Versatility of *nido*-Monophosphinocarboranes as Ligands. Tricoordination via PPh_2 and BH in Rhodium(I) Complexes

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Summary: Reaction of $[NMe_4][7\text{-}PPh_2\text{-}8\text{-}R\text{-}7,8\text{-}C_2B_9H_{10}]$ *(R = H, Me) with* $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ *in dichloromethane yielded* $[Rh(7\text{-}PPh_2\text{-}8\text{-}R\text{-}7,8\text{-}C_2B_9H_{10})(cod)]$ *(R = H, Me). The carborane ligand coordinates the Rh through Cc−*PPh_2*, B(11)−H, and B(2)−H. The Rh(I) atom is pentacoordinated, assuming that cod is bidentate. The B−H→Rh resonances in the* ^1H *NMR spectra appear in the interval between +1 and +3 ppm, as a consequence of the trans influence generated by cod. The structure was fully elucidated by a crystal diffraction analysis of* $[Rh(7\text{-}PPh_2\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_{10})(cod)]$*. The B−H→Rh agostic bonds exist both in the solid state and in solution, as was proven by* ^{11}B *NMR.*

Introduction

Rhodacarboranes[1,2] containing phosphine or alkene ligands showed exceptional activity in the hydrogenation of terminal[3,4] and internal alkenes,[5,6] respectively. In earlier papers, we described the syntheses of rhodacarboranes based on *nido*-dithiocarborane[7] and *nido*-diphosphinocarborane[8] ligands. In both cases, the *nido*-carborane cage is chelated to Rh(I) through the two S or P atoms, giving the metal a square-planar geometry. Recently, we have reported[9,10] the synthesis of new Cc−S or Cc−P (Cc = cluster carbon) *exo-nido*-rhodacarborane complexes whose general formula is $[Rh(7\text{-}SR\text{-}8\text{-}R'\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ or $[Rh(7\text{-}PR_2\text{-}8\text{-}R'\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$. These complexes have the necessary B−H→M interactions in the *exo-nido* species to prevent the formation of *closo* tautomers. The *nido*-carborane is bonded to the square-planar Rh(I) through the Cc−PPh_2 phosphorus atom and the B(11)−H group. They are active catalysts in the hydrogenation of terminal alkenes. Up to now, in every Rh(I) complex containing a C_2B_9 *nido* cluster, this had been found coordinated to Rh(I) as a bidentate ligand.[3−11] Here, we report on the synthesis and crystallographic characterization of the first Rh(I) complex where the carborane ligand acts as a tricoordinating moiety. Moreover, this unique complex contains two B−H→Rh interactions and is the first *exo-nido* complex with cycloocta-1,5-diene as ancillary ligand.

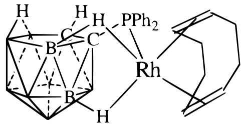

Figure 1. Structure proposed for the rhodium complex **1**.

Results and Discussion

The ligand $[NMe_4][7\text{-}PPh_2\text{-}8\text{-}H\text{-}7,8\text{-}C_2B_9H_{10}]$ reacts with $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$, giving rise to the complex $[Rh(7\text{-}PPh_2\text{-}8\text{-}H\text{-}7,8\text{-}C_2B_9H_{10})(cod)]$ (**1**) (Figure 1). The IR spectrum of **1** showed the ν(B−H) band at 2546 cm^{-1} and a low-intensity band at 2101 cm^{-1} which can be assigned to the B−H→Rh bond. The ^1H NMR spectrum displayed a broad resonance centered at −2.84 ppm assigned to the B−H−B bridge, and no further resonances were found at higher field. Resonances centered at 7.45 ppm characteristic of phenyl groups indicated the presence of the *nido*-carborane in the complex. Resonances at 2.31, 3.79, 4.02, and 5.45 ppm were attributed to the cycloocta-1,5-diene ligand. The $^{31}P\{^1H\}$ NMR spectrum showed only a doublet at δ 23.67 ppm ($^1J(Rh,P) = 121$ Hz), attributed to the unique phosphorus atom in the cluster. The $^{11}B\{^1H\}$ NMR spectrum pattern 1:1:1:1:1:1:2:1 is similar to that of the free ligand (1:1:1:1:3:2), although some resonances were noticeably altered. These data confirmed the PPh_2 coordination to the Rh(I); however, they were in apparent contradiction with earlier data obtained by our group which indicated that $[7\text{-}PR_2\text{-}8\text{-}R'\text{-}7,8\text{-}C_2B_9H_{10}]^-$ or

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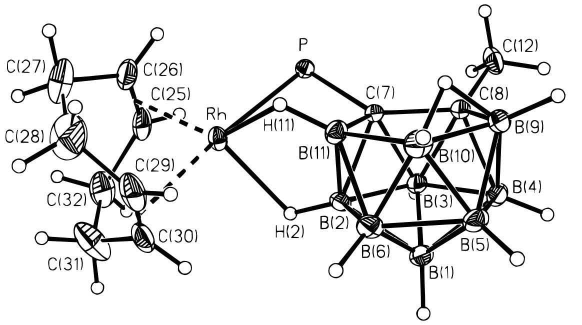

Figure 2. Simplified drawing of [Rh(7-PPh$_2$-8-Me-7,8-C$_2$B$_9$H$_{10}$)(cod)] (**2**). Phenyl groups are omitted. Thermal displacement ellipsoids are drawn at the 20% probability level.

[7,8-(PR$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$]$^-$ were at least dicoordinating and chelating.[8−10] In [7-PR$_2$-8-R′-7,8-C$_2$B$_9$H$_{10}$]$^-$ chelation originates in Cc−PR$_2$ and B(11)−H. The absence of resonances at the negative region in the ^{1}H NMR of **1** suggested the absence of B−H→Rh interactions, in which case the Rh(I) would be tricoordinated if it is assumed that cod occupies two coordination sites. Furthermore, it was obvious from the ^{1}H NMR that the two double bonds in cod were clearly different. These confusing data did not permit us to draw a structure proposal for this complex, and X-ray crystal data were required. Unfortunately, we were not able to grow adequate crystals for this analysis.

The reaction of [NMe$_4$][7-PPh$_2$-8-Me-7,8-C$_2$B$_9$H$_{10}$] with [Rh$_2$(μ-Cl)$_2$(cod)$_2$] was conducted under conditions similar to those utilized for **1** except for the reaction time (10 min). The compound [Rh(7-PPh$_2$-8-Me-7,8-C$_2$B$_9$H$_{10}$)-(cod)] (**2**) was obtained. Besides some minor changes, the NMR data confirmed the similarity of compounds **1** and **2**. In this case, the complex **2** crystallizes from CHCl$_3$ to give good-quality orange crystals for X-ray diffraction analysis. The simplified drawing of **2** is shown in Figure 2. The molecule consists of a pentacoordinated Rh(I) atom bonded to a tridentate *nido*-carborane cage and to one cycloocta-1,5-diene. The three cluster bonds to Rh(I) are made by Cc−PPh$_2$, B(2)−H, and B(11)−H. The two remaining Rh(I) positions are filled by the alkene ligand. Interestingly, the coordination motif presented by the cluster is identical with that found for Ru(II).[12] In this case, too, the participating elements in coordination were Cc−PR$_2$, B(2)−H, and B(11)−H. However, in [RuCl(7-PPh$_2$-8-Me-7,8-C$_2$B$_9$H$_{10}$)(PPh$_3$)$_2$] (**3**), the B−H→Ru resonances in the ^{1}H NMR spectra were found in the range between −3.0 and −14.5 ppm for the complexes.

Thus, although the ^{1}H NMR spectroscopic data for the complex **2** in solution show no evidence of B−H→Rh agostic bonds in the negative zone, the resolution of the crystallographic structure revealed two of them. The Rh−P distance (2.293(9) Å) is close to that observed in [Rh(7-PPh$_2$-8-H-7,8-C$_2$B$_9$H$_{10}$)(PPh$_3$)$_2$][10] (**4**), which is 2.276-(3) Å. The Rh−B(11) distance in **2** (2.538(4) Å) was a slightly shorter than in **4** (2.643 Å). The major discrepancy was with the Rh−B(2) distance. In complex **2** this is a bond distance (2.521(4) Å), while in **4** it was out of bonding range (3.586(8) Å). On the other hand, these distances in **2** are slightly longer that those found in **3**, which are 2.473(2) Å for Ru−B(11) and 2.422(8) Å for Ru−B(2).

As mentioned, the ^{1}H NMR resonances assigned to B−H→Ru in **3** and B−H→Rh in **4** were prominent in the negative zone of the spectrum. In contrast, this has not been the case for **1** or **2**. Variable-temperature ^{1}H NMR spectra down to 179 K did not produce any new resonances. The ^{11}B NMR is, on the other hand, fully supportive of B−H→Rh interactions. This is supported by a shift and sharpening of the B(11)−H resonance and a higher field shift of the extra B−H, in this case B(2). The absence of B−H→Rh resonances at the negative zone of the ^{1}H NMR spectrum is not in contradiction with previous data obtained by our group. It was observed in octahedral Ru(II) complexes that the trans ancillary ligand to the B−H→Ru groups modulated its position. It was also found that the effect did follow fairly well the *trans influence*. By comparison of complexes **4** and **1** or **2** an explanation of the lack of B−H→Rh in the last two can be found. In **4** B−H→Rh is trans to PPh$_3$. The *trans influence* of alkenes is larger than that of PR$_3$, and we found that the greater the *trans influence*, the more positive the positions of the B−H→Rh resonances would be.[12] Then, it was expected that these would appear at the same region as a noncoordinated B−H. The several resonances which appear in this region in the spectra of **1** or **2** did not permit a correct assignment. Thus, these signals are present, but they are in the region between +1 and +3 ppm of the spectrum.

The tricoordinating capacity of [7-PPh$_2$-8-R-7,8-C$_2$B$_9$H$_{10}$]$^-$ in Rh(I) complexes can be understood by comparing **1** and **4**. In **4** the Rh(I) electronic requirements are satisfied by the σ-donor capacity of two PPh$_3$ groups, Cc−PPh$_2$, and one B−H. In contrast, in **1** the cycloocta-1,5-diene is mainly a π-acceptor, which removes electron density from Rh. To maintain the right Rh(I) electronic balance, an extra source of electrons is required, and this is provided by an extra B−H adequately placed in the cluster to form B−H→Rh. On the other hand, the angle values around Rh suggest that the B(2)−H→Rh interaction is facilitated for the complex to release steric crowding caused by the two aromatic rings on phosphorus.

Experimental Section

All reactions were performed under a dinitrogen atmosphere using Schlenk techniques. Solvents were purified by distillation from appropriate drying agents before use. [NMe$_4$][7-PPh$_2$-7,8-C$_2$B$_9$H$_{10}$] and [NMe$_4$][7-PPh$_2$-8-Me-7,8-C$_2$B$_9$H$_{10}$] were synthesized as described in the literature.[13] [Rh$_2$(μ-Cl)$_2$(cod)$_2$] was synthesized according to the literature procedure. Elemental analyses were performed in our analytical laboratory using a Carlo Erba EA1108 microanalyzer. IR spectra were obtained with KBr pellets on a Nicolet 710-FT spectrophotometer. The ^{1}H NMR, ^{11}B NMR, ^{13}C{^{1}H} NMR, and ^{31}P{^{1}H} NMR spectra were recorded on Bruker AM 400WB and a Bruker ARX 300 instruments. ^{1}H 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 NMR spectra to 85% H$_3$PO$_4$ and BF$_3$·Et$_2$O, respectively.

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Table 1. Crystallographic Data for [Rh(7-PPh$_2$-8-Me-7,8-C$_2$B$_9$H$_{10}$)(cod)] (2)

chem formula	$C_{23}H_{35}B_9PRh$
fw	542.68
T, °C	20
λ, Å	0.710 69
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	12.925(2)
b, Å	10.568(2)
c, Å	19.3520(10)
β, deg	90.438(6)
V, Å^3	2643.2(7)
Z	4
D_{calcd}, g cm^{-3}	1.364
μ, mm^{-1}	0.718
F(000)	1112
no. of indep rflns	5188
no. of params	323
goodness of fit on F^2	0.988
R1[a] [$I > 2\sigma(I)$]	0.0379
wR2[b] [$I > 2\sigma(I)$]	0.0852
largest diff peak/hole, e Å^{-3}	+0.433 and −0.339

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

Table 2. Selected Interatomic Distances (Å) and Angles (deg) (Esd's in Parentheses) for [Rh(7-PPh$_2$-8-Me-7,8-C$_2$B$_9$H$_{10}$)(cod)] (2)

Rh−P	2.2933(9)	Rh−B(2)	2.521(4)
Rh−C(25)	2.106(4)	Rh−B(11)	2.538(4)
Rh−C(26)	2.104(4)	Rh−H(2)	1.97(3)
Rh−C(29)	2.255(4)	Rh−H(11)	2.03(3)
Rh−C(30)	2.272(4)		
Rh−P−C(7)	88.75(10)	P−C(7)−B(3)	117.5(2)
P−C(7)−C(8)	132.4(2)	P−C(7)−B(11)	104.8(2)
P−C(7)−B(2)	104.5(2)		

Preparation of [Rh(7-PPh$_2$-8-H-7,8-C$_2$B$_9$H$_{10}$)(cod)] (1). To a deoxygenated dichloromethane solution (8 mL) containing [NMe$_4$][7-PPh$_2$-8-H-7,8-C$_2$B$_9$H$_{10}$] (50 mg, 0.125 mmol) was added [Rh$_2$(μ-Cl)$_2$(cod)$_2$] (31 mg, 0.062 mmol), and the mixture was stirred at room temperature for 24 h. At this point a solid was obtained, which was filtered. The yellow solid was washed with water (15 mL) to produce the analytically pure solid [Rh-(7-PPh$_2$-8-H-7,8-C$_2$B$_9$H$_{10}$)(cod)] (**1**): (yield 34 mg, 56%). ^{1}H NMR (CDCl$_3$, ppm): δ −2.84 (br, 1H, B−*H*−B); 2.31 (m, 8H, C*H*$_2$), 3.79 (m, 2H, C*H*═CH), 4.02 (m, 1H, CH═C*H*), 5.45 (s, 1H, C*H*═CH), 7.45 (m, 10H, C$_6$*H*$_5$). ^{31}P{^{1}H} NMR (CDCl$_3$, ppm): δ 23.67 (d, ^1J(P,Rh) = 121 Hz). ^{11}B NMR (CDCl$_3$, ppm): δ 0.3 (d, ^1J(B,H) = 144 Hz, 1B), −12.9 (d, ^1J(B,H) = 154 Hz, 1B), −16.9 (1B), −18.4 (d, ^1J(B,H) = 115 Hz, 1B), −24.2 (d, ^1J(B,H) = 154 Hz, 1B), −26.3 (1B), −32.0 (d, ^1J(B,H) = 125 Hz, 2B), −34.9 (d, ^1J(B,H) = 154 Hz, 1B). FTIR (KBr, cm^{-1}): 2101 ν(B−H−Rh), 2546 ν(B−H). Anal. Calcd for $C_{22}H_{33}B_9PRh$: C, 49.99; H, 6.25. Found: C, 50.12; H, 6.15.

Preparation of [Rh(7-PPh$_2$-8-Me-7,8-C$_2$B$_9$H$_{10}$)(cod)] (2). The reaction of [NMe$_4$][7-PPh$_2$-8-Me-7,8-C$_2$B$_9$H$_{10}$] (100 mg, 0.246 mmol) with [Rh$_2$(μ-Cl)$_2$(cod)$_2$] (60.7 mg, 0.123 mmol) was conducted under conditions similar to those utilized for **1**, except for the reaction time (10 min): yield 61 mg, 44%. ^{1}H NMR (CDCl$_3$, ppm): δ −2.45 (br, 1H, B−*H*−B); 1.29 (s, 3H, Cc−C*H*$_3$), 2.37 (m, 8H, C*H*$_2$), 3.57 (m, 2H, C*H*═CH), 5.30 (m, 2H, CH═C*H*), 7.50 (m, 10H, C$_6$*H*$_5$). ^{31}P{^{1}H} NMR (CDCl$_3$, ppm): δ 30.90 (d, ^1J(P,Rh) = 114 Hz). ^{11}B NMR (CDCl$_3$, ppm): δ −0.51 (d, ^1J(B,H) = 125 Hz, 1B), −8.27 (1B), −10.78 (1B), −12.67 (1B), −18.33 (d, ^1J(B,H) = 135 Hz, 1B), −27.67 (d, ^1J(B,H) = 139 Hz, 1B), −26.78 (1 B), −31.45 (d, ^1J(B,H) = 109 Hz, 1B), −34.06 (d, ^1J(B,H) = 145 Hz, 1B). FTIR (KBr, cm^{-1}): 2101 ν(B−H−Rh), 2586, 2544 ν(B−H). Anal. Calcd for $C_{23}H_{35}B_9PRh$: C, 50.91; H, 6.46. Found: C, 49.84; H, 6.25.

X-ray Data Collection, Structure Determination, and Refinement for 2. Orange crystals of **2** were grown from CDCl$_3$ by slow evaporation. Single-crystal data collection for [Rh(7-PPh$_2$-8-Me-7,8-C$_2$B$_9$H$_{10}$)(cod)] 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 were collected by the ω−2θ technique to a maximum 2θ value of 50°. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods by using the SHELXS86 program,[14] and full-matrix least-squares refinements on F^2 were performed using the SHELXL-93 program.[15] Non-hydrogen atoms were refined with anisotropic displacement parameters, but hydrogen atoms were included in the calculations at fixed distances from their host atoms (riding model). Crystallographic data for [Rh(7-PPh$_2$-8-Me-7,8-C$_2$B$_9$H$_{10}$)(cod)] are presented in Table 1, and selected interatomic distances and angles are given in Table 2.

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Supporting Information Available: Tables giving detailed crystallographic data, atomic positional and thermal displacement parameters, and bond distances and angles for [Rh(7-PPh$_2$-8-Me-7,8-C$_2$B$_9$H$_{10}$)(cod)] (**2**) (11 pages). Ordering information is given on any current masthead page.

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