ppm) −11.7 (2B), −14.5 (2B), −17.4 (1B), −19.6 (2B), −30.6 (d, ^1J(B,H) = 99.9 Hz, 1B), −36.0 (d, ^1J(B,H) = 115.5 Hz, 1B). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 26.8 (ddd, ^2J_t(P,P) = 297 Hz, ^1J(P,Rh) = 133 Hz, ^2J_c(P,P) = 40 Hz, 1P, PPh$_3$), 39.4 (dt, ^1J(P,Rh) = 168 Hz, ^2J_c(P,P) = 34 Hz, 1P, PPh$_3$), 76.2 (ddd, ^2J_t(P,P) = 297 Hz, ^1J(P,Rh) = 140 Hz, ^2J_c (P,P) = 32 Hz, 1P, −PPh$_2$).

Synthesis of [Rh(7-PPh$_2$-8-S*i*Pr-7,8-C$_2$B$_9$H$_{10}$)(cod)] (2). [RhCl(cod)]$_2$ (26.4 mg, 0,054 mmol) was added to a solution of [NMe$_4$][7-PPh$_2$-8-S*i*Pr-7,8-C$_2$B$_9$H$_{10}$] (50 mg, 0.11 mmol) in hot deoxygenated ethanol (5 mL). The orange slurry was refluxed for 1 h:30 min. The resulting orange precipitate was isolated by filtration, washed with hot ethanol (5 mL) and diethyl ether (5 mL), and dried in a vacuum to yield 34.7 mg (52%). Recrystalization from dichloromethane/*n*-heptane (1:1) gave orange microcrystals. Anal. Calcd for $C_{25}H_{39}B_9PRhS$: C, 49.81; H, 6.52; S, 5.32. Found: C, 49.46; H, 6.34; S, 5.50. FTIR (KBr): ν(B−H) (cm^{-1}) 2530. ^{1}H {^{11}B} NMR (CD_2Cl_2): δ (ppm) −2.5 (bs, 1H, B*H*B), 1.4 (d, ^1J(H, H) = 6.0 Hz, 6H, C*H*$_3$), 1.9−2.3 (m, 8H, −C*H*$_2$ (cod)), 3.3 (m, 1H, −S−C*H*), 4.3 (bs, 1H, C*H*= (cod)), 4.4 (br, 1H, C*H*= (cod)), 4.6 (bs, 1H, C*H*= (cod)), 5.5 (bs, 1H, C*H*= (cod)), 7.3−7.7 (m, 10 H, C$_{aryl}$−*H*). ^{11}B NMR (CD_2Cl_2): δ (ppm) −12.9 (1B), −15.3 (1B), −17.8 (1B), −19.1 (2B), −20.1 (1B), −22.4 (1B), −33.1 (d, ^1J(B,H) = 97.5 Hz, 1B), −38.9 (d, ^1J(B,H) = 141.8 Hz, 1B). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 67.4 (d, *J*(P,Rh) = 145.2 Hz, *P*Ph$_2$).

X-ray Structure Determination of [Rh(7-PPh$_2$-8-SiPr−C$_2$B$_9$H$_{10}$)(cod)]. 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. A correction for empirical absorption (ψ scan) was also applied. A total of 5560 independent reflections were collected by $\omega/2\theta$ scan mode ($2\theta_{max}$ = 50°). Of those, 3336 were considered as observed according to the criterion $I > 2\sigma(I)$. Crystallographic data are presented in Table 1. Selected bond lengths and angles are given in Table 2.

The structure was solved by direct methods by using the MITRIL program,[9] and least-squares refinements were performed using the SHELXL-93 program.[10] Boron atoms were refined with isotropic, but the rest of the non-hydrogen atoms, with anisotropic displacement parameters. Hydrogen atoms were included in the calculations at fixed distances from their host atoms and treated as riding atoms using the SHELXL-93 default parameters.

Table 1. Crystallographic Data and Structure Refinement for [Rh(7-PPh$_2$-8-S*i*Pr-7,8-C$_2$B$_9$H$_{10}$)(cod)]

chem formula	$C_{25}H_{39}B_9PRhS$
fw	602.79
T, °C	21
λ, Å	0.710 69
cryst syst	orthorhombic
space group	*Pna*2(1) (No. 33)
a, Å	37.54(3)
b, Å	13.376(8)
c, Å	11.93(2)
β, deg	90
V, Å^3	5992(9)
Z	8
D_{calcd}, g cm^{-3}	1.336
μ, mm^{-1}	0.708
F(000)	2480
independent reflect	5560
parameters	604
R1[a] [$I > 2\sigma(I)$]	0.0547
wR[b] [$I > 2\sigma(I)$]	0.0986
larg diff peak/hole, e Å^{-3}	0.501 and −0.450

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

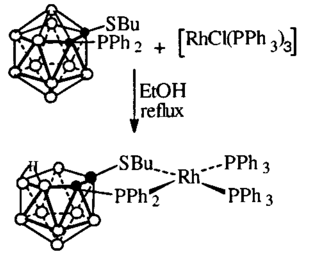

Figure 1. Schematic reaction of 1-PPh$_2$-2-SBu-1,2-C$_2$B$_{10}$H$_{10}$ with [RhCl(PPh$_3$)$_3$].

Table 2. Selected Bond Lengths [Å] and Angles [deg] for [Rh(7-PPh$_2$-8-S*i*Pr-7,8-C$_2$B$_9$H$_{10}$)(cod)]

Rh(1A)−C(32A)	2.171(14)	Rh(1B)−C(33B)	2.17(2)
Rh(1A)−C(33A)	2.18(2)	Rh(1B)−C(32B)	2.21(2)
Rh(1A)−C(29A)	2.20(2)	Rh(1B)−C(29B)	2.23(2)
Rh(1A)−C(28A)	2.227(14)	Rh(1B)−C(28B)	2.26(2)
Rh(1A)−P(1A)	2.300(3)	Rh(1B)−P(1B)	2.309(3)
Rh(1A)−S(1A)	2.361(4)	Rh(1B)−S(1B)	2.354(4)
S(1A)−C(8A)	1.773(13)	S(1B)−C(8B)	1.797(13)
S(1A)−C(25A)	1.84(2)	S(1B)−C(25B)	1.861(13)
P(1A)−C(13A)	1.802(14)	P(1B)−C(19B)	1.814(12)
P(1A)−C(19A)	1.833(13)	P(1B)−C(7B)	1.829(12)
P(1A)−C(7A)	1.832(13)	P(1B)−C(13B)	1.837(13)
C(7A)−C(8A)	1.57(2)	C(7B)−C(8B)	1.60(2)
C(32A)−Rh(1A)−P(1A)	95.5(4)	C(33B)−Rh(1B)−P(1B)	97.2(4)
C(33A)−Rh(1A)−P(1A)	103.2(5)	C(32B)−Rh(1B)−P(1B)	99.6(5)
C(29A)−Rh(1A)−S(1A)	92.4(5)	C(29B)−Rh(1B)−S(1B)	91.3(5)
C(28A)−Rh(1A)−S(1A)	88.0(5)	C(28B)−Rh(1B)−S(1B)	90.2(5)
P(1A)−Rh(1A)−S(1A)	85.15(12)	P(1B)−Rh(1B)−S(1B)	85.37(12)
C(8A)−S(1A)−Rh(1A)	106.2(4)	C(8B)−S(1B)−Rh(1B)	107.4(4)
C(7A)−P(1A)−Rh(1A)	107.4(4)	C(7B)−P(1B)−Rh(1B)	108.8(4)
C(8A)−C(7A)−P(1A)	114.4(9)	C(8B)−C(7B)−P(1B)	114.1(8)
C(7A)−C(8A)−S(1A)	117.8(9)	C(7B)−C(8B)−S(1B)	116.8(9)

Results and Discussion

The "Rh(PPh$_3$)$_2$" Fragment as a Probe To Compare the C−SR and C−PPh$_2$ Coordinating Capacity. The reaction of 1-PPh$_2$-2-SBu-1,2-C$_2$B$_{10}$H$_{10}$ with [RhCl(PPh$_3$)$_3$] in refluxing ethanol yields the rhodium complex [Rh(7-PPh$_2$-8-SBu-7,8-C$_2$B$_9$H$_{10}$)(PPh$_3$)$_2$] (Figure 1). The spectroscopic data and elemental analysis were consistent with the deboronation of the cluster to yield a *nido* carborane. The cluster's negative charge compensates the positive rhodium. The IR displayed a ν (B−H) band at 2530 cm^{-1}, which is consistent with the

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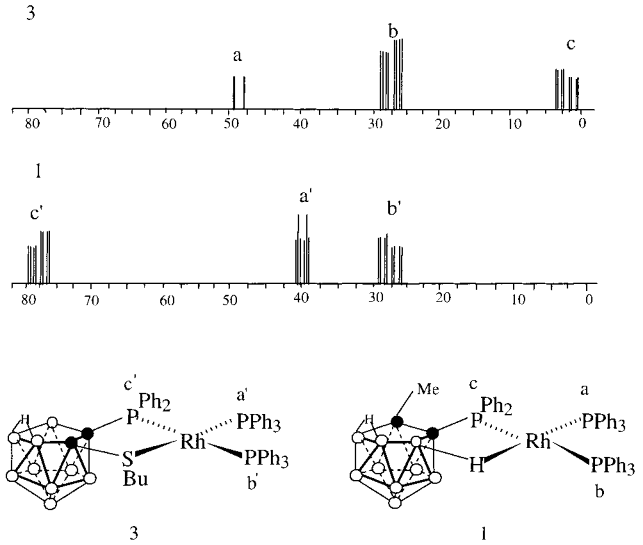

Figure 2. Schematic representation of the $^{31}P\{^1H\}$ NMR spectra of $[Rh(7\text{-}PPh_2\text{-}8\text{-}SBu\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ (**1**) and $[Rh(7\text{-}PPh_2\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ (**3**).

nido fragment. In agreement with this, the ^1H NMR spectrum displays a broad resonance at ca. −2.6 ppm, corresponding to the B−H−B bridge. No resonances were found at field higher than −2.6 ppm, which would have been indicative of B−H−M interactions. The $^{31}P\{^1H\}$ NMR spectrum (Figure 2) displays three sets of resonances, indicating three different phosphorus atoms in the molecule. The highest field resonance is a doublet of doublet of doublets centered at $\delta = 26.8$ ppm. A second doublet of doublet of doublets is observed at the lowest field resonance ($\delta = 76.2$ ppm). Those two sets of resonances shall be asigned to $C-PPh_2$ and PPh_3 in a trans disposition. Finally at $\delta = 39.4$ ppm a doublet of triplets is observed, which is assigned to the PPh_3 ligand cis to both the $-PPh_2$ group and the PPh_3 trans to the $-PPh_2$ group. The solution of $[Rh(7\text{-}PPh_2\text{-}8\text{-}SBu\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ is air sensitive, as it is evidenced by the $^{31}P\{^1H\}$ NMR and the ^{11}B NMR, displaying only one broad singlet signal attributable to $OPPh_3$ and $B(OEt)_3$, respectively.

To assign the $^{31}P\{^1H\}$ NMR resonances, it was required to compare the spectrum of $[Rh(7\text{-}PPh_2\text{-}8\text{-}SBu\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ (**1**) to that of the monosubstituted $[Rh(7\text{-}PPh_2\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ (**3**).[4c] Both compounds are indicated in Figure 2.

The ^{31}P NMR spectrum of $[Rh(7\text{-}PPh_2\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ displays a broad doublet at 50.1 ppm and two doublet of doublet of doublets at 30.2 and at 4.55 ppm, respectively. Thus the two phosphorus atoms in trans disposition display their $^{31}P\{^1H\}$ NMR resonances at 30.2 and 4.55 ppm. For **1** these are at 26.8 and 76.2 ppm. If the trans influence is dominating in these compounds,[11] a noticeable discrepancy in chemical shifts is expected for phosphorus a and a′ which are trans to B−H and SBu, respectively. This is the case since resonances at 50.1 and 39.4 ppm are observed, respectively. Resonances corresponding to b and b′ should be less influenced since both are trans to $C-PPh_2$; thus it is expected that both should appear at similar chemical shifts, 30.2 and 26.8, respectively. As a result, the $C-PPh_2$ resonance should be at 76.2 ppm in **1**. The corresponding one in $[Rh(7\text{-}PPh_2\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ is at 4.55 ppm. This enormous difference shall be attributed to the electron-withdrawing effect induced by the −SR group,[12] which depletes $-PPh_2$ of electron density, consequently shifting its position to lower field, and turns the −SR into a strong coordinating group. This will later be discussed when dealing with the dialkene ligand (cod).

The metal-driven partial degradation of $1\text{-}PPh_2\text{-}2\text{-}SBu\text{-}1,2\text{-}C_2B_{10}H_{10}$ to $[7\text{-}PPh_2\text{-}8\text{-}SBu\text{-}7,8\text{-}C_2B_9H_{10}]^-$ found in this reaction provides useful information on the role the C−SR moiety is playing in this deboronation reaction. In general no deboronation has been achieved upon the reaction of $1\text{-}PR_2\text{-}2\text{-}R'\text{-}1,2\text{-}C_2B_{10}H_{10}$ or $1\text{-}SR\text{-}2\text{-}R'\text{-}1,2\text{-}C_2B_{10}H_{10}$ with transition metal complexes, and although $1,2\text{-}(PR_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (R = alkyl or aryl) compounds are ready to deboronate to $[7,8\text{-}(PR_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ by reaction with a transition metal complex, not all metals can do it. For instance $[AuCl(PPh_3)]$, $[AgCl(PPh_3)]$, or $[MCl_2(PPh_3)_2]$ (M = Pd, Pt) are successful in deboronating the cluster but not $[RhCl(PPh_3)_3]$.[13] This is why this was chosen to perform the metal-driven deboronation and prove that although carborane monophosphine ligands were not ready for deboronation upon reaction with $[RhCl(PPh_3)]$, the contribution of the C−SR moiety facilitated it.

The "Rh(cod)" Fragment as a Probe. The C−P bond is highly susceptible to nucleophilic attack, producing the breaking of the bond. Thus the synthesis of $[7\text{-}PPh_2\text{-}8\text{-}SR\text{-}7,8\text{-}C_2B_9H_{10}]^-$ anionic ligands from the $1\text{-}PPh_2\text{-}2\text{-}SR\text{-}1,2\text{-}C_2B_{10}H_{10}$ neutral compounds is not a straightforward procedure in the absence of metals, and conventional methods of partial degradation could not be utilized. Recently, a procedure to synthesize *nido* diphosphino[3a] ligands was reported which is also operative for these heterodisubstituted compounds. The availability of these $[7\text{-}PPh_2\text{-}8\text{-}SR\text{-}7,8\text{-}C_2B_9H_{10}]^-$ ligands in pure form motivated us to use them and compare their behavior with respect to the *closo* analogues. Furthermore and complementing the discussion early initiated with regard to the comparative bonding capacity of C−SR vs $C-PPh_2$ complex, $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ provided a homodilegged π-ligand which upon coordination and presumably Cl replacement would bring valuable information on the relative bonding capacity of the two distinct coordinating groups present in these $[7\text{-}PPh_2\text{-}8\text{-}SR\text{-}7,8\text{-}C_2B_9H_{10}]^-$ molecules. Reaction of $[NMe_4][7\text{-}PPh_2\text{-}8\text{-}S\mathit{i}Pr\text{-}7,8\text{-}C_2B_9H_{10}]$ with $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ in 2:1 molar ratio in refluxing ethanol led to the isolation of the cyclooctadiene rhodium complex $[Rh(7\text{-}PPh_2\text{-}8\text{-}S\mathit{i}Pr\text{-}7,8\text{-}C_2B_9H_{10})(cod)]$ (**2**). The IR spectra shows an absorption at 2530 cm^{-1} attributable to B−H, and the $^1H\{^{11}B\}$ NMR spectrum showed a broad resonance at −2.5 ppm characteristic of B−H−B. The ^{11}B NMR is also consistent with the *nido* nature of the ligand in the complex. The same results are obtained starting either from the *closo* compound or from the *nido* one, but a better yield is obtained when the *nido* ligand is used instead of the *closo*. Although the molecular structure could be in-

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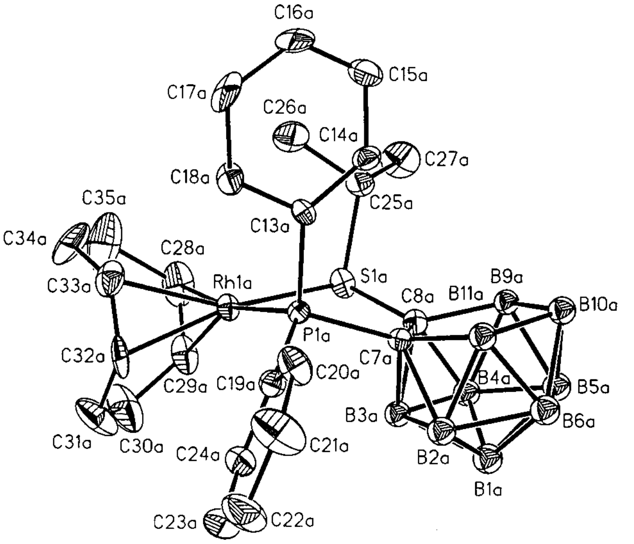

Figure 3. ORTEP plot of [Rh(7-PPh$_2$-8-S*i*Pr-7,8-C$_2$B$_9$H$_{10}$)(cod)] showing 30% displacement ellipsoids.

ferred from the spectroscopic data, suitable crystals were required to know structural parameters which could provide information on the $-PR_2$ and $-SR$ σ bonding capacity. Adequate crystals were grown from dichloromethane/*n*-heptane (Figure 3). The homodilegged nature of cod and its π ligand character is adequate to sense the σ bonding capacity of the respective trans coordinating groups. The asymmetric unit of the structure consists of two approximately similar [Rh(7-PPh$_2$-8-SiPr$-$C$_2$B$_9$H$_{10}$)(cod)] complex units, labeled **A** and **B**. In each unit the carborane cage is coordinated bidentately through the P and S atoms to the Rh(I) ion, while cod is η^4-coordinated to the metal. In Table 2 the C(cod)$-$Rh distance trans to C$-$SR averages 2.17 Å in molecule **A** and 2.19 Å in molecule **B**. On the contrary the average C(cod)$-$Rh distance trans to C$-$PPh$_2$ is 2.21 Å in **A** and 2.24 Å in **B**. Thus either in **A** or in **B** the C(cod)$-$Rh distance trans to C$-$SR is approximately 0.04 Å shorter than that trans to C$-$PPh$_2$. This can be interpreted as if excess electron density from the Rh provided by a determined carborane coordinating fragment is offloaded onto its trans alkene leg. The more extensive the back-donation, the shorter the Rh$-$alkene distance will be found. Thus higher contribution by back-donation is found in the alkene fragment trans to C$-$SR. This suggests that this fragment loads more electron density into Rh than C$-$PPh$_2$, in agreement with the ^{31}P NMR spectrum of [Rh(7-PPh$_2$-8-S*i*Pr-7,8-C$_2$B$_9$H$_{10}$)(cod)].

Additional Details on the [Rh(7-PPh$_2$-8-S*i*Pr-7,8-C$_2$B$_9$H$_{10}$)(cod)] Molecule Structure. In each complex unit the orientation of the metal is anti with respect to the C$_2$B$_3$ open face, and the bridging H atom at the open face is connected to B(10) and B(11). Bond lengths in the two coordination spheres are equal within experimental error (cf. Table 2), and also the geometry of the two [Rh(7-PPh$_2$-8-SiPr$-$C$_2$B$_9$H$_{10}$)] moieties is very similar, although a few significant differences can be obtained. Typical parameters observed for the 7,8-disubtituted *nido* carborane moieties are the P$-$C(7)$-$C(8)$-$S torsion angle values of $-0.5(13)°$ and $0.3(12)°$ and the C(7)$-$C(8) distances of 1.57(2) and 1.60(2) Å for units **A** and **B**, respectively.

The most remarkable difference between the two complex units is in the orientation of (cod) ligands with respect to the plane through the central atom and the coordinating P and S atoms. For unit **A** deviations of the atoms C(28a), C(29a), C(32a), and C(33a) from the plane are 0.33(3), $-0.97(2)$, $-0.45(2)$, and 0.86(2) Å, respectively. In unit **B** the relevant deviations for C(28b), C(29b), C(32b), and C(33b) atoms are 0.61(3), $-0.73(3)$, $-0.58(2)$, and 0.77(2) Å, respectively. Thus (cod) is more symmetrically coordinated in **B**, but generally small deviations in η^4 bonding are possible and these kind of deviations arise from packing effects.

Conclusion

Heterodisubstituted C$-$PPh$_2$ and C$-$SR *o*-carborane derivative ligands sharing exactly the same structural moiety, the carborane, have provided a unique way to precisely compare the coordinating and electronic characteristic of both groups. The C$-$SR has a stronger capacity than C$-$PPh$_2$ to polarize electron density, which in turn makes the C$-$SR a better σ donor.

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Supporting Information Available: X-ray tables of experimental details, hydrogen atom positional parameters and thermal parameters, anistropic thermal parameters, and interatomic distances and angles for [Rh(7-PPh$_2$-8-S*i*Pr-7,8-C$_2$B$_9$H$_{10}$)(cod)] (12 pages). Ordering information is given on any current masthead page.

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