Rhodium Complexes with the New Anionic Diphosphine [7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$]$^-$ Ligand

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New rhodium complexes with the eclipsed anionic diphosphine **[7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$]**$^-$ are described. These were prepared from the neutral cod complex [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(cod)] either directly or via the complex [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)$_2$], which was obtained by bubbling CO through a suspension of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(cod)] in deoxygenated methanol. The CO ligands may be readily replaced by monophosphines, chelating diphosphines, monoamines, and chelating diamines. CO substitution by monophosphines depends on the phosphine cone angle more than the phosphine basicity. Both CO ligands can be replaced in [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)$_2$] by monophosphines with small cone angles, while monophosphines with large cone angles are only able to displace one CO ligand. Thus [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)(phosphine)] and [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(phosphine)$_2$] can be obtained. By contrast, with chelating diamines, carbamoyl complexes have been obtained.

It is well-known that the tris(triphenylphosphino)chlororhodium(I) complex is an active catalyst for the homogeneous hydrogenation of unsaturated compounds containing olefinic and acetylenic linkages.[1] The effect of the aryl- and alkyl- substituted tertiary phosphine groups in tris(tertiaryphosphino)chlororhodium(I) complexes on the rate of catalytic homogeneous hydrogenation of substrates[2] is well established.

The relevance of selective catalytic hydrogenation to asymmetric synthesis has led to a spectacular proliferation of rhodium complexes with a great variety of chelating neutral diphosphines.[3] Catalysts with a chelating diphosphine can be formed by treatment of (diene)rhodium complexes with the appropriate diphosphine, among other procedures. They behave differently from those formed from monodentate tertiary phosphines, a feature understood in terms of stereochemical arguments.[4]

The advantage of these over the monophosphines has to do with their chelating capacity, which ensures greater robustness of the complex. To this aim the anionic diphosphine 7,8-bis(diphenylphosphino)-7,8-dicarba-*nido*-undecaborate(1−), [7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$]$^-$, has been recently prepared.[5]

In transition metal complexes with this anionic diphosphino ligands, the proximity of the anionic cluster to the metal is thought to induce a greater stability to the chelate. In addition, the anionic nature of the ligand should prevent the approach of other anionic coordinating ligands to the metal.

The catalytic characteristics of rhodium complexes with the unsubstituted carborane have been previously studied.[6] These complexes are catalytically active in the hydrogenation of olefins, including stereoselective hydrogenation.[7] The catalytic properties of rhodium complexes based on the neutral *closo*-carboranyldiphosphines have also been noted.[8]

As a consequence, the eclipsed anionic diphosphine **[7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$]**$^-$ was synthesized and structurally characterized to understand the influence of the ligand's negative charge on the P-Rh bonds, without the interference of other charge-compensating anionic ligands.[5]

Here we report the synthesis of Rh(I) complexes based on the eclipsed anionic diphosphine [7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$]$^-$. From the species [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(diene)], Rh(I) complexes have been obtained by displacement of the diolefinic ligand. They are formally similar to Wilkinson's catalyst via substitution of the PPh$_3$ and Cl$^-$ ligands by the diphosphine [**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**]$^-$. Their spectroscopic and chemical properties have also been studied.

Results and Discussion

The reaction of the dimeric rhodium complex [Rh$_2$(μ-Cl)$_2$(cod)$_2$] (cod = 1,5-cyclooctadiene) with the anionic diphosphine [**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**]$^-$ induces the cleavage of the initial dimer and the formation of a neutral monomeric complex, [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(cod)]. (See eq 1.)

$$\begin{aligned}&{}^{1}\!/_{2}[\mathrm{Rh_2(\mu\text{-}Cl)_2(cod)_2}] + \\ &\qquad [\mathrm{NMe_4}][\mathbf{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}}] \rightarrow \\ &\quad [\mathrm{Rh}\{\mathbf{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}}\}(\mathrm{cod})] + [\mathrm{NMe_4}]\mathrm{Cl} \quad (1)\end{aligned}$$

The ligand [**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**]$^-$ contains three competing sites of coordination: the cluster's open face

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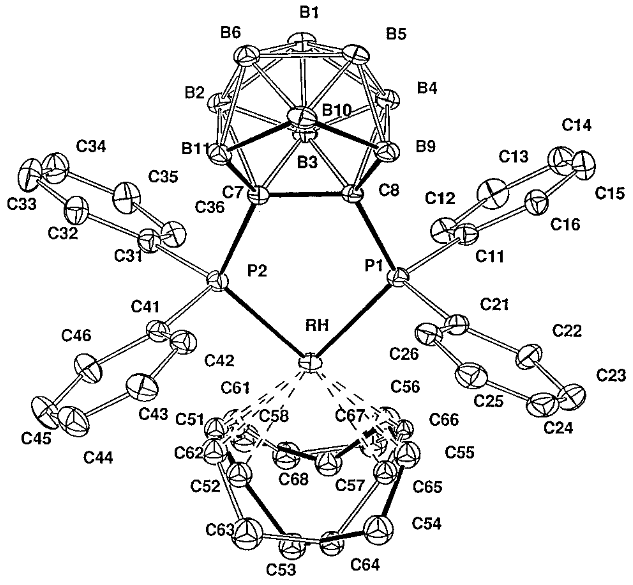

Figure 1. ORTEP molecular plot, with 20% probability thermal ellipsoids, showing labeling scheme. Hydrogens atoms have been omitted for clarity.

C_2B_3, the two exocluster phosphorus atoms, and the BH's, in which case exo−*nido* coordination might take place. In the absence of the two P elements connected to the *nido*-carborane cluster, an η^5 coordination to the C_2B_3 open face[6b,9] or an exo−*nido* coordination[10] would be expected upon reaction with Rh(I) complexes. The spectroscopic characterization of this complex shows that only the phosphorus groups of the ligand [**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**]$^-$ participate in the coordination to the cation Rh(I). The characteristic 2:5:1:1 pattern in the $^{11}B\{^1H\}$-NMR spectrum in the range −11/−36 ppm, and the lack of any absorption at higher field than −2.6 ppm in the ^1H-NMR spectrum, rules out any B(3)-H→Rh interaction[11] and η^5 rhodium coordination to the C_2B_3 open face. The $^{11}B\{^1H\}$-NMR spectrum range also rules out an η^5 rhodium coordination to the C_2B_3 open face.

The X-ray structure determination of the complex supports the spectral data. In contrast with the structure of an equivalent rhodium dithiocarborane complex previously studied by our group, in the current molecule there is no close contact between the hydrogen atom of B3 and the rhodium atom, as the carborane cage lies well away from the Rh(cod) unit.[12] The [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(cod)] molecule exhibits rotational disorder in the cod ligand positions, the two groups of cod atoms being labeled C(51)−C(58) (conformer 1) and C(61)−C(68) (conformer 2) (C(51)−C(58) (pop = 0.6852) and C(61)−C(68) (pop = 1 − 0.6852)) (see Figure 1). The average geometry for the rhodium atom is approximately square planar, the average P−Rh−C=C angle being 94.62°, C=C−Rh−C=C being 86.34°, and P(1)−Rh−P(2) being 85.33(3)° and the rhodium atom lies within the plane described by the atoms P(1), P(2), C(7), and C(8). In contrast, a copper complex with the same [**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**]$^-$ ligand involves coordination of the metal atom at an angle of 20.4° to the plane of the P(1), P(2), C(7), C(8) atoms,[13] allowing a distorted tetrahedral coordination environment for the copper atom. Crystallographic data are given in Table 1, and selected bond distances and angles for the two conformers are reported in Table 2.

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

mol formula: $C_{34}H_{42}B_9P_2Rh$	density $\rho_c = 1.16$ g cm^{-3}
MW 712.85	space group; P4$_3$, No. 78.
$F(000) = 1464$	$Z = 4$
cell params	cryst dimens: 0.36 × 0.20 × 0.63
a, b = 18.084(3) Å	abs coeff: μ(Mo Kα) = 5.20 cm^{-1}
c = 12.493(1) Å	
V = 4086(1) Å^3	
Data Collection	
diffractometer: Enraf-Nonius CAD4	θ meas range: 2.17 ≤ θ ≤ 30.44°
	Range h, k, l: 0/25, −25/25, 0/17
T = 23 °C	no. of reflcns measd: = 13185
Refinement	
no. of obsd reflcns: 10220 with $I \geq 3\sigma(I)$	R Factors
	R = 0.040
no. of params refined: 407	R$_w$ = 0.054

The complex [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(cod)] is a good starting material to prepare other Rh(I) complexes based on [**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**]$^-$, by replacing the weakly coordinated cod by other ligands, such as carbon monoxide or phosphines (Figure 2).

Bubbling carbon monoxide through a slurry of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(cod)] yields the corresponding dicarbonyl species. (See eq 2.)

$$[\mathrm{Rh}\{\mathbf{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}}\}(\mathrm{cod})] \xrightarrow[+\,\mathrm{cod}]{\mathrm{CO\ gas}} [\mathrm{Rh}\{\mathbf{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}}\}(\mathrm{CO})_2] \quad (2)$$

In the IR spectrum of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)$_2$] the ν(CO) frequencies occur at 2087 and 2054 cm^{-1}. The CO absorption process is reversible, and in solution in the absence of a CO atmosphere, the initial cod complex is recovered. The ^1H-NMR spectrum of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)$_2$] confirms the removal of the starting cod ligand and the presence of the BHB bridge (δ = −2.1 ppm) in the *nido* cluster. The $^{11}B\{^1H\}$-NMR spectrum shows the typical 2:3:2:1:1 pattern between −9.7 and −35.1 ppm.

This dicarbonylic complex is suitable as a starting material for the synthesis of a new series of Rh(I) complexes. Its reaction with monophosphines varying in steric and electronic properties, with neutral and anionic diphosphines, and with monodentate and bidentate N-donor ligands, leads easily and quantitatively to new complexes by displacement of one or two CO molecules. Figures 2 and 3 show the synthetic procedures which are reported in detail in the Experimental Section.

In all cases, the coordination of the ligand [**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**]$^-$ takes place through the exoclus-

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

Conformer 1: Population C(51)−C(58) = 0.6852

Bond Distances

Rh−P(1)	2.2886(9)	Rh−P(2)	2.2843(9)
Rh−C(51)	2.240(7)	Rh−C(52)	2.262(6)
Rh−C(55)	2.309(7)	Rh−C(56)	2.319(7)

Bond Angles

P(1)−Rh−P(2)	85.33(3)	P(1)−Rh−C(51)	170.1(2)
P(1)−Rh−C(52)	154.2(2)	P(1)−Rh−C(55)	91.0(2)
P(1)−Rh−C(56)	100.2(2)	P(2)−Rh−C(51)	89.6(2)
P(2)−Rh−C(52)	98.3(2)	P(2)−Rh−C(55)	167.0(2)
P(2)−Rh−C(56)	156.7(2)	C(51)−Rh−C(52)	35.2(2)
C(51)−Rh−C(55)	95.7(2)	C(51)−Rh−C(56)	81.3(3)
C(52)−Rh−C(55)	79.7(2)	C(52)−Rh−C(56)	86.5(2)
C(55)−Rh−C(56)	36.4(3)	Rh−C(51)−C(58)	105.6(5)
C(52)−C(51)−C(58)	126.6(6)	Rh−C(52)−C(53)	110.8(4)
C(51)−C(52)−C(53)	126.2(6)	C(52)−C(53)−C(54)	114.8(6)
C(53)−C(54)−C(55)	113.4(6)	Rh−C(55)−C(54)	106.3(5)
C(54)−C(55)−C(56)	126.9(6)	Rh−C(56)−C(57)	106.8(4)
C(55)−C(56)−C(57)	123.0(6)	C(56)−C(57)−C(58)	115.3(6)
C(51)−C(58)−C(57)	113.2(6)		

Conformer 2: Population C(61)−C(68) = 0.3148

Bond Distances

Rh−P(1)	2.2886(9)	Rh−P(2)	2.2843(9)
Rh−C(61)	2.30(1)	Rh−C(62)	2.29(2)
Rh−C(65)	2.27(1)	Rh−C(66)	2.22(1)

Bond Angles

P(1)−Rh−P(2)	85.33(3)	P(1)−Rh−C(61)	157.2(4)
P(1)−Rh−C(62)	170.3(4)	P(1)−Rh−C(65)	97.9(3)
P(1)−Rh−C(66)	91.5(3)	P(2)−Rh−C(61)	98.9(4)
P(2)−Rh−C(62)	89.6(4)	P(2)−Rh−C(65)	152.2(3)
P(2)−Rh−C(66)	171.9(3)	C(61)−Rh−C(62)	32.0(6)
C(61)−Rh−C(65)	88.8(5)	C(61)−Rh−C(66)	81.3(5)
C(62)−Rh−C(65)	82.8(5)	C(62)−Rh−C(66)	94.6(5)
C(65)−Rh−C(66)	35.7(4)	Rh−C(61)−C(68)	111(1)
C(62)−C(61)−C(68)	131(1)	Rh−C(62)−C(63)	105(1)
C(61)−C(62)−C(63)	121(1)	C(62)−C(63)−C(64)	117(1)
C(63)−C(64)−C(65)	120(1)	Rh−C(65)−C(64)	108.3(8)
C(64)−C(65)−C(66)	123(1)	Rh−C(66)−C(67)	105.7(8)
C(65)−C(66)−C(67)	128(1)	C(66)−C(67)−C(68)	114(1)
C(61)−C(68)−C(67)	118(1)		

Overall Molecular Geometry

Rh−P(1)	2.2886(9)	Rh−P(2)	2.2843(9)
Rh−C(av)	2.276	Rh−C range	2.22(1)−2.319(7)
P(1)−C(8)	1.846(3)	P(1)−C(11)	1.810(3)
P(1)−C(21)	1.826(3)	P(2)−C(7)	1.849(3)
P(2)−C(31)	1.821(4)	P(2)−C(41)	1.820(3)
C(7)−C(8)	1.614(4)	B−C(av)	1.697
B−C range	1.617(5)−1.739(5)	B−B(av)	1.782
B−B range	1.732(6)−1.863(6)	C−C(phenyl av)	1.386

P(1)−Rh−P(2)	85.33(3)	P−Rh−C═C	94.62
C═C−Rh−C═C	86.34	Rh−P(1)−C(8)	113.4(1)
Rh−P(1)−C(11)	116.7(1)	Rh−P(1)−C(21)	110.6(1)
Rh−P(2)−C(7)	113.9(1)	Rh−P(2)−C(31)	115.7(1)
Rh−P(2)−C(41)	110.8(1)	P(2)−C(7)−C(8)	113.3(2)
P(1)−C(8)−C(7)	114.1(2)		

ter phosphorus atoms. The IR spectra show the B-H stretching frequency at the expected position for a *nido* carborane cluster (ν < 2550 cm^{-1}) and confirm the presence or absence of CO as ligands in the new complexes. As a general observation, it appears that the less basic monophosphines are capable of displacing only one CO, while the more basic ones may displace both, e.g. PPh$_3$ and PMePh$_2$ displace one CO, while PMe$_2$Ph displace two. Phosphites are an exception since they displace the two CO groups. As discussed below this reaction is more related to steric hindrance than electronic effects. The IR spectra of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)(PPh$_3$)] and [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)(PMePh$_2$)] show a single CO band at 2032 and 2009 cm^{-1}, respectively. Diphosphines are able of displacing the two CO molecules of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)$_2$]. If neutral diphosphines such as diphos and **1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$** or anionic diphosphines such as [**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**]$^-$ are used, complete substitution of the CO molecules is observed. Probably the chelating effect is the driving force for this process, providing additional stability for the formation of compounds of the type [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(PP)]^n (n = 0 if PP = diphos or **1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$**; $n = -1$ if PP = [**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**]$^-$).

The situation is different when N-donor ligands are used (Figure 3). The removal of both CO molecules in [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)$_2$] by amines follows the expected path only with monodentate ligands such as pyridine. In this case, [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(py)$_2$] is isolated. The ^{31}P-NMR in DMSO is explained by substitution of one pyridine by DMSO, producing [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(py)(DMSO)] in solution. When chelating N-donor ligands such as phenanthroline or bipyridine are used, monocarbamoyl derivatives are formed instead of total substitution of both CO ligands.

Many metal carbonyl complexes are known to react directly with nucleophiles such as ammonia or secondary amines to yield carbamoyl complexes[14] (Figure 4). However, only a few examples of the analogous reactions with diamines have been noted,[15] and in those cases dinuclear dicarbamoyl complexes have been reported, in which the two metal centers were linked via a dicarbamoyl bridge. In the example reported here, a monocarbamoyl moiety has been formed which acts as a chelating ligand. We do not fully rule out that the formation of a dicarbamoyl ligand may take place, but chemical analysis better support the monocarbamoyl, though variations between one or the other are so small that they are not conclusive. The CO complexes stretching frequency of the IR spectra moves from 2080 cm^{-1}, observed for [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)$_2$] to approximately 1650 cm^{-1}, the typical range for >N−C═O groups.

The ^{1}H-NMR spectrum confirms the coordination of the carborane cluster to Rh(I). The characteristic broad band of the BHB hydrogen bridge appears in all cases between −2.0 and −2.6 ppm. The multiplets due to aromatic hydrogen atoms of the phenylphosphines and N-donor ligands appear in the range between 6.69 and 8.52 ppm, and the complexes containing alkyl groups resonate at the expected frequencies.

The ^{11}B-NMR spectra of these complexes also confirm the participation of the cluster in the Rh(I) coordination. The spectrum pattern and frequency range are quite similar to the ligand. In several cases minor variations are observed due to a reduction of symmetry of the ligand.

The ^{31}P{^{1}H}-NMR spectra support the proposed stoichiometries. We propose monocarbamoyl ligands and not dicarbamoyl because the number of resonances and the coupling constants observed require complex asymmetry. The high insolubility of these complexes required to use a good solvating agent such as DMSO. Total substitution of the chelating carbamoyl ligand in

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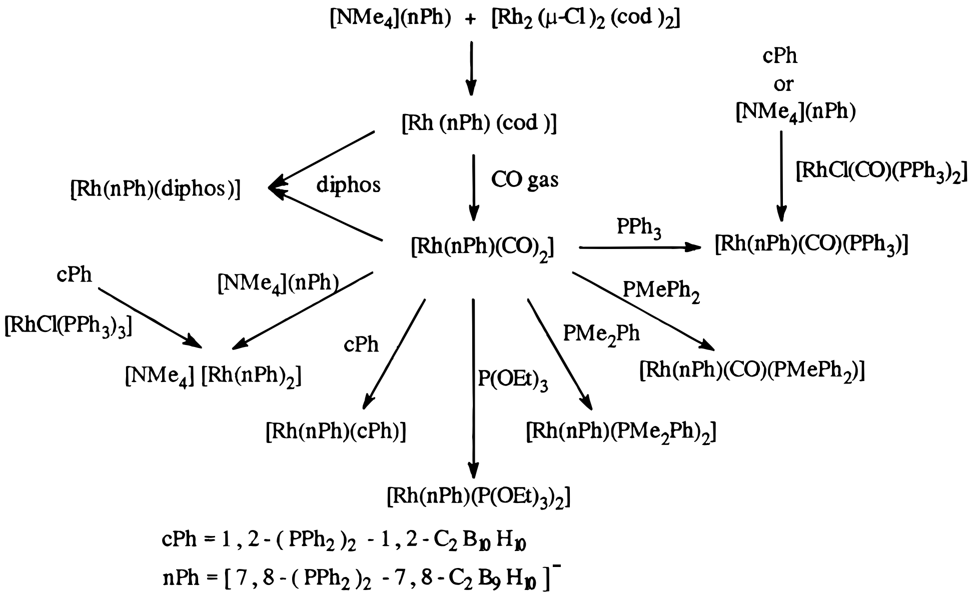


Figure 2. Schematic representation of $[Rh\{\mathbf{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}}\}(cod)]$ reactivity and CO displacement reactions by P-donor ligands at $[Rh\{\mathbf{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}}\}(CO)_2]$.

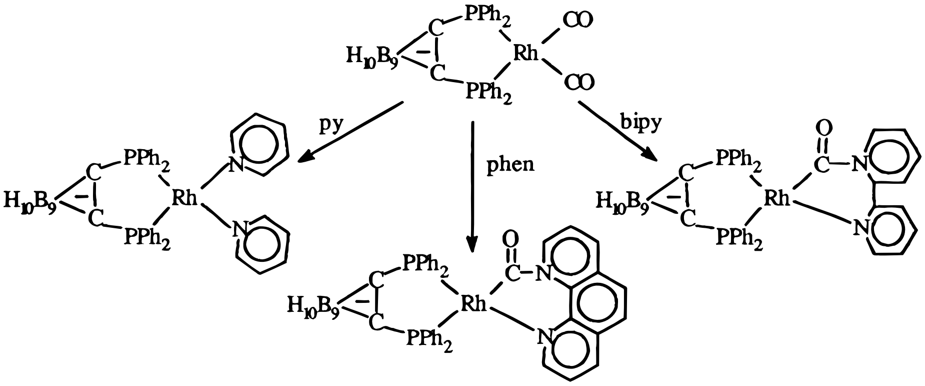
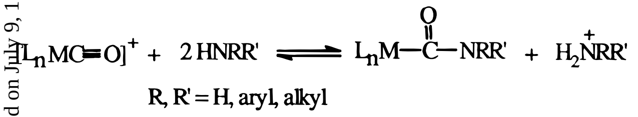


Figure 3. Schematic representation of the reactivity of $[Rh\{\mathbf{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}}\}(CO)_2]$ versus N-donor ligands.



$$[L_nMC{\equiv}O]^+ + 2\,HNRR' \rightleftharpoons L_nM{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NRR' + H_2\overset{+}{N}RR'$$

R, R' = H, aryl, alkyl

Figure 4. Carbamoyl derivatives.

some of the molecules by DMSO explains the $^{31}P\{^1H\}$-NMR spectra. The values of chemical shifts and coupling constants are similar to those registered in the literature for Rh(I) complexes.[16]

The starting complex $[Rh\{\mathbf{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}}\}(cod)]$ is an excellent precursor to synthesize a new series of Rh(I) complexes, first by replacement of the diolefinic cod ligand by CO, and second by P-donor or N-donor ligands. In the case of replacement by P-donor ligands, the rate of carbonyl substitution may depend on the electronic and steric effects of the phosphines. As mentioned, with PPh_3 and $PMePh_2$, even in excess, only monosubstitution is observed, while with PMe_2Ph and $P(OEt)_3$ disubstitution is always found. These three monophosphines and the monophosphite have different electronic properties: the basicity of alkylphosphines is higher than the aryl ones, but the steric effect seems to be the dominant factor in the rate of CO substitution in $[Rh\{\mathbf{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}}\}(CO)_2]$. From Tolman's cone angle data,[17] the steric constrains imposed by the phosphorus ligands decrease in the following order:

$$PPh_3 > PMePh_2 > \text{diphos} > PMe_2Ph > P(OEt)_3$$

The cone angle explains the ability of the low-angle phosphines to substitute both CO groups, while the high-angle phosphines only replace one CO. It has not been possible to prepare the complex analogous to Wilkinson's catalyst by direct substitution of Cl^- and PPh_3 by the anionic diphosphine $[\mathbf{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}}]^-$. Steric requirements may not allow the formation of "$[Rh\{\mathbf{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}}\}(PPh_3)_2]$", although the analogous exodithiocarborane complexes are well-known.[18]

For chelating diphosphines, two additional factors must be considered: first, the additional stability conferred by their chelating capacity as compared to two carbon monoxide molecules and, second, their minor steric hindrance in comparison with the two analogous monophosphines. These aspects favor the disubstitution of the two CO molecules of $[Rh\{\mathbf{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}}\}(CO)_2]$ independently of their electronic properties or their neutral or anionic charge.

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With monodentate N-donor ligands, disubstitution occurs, but in contrast, the reaction with chelating diamines, such as bipy and phen, is an exception, leading to the formation of chelating monocarbamoyl derivatives.

As a conclusion, a family of new Rh(I) complexes formally analogous to Wilkinson's catalyst by substitution of Cl$^-$ and PPh$_3$ for the anionic diphosphine [**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**]$^-$, has been accomplished. Using [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(cod)] as a starting material, replacement of the olefinic ligand by CO and then by phosphines, diphosphines, and N-donor ligands has yielded this series of Rh(I) complexes. The most important factor in the replacement of the CO molecules is the steric hindrance of the phosphines. With the highly hindered phosphines, only monosubstitution is observed, while with the less hindered ones, disubstitution is observed. The chelating diphosphines in each case produce disubstitution. Electronic effects of the phosphines seem to be of lesser importance in the formation of these complexes.

Variations in the nature of the ancillary ligands bound to Rh(I) will enable a detailed study of their effect on the catalytic properties of these complexes. The results of this study will be the subject of a subsequent publication.

Experimental Section

General Methods. 1,2-Dicarba-*closo*-dodecaborane was sublimed under high vacuum before use. **1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$** and [NMe$_4$][**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**] were prepared from 1,2-dicarba-*closo*-dodecaborane according to the literature procedure.[5] A 1.6 M solution of *n*-butyllithium in hexane (Fluka) was used as purchased. [RhCl(PPh$_3$)$_3$],[19] [RhCl(CO)(PPh$_3$)$_2$],[20] and [Rh$_2$(μ-Cl)$_2$(cod)$_2$][21] were synthesized according to the literature procedures. Solvents, inorganic salts, and organic reagents were analytical reagent grade from Fluka or Aldrich and were used as purchased.

All reactions were carried out under a dinitrogen atmosphere employing Schlenk techniques.

Microanalyses were performed in our analytical laboratory by using a Perkin-Elmer 240B microanalyzer. IR spectra were obtained with KBr pellets on a Nicolet 710-FT spectrophotometer. The ^{1}H-NMR, ^{11}B-NMR, and ^{31}P-NMR spectra were recorded on Bruker AM 400WB or AC 250WB instruments.

Synthesis of [Rh{7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$}(cod)]. [Rh$_2$(μ-Cl)$_2$(cod)$_2$] (26 mg, 0.053 mmol) was added to 15 mL of a solution of [NMe$_4$]][**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**] 26 mg (0.053 mmol), in deoxygenated refluxing ethanol, and the mixture was refluxed for 1 h. An orange solid precipitated from the warm mixture. The orange solid was separated by filtering under nitrogen and then washed with ethanol (10 mL) and a mixture of ethanol/water (2/1), giving [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(cod)], 62 mg (87%). Anal. Calcd for C$_{34}$H$_{42}$B$_9$P$_2$Rh: C, 57.29; H, 5.94. Found: C, 57.45; H, 6.34. IR (KBr): υ_{max}(B$-$H) = 2578, 2525 cm^{-1}. ^{1}H-NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ -2.6 (br, 1 H, B**H**B), 1.97$-$2.34 (q, 8 H, C**H**$_2$), 4.55 and 4.69 (s, 4 H, C**H**), 7.25$-$7.29, 7.41$-$7.45, 7.58$-$7.65 (m, 20 H, C$_{aryl}$$-$**H**). ^{11}B-NMR (128 MHz, CH$_2$Cl$_2$, 25 °C, BF$_3$·Et$_2$O): $\delta = -10.9$ (d, ^1J(BH) = 123 Hz, 2 B), -16.1 (d, ^1J(BH) = 135 Hz, 5 B), -29.2 (1 B), -35.3 (d, ^1J(BH) = 142 Hz, 1 B). ^{31}P{^{1}H}-NMR (162 MHz, CD$_2$Cl$_2$, 25 °C, H$_3$PO$_4$): $\delta = 74.33$ (d, ^1J(RhP) = 148 Hz).

Orange crystals suitable for X-ray analysis were grown from a dichloromethane/heptane solution (3:1) after partial evaporation of the solvent.

Synthesis of [Rh{7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$}(CO)$_2$]. A yellow solid was obtained when carbon monoxide was bubbled for a few minutes through a suspension of 150 mg (0.210 mmol) of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(cod)] in deoxygenated methanol (25 mL). The resulting yellow solid was filtered off, washed with methanol, and dried in vacuum to afford 115 mg of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)$_2$] (97%). Anal. Calcd for C$_{28}$H$_{30}$B$_9$P$_2$O$_2$Rh: C, 50.90; H, 4.58. Found: C, 50.49; H, 4.81. IR (KBr): υ_{max}(B$-$H)= 2584, 2580, 2532 cm^{-1}; υ_{max}(C$\equiv$O)= 2087, 2054 cm^{-1}. ^{1}H-NMR (400 MHz, acetone-d_6, 25 °C, TMS): δ -2.1 (br, 1 H, B**H**B), 7.44$-$7.87 (m, 20 H, C$_{aryl}$$-$**H**). ^{11}B-NMR (128 MHz, acetone-d_6, 25 °C, BF$_3$·Et$_2$O): $\delta = -9.7$ (d, ^1J(BH) = 137 Hz, 2 B), -14.0 (d, ^1J(BH) = 143 Hz, 3 B), -16.3 (2 B), -27.9 (d, ^1J(BH) = 104 Hz, 1 B), -35.1 (d, ^1J(BH) = 144 Hz, 1 B). ^{31}P{^{1}H}-NMR (162 MHz, acetone, 25 °C, H$_3$PO$_4$): $\delta = 79.34$ (d, ^1J(RhP) = 121 Hz).

Synthesis of [Rh{7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$}(CO)(PPh$_3$)]. Method 1. An excess of PPh$_3$ was added to 10 mL solution of 30 mg (0.045 mmol) of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)$_2$] in deoxygenated refluxing dichloromethane, and the mixture was refluxed for 1 h. The solution was evaporated to dryness. The excess PPh$_3$ was dissolved in hexane/dichloromethane, and the yellow solid was separated by filtering under nitrogen and was washed with hexane. Yield of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)(PPh$_3$)]: 30 mg (75%).

Method 2. First, 50 mg (0.087 mmol) of [RhCl(CO)(PPh$_3$)$_2$] was added to 20 mL solution of 50 mg (0.087 mmol) of [NMe$_4$][**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**] in deoxygenated refluxing ethanol and the mixture was refluxed for 1.5 h. The resulting yellow solid was filtered, washed with hot ethanol and dried in vacuum to afford 58 mg of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)(PPh$_3$)] (74%).

Method 3. This compound can be synthesized as described[22] from **1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$** and [RhCl(CO)(PPh$_3$)$_2$] in molar ratio 1:1, in refluxing ethanol. Yield: 55%.

Anal. Calcd for C$_{45}$H$_{45}$B$_9$P$_3$ORh: C, 60.39; H, 5.07. Found: C, 58.37; H, 4.99. IR (KBr): υ_{max}(B$-$H)= 2582, 2538, 2524 cm^{-1}; υ_{max}(C$\equiv$O)= 2032, 2014 cm^{-1}. ^{1}H-NMR (400 MHz, acetone-d_6, 25 °C, TMS): δ -2.5 (br, 1 H, B**H**B), 6.93, 7.28$-$7.33, 7.64 (m, 35 H, C$_{aryl}$$-$**H**). ^{11}B-NMR (128 MHz, CD$_2$Cl$_2$, 25 °C, BF$_3$·Et$_2$O): $\delta = -10.5$ (1 B), -13.2 (3 B), -15.0 (2 B), -17.9 (d, ^1J(BH) = 144 Hz, 2 B), -31.5 (d, ^1J(BH) = 90 Hz, 1 B), -35.9 (d, ^1J(BH) = 120 Hz, 1 B).

Synthesis of [Rh{7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$}(CO)(PMePh$_2$)]. An excess of PMePh$_2$ was added to a 10 mL solution of 30 mg (0.045 mmol) of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)$_2$] in deoxygenated refluxing dichloromethane and the yellow solution was refluxed for 3 h, yielding a yellow solid. The solid was filtered and washed with dichloromethane. Yield: 36 mg of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)(PMePh$_2$)] (96%). Anal. Calcd for C$_{40}$H$_{43}$B$_9$P$_3$ORh: C, 57.68; H, 5.20. Found: C, 56.70; H, 5.22. IR (KBr): υ_{max}(B$-$H) = 2571, 2537 cm^{-1}; υ_{max} (C$\equiv$O)= 2009 cm^{-1}. ^{1}H-NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ -2.4 (br, 1 H, B**H**B), 1.21 (m, 3 H, C**H**$_3$), 6.98$-$7.68, 8.11$-$8.16 (m, 30 H, C$_{aryl}$$-$**H**). ^{11}B-NMR (128 MHz, CHCl$_3$, 25 °C, BF$_3$·Et$_2$O): $\delta = -10.7$ (1 B), -11.7 (2 B), -13.6 (2 B), -16.8 (3 B), -29.4 (1 B), -36.4 (d, ^1J(BH) = 137 Hz, 1 B). ^{31}P{^{1}H}-NMR (162 MHz, CDCl$_3$, 25 °C, H$_3$PO$_4$): $\delta = 10.49$ (two dd, ^2J(PP)$_c$ = 39 Hz, ^2J(PP)$_t$ = 244 Hz, ^1J(RhP) = 127 Hz), 67.89 (dt, ^2J(PP)$_c$ = 39 Hz, ^1J(RhP) = 127 Hz), 83.02 (two dd, ^2J(PP)$_c$ = 39 Hz, ^2J(PP)$_t$ = 244 Hz, ^1J(RhP) = 127 Hz).

Synthesis of [Rh{7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$}(PMe$_2$Ph)$_2$]. An excess of PMePh$_2$ was added to 8 mL of a solution of 30 mg (0.045 mmol) of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)$_2$] in deoxygenated refluxing dichloromethane and the yellow solution was refluxed for 1 h. After addition of hexane (4 mL) and storing at -4 °C, a microcrystalline orange solid separated, filtered, washed with a mixture of hexane/diethyl ether (1:1),

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and dried in vacuum. Yield: 23 mg of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(PMe$_2$Ph)$_2$] (58%). Anal. Calcd for $C_{42}H_{52}B_9P_4Rh$: C, 57.26; H, 5.95. Found: C, 57.35; H, 6.12. IR (KBr): υ_{max}(B–H) = 2591, 2545, 2516, 2506 cm^{-1}. ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$, 25 °C, TMS): δ −2.6 (br, 1 H, B**H**B), 1.66 and 1.69 (s, 12 H, C**H**$_3$), 7.17–7.71, 7.96 (m, 30 H, C$_{aryl}$–**H**). ^{11}B-NMR (128 MHz, acetone, 25 °C, BF$_3$·Et$_2$O): δ = −11.3 (d, ^1J(BH) = 140 Hz, 2 B), −17.0 (d, ^1J(BH) = 121 Hz, 5 B), −30.8 (d, ^1J(BH) = 111 Hz, 1 B), −36.0 (d, ^1J(BH) = 143 Hz, 1 B). ^{31}P{^{1}H}-NMR (162 MHz, acetone-d_6, 25 °C, H$_3$PO$_4$): δ = −4.29 (dd, ^2J(PP)$_t$ = 133 Hz, ^1J(RhP) = 227 Hz), 82.17 (dd, ^2J(PP)$_t$ = 133 Hz, ^1J(RhP) = 227 Hz).

Synthesis of [Rh{7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$}(P{OEt}$_3$)$_2$]. An excess of P(OPh)$_3$ was added to 8 mL of a solution of 30 mg (0.045 mmol) of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)$_2$] in deoxygenated refluxing dichloromethane, and the yellow solution was refluxed for 30 min. After evaporation to ca 3 mL, a mixture of hexane/ethyl ether (2:1) was added and a yellow solid precipitated. This was filtered and washed with hexane/ether (2:1). Yield: 23 mg of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(P{OEt}$_2$)$_2$] (78%). Anal. Calcd for $C_{38}H_{60}B_9P_4O_6Rh$: C, 48.71; H, 6.45. Found: C, 48.35; H, 6.47. IR (KBr): υ_{max}(B–H) = 2577, 2531, 2522 cm^{-1}. ^{1}H-NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ −2.5 (br, 1 H, B**H**B), 0.91 (br, 18 H, C**H**$_3$), 3.62 (br, 12 H, C**H**$_2$), 7.17, 7.28, 7.59, 7.93 (m, 20 H, C$_{aryl}$–**H**). ^{11}B-NMR (128 MHz, CHCl$_3$, 25 °C, BF$_3$·Et$_2$O): δ = −10.7 (2 B), −15.8 (5 B), −29.5 (1 B), −35.7 (d, ^1J(BH) = 112 Hz, 1 B). ^{31}P{^{1}H}-NMR (162 MHz, CDCl$_3$, 25 °C, H$_3$PO$_4$): δ = 78.95 (dd, ^2J(PP)$_t$ = 357 Hz, ^1J(RhP) = 122 Hz), 129.95 (dd, ^2J(PP)$_t$ = 357 Hz, ^1J(RhP) = 222 Hz).

Synthesis of [Rh{7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$}{1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$)]. First, 19 mg (0.038 mmol) of **1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$** was added to a 15 mL solution of 25 mg (0.038 mmol) of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)$_2$] in deoxygenated refluxing dichloromethane, and the yellow solution was refluxed for 30 min. After evaporation to ca 8 mL, hexane was added. The yellow solution was stored at −4 °C and a yellow microcrystalline solid precipitated. This was filtered and washed with hexane. Yield: 38 mg of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}{**1,2-(PPh$_2$)$_2$-1,2-C$_2$B$_{10}$H$_{10}$**}] (90%). Anal. Calc for $C_{52}H_{60}B_{19}P_4Rh$: C, 55.90; H, 5.41. Found: C, 56.68; H, 5.50. IR (KBr): υ_{max}(B–H) = 2563, 2546, 2528, 2520 cm^{-1}. ^{1}H-NMR (400 MHz, CDCl$_3$, 25 °C, TMS): δ −2.6 (br, 1 H, B**H**B), 6.81–7.62, 8.07 (m, 40 H, C$_{aryl}$–**H**). ^{11}B-NMR (128 MHz, CH$_2$Cl$_2$, 25 °C, BF$_3$·Et$_2$O): δ = −1.8 (2 B), −4.1 (4 B), −8.7 (2 B), −10.9 (6 B), −15.9 (d, ^1J(BH) = 102 Hz, 3 B), −29.1 (1 B), −35.7 (d, ^1J(BH) = 131 Hz, 1 B). ^{31}P{^{1}H}-NMR (162 MHz, acetone-d_6, 25 °C, H$_3$PO$_4$): δ = 73.88 (two dd, ^2J(PP)$_c$ = 25 Hz, ^2J(PP)$_t$ = 131 Hz, ^1J(RhP) = 269 Hz), 84.45 (two dd, ^2J(PP)$_c$ = 25 Hz, ^2J(PP)$_t$ = 131 Hz, ^1J(RhP) = 266 Hz).

Synthesis of [NMe$_4$][Rh{7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$}$_2$]. Method 1. First, 26 mg (0.045 mmol) of [NMe$_4$]][**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**] was added to a 10 mL solution of 30 mg (0.045 mmol) of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)$_2$] in deoxygenated refluxing dichloromethane, and the yellow solution was refluxed for 30 min. After evaporation to dryness, chloroform and heptane were added and an orange microcrystalline solid separated. This was filtered and washed with heptane and diethyl ether to yield 41 mg of [NMe$_4$][Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}$_2$] (77%).

Method 2. This product can be obtained from [NMe$_4$][**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**] and [RhCl(PPh$_3$)$_3$] in molar ratio 1:1 or 2:1 in refluxing ethanol, but the yield is only 55%.

Anal. Calcd for $C_{56}H_{72}B_{18}P_4NRh$: C, 56.97; H, 6.15; N, 1.19. Found: C, 54.53; H, 6.11; N, 1.17. IR (KBr): υ_{max}(B–H)= 2527 cm^{-1}. ^{1}H-NMR (400 MHz, acetone-d_6, 25 °C, TMS): δ −2.2 (br, 2 H, B**H**B), 3.52 (s, 12 H, C**H**$_3$), 6.69–8.19, 8.52 (m, 40 H, C$_{aryl}$–**H**). ^{11}B-NMR (128 MHz, CH$_2$Cl$_2$, 25 °C, BF$_3$·Et$_2$O): δ = −11.0 (2 B), −16.0 (5 B), −29.7 (1 B), −36.1 (1 B). ^{31}P{^{1}H}-NMR (162 MHz, acetone-d_6, 25 °C, H$_3$PO$_4$): δ = 78.46 (d, ^1J(RhP)= 138 Hz), 80.78 (d, ^1J(RhP) = 138 Hz).

Synthesis of [Rh{7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$}(diphos)]. Method 1. 1,2-Bis(diphenylphosphine)ethane, diphos (12 mg, 0.030 mmol), was added to a refluxing solution of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)$_2$] (20 mg, 0.030 mmol) in deoxygenated dichloromethane (8 mL). The yellow solution was refluxed for 30 min, and a yellow solid was separated, filtered, washed with dichloromethane, and dried in vacuum to afford 16 mg of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(diphos)] (88%).

Method 2. This product can be obtained from [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(cod)] and diphos under the same reaction conditions with similar yield.

Anal. Calcd for $C_{51}H_{54}B_9P_4Rh$: C, 61.81; H, 5.49. Found: C, 61.81; H, 5.49. IR (KBr): υ_{max}(B–H) = 2580, 2543, 2518 cm^{-1}.

Synthesis of [Rh{7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$}(CObipy)]·$^1/_3$CH$_2$Cl$_2$. 2,2′-Bipyridine (12 mg, 0.072 mmol) was added to a refluxing solution of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)$_2$] (40 mg, 0.060 mmol) in deoxygenated dichloromethane (10 mL). The mixture was refluxed for 30 min, and stirred at room temperature for a further 2 h. The resulting ivory solid was filtered, washed with hexane and diethyl ether, and dried in vacuum to afford 45 mg of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CObipy)]. $^1/_3$CH$_2$Cl$_2$ (92%). Anal. Calcd for $C_{37}H_{38}B_9P_2N_2ORh$. 1/3 CH$_2$Cl$_2$: C, 54.87; H, 4.77; N, 3.43. Found: C, 55.25; H, 4.26; N, 2.85. IR (KBr): υ_{max}(B–H) = 2586, 2537 cm^{-1}; υ_{max}(C=O) = 1682, 1629 cm^{-1}.

Synthesis of [Rh{7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$}(COphen)]·$^1/_2$CH$_2$Cl$_2$. 1,10-Phenanthroline (20 mg, 0.092 mmol) was added to a refluxing solution of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)$_2$] (60 mg, 0.090 mmol) in deoxygenated dichloromethane (10 mL). The mixture was refluxed for 30 min and stirred at room temperature for a further 2 h. It was then evaporated to approximately $^1/_2$ of the volume, and hexane was added until a solid precipitated. Upon recrystallization from dichloromethane/heptane, a yellow solid was obtained. This was filtered, washed with heptane and diethyl ether and dried in vacuum to afford 62 mg of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(COphen)]·$^1/_2$CH$_2$Cl$_2$ (82%). Anal. Calcd for $C_{39}H_{39}B_9P_2N_2ORh$·$^1/_2$CH$_2$Cl$_2$: C, 55.40; H, 4.71; N, 3.27. Found: C, 55.50; H, 4.56; N, 3.13. IR (KBr): υ_{max}(B–H) = 2563, 2546, 2528, 2520 cm^{-1}; υ_{max}(C=O) = 1674, 1628 cm^{-1}. ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$, 25 °C, TMS): δ −2.1 (br, 1 H, B**H**B), 6.40, 6.88–7.75, 7.91, 8.49, 9.39 (m, 28 H, C$_{aryl}$–**H**). ^{11}B-NMR (128 MHz, CH$_2$Cl$_2$, 25 °C, BF$_3$·Et$_2$O): δ = −9.1 (2 B), −14.3 (1 B), −16.3 (5 B), −28.4 (1 B), −35.1 (1 B). ^{31}P{^{1}H}-NMR (162 MHz, DMSO-d_6, 25 °C, H$_3$PO$_4$): δ = 68.6 (dd, ^2J(PP)$_c$ = 30 Hz, ^1J(RhP) = 230 Hz, PPh$_2$), 75.7 (dd, ^2J(PP)$_c$ = 30 Hz, ^1J(RhP) = 148 Hz, PPh$_2$), 96.27 (d, ^1J(RhP) = 311 Hz, PPh$_2$).

Synthesis of [Rh{7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$}(py)$_2$]·$^1/_3$CH$_2$Cl$_2$. Excess pyridine was added to a refluxing solution of [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(CO)$_2$] (30 mg, 0.045 mmol) in deoxygenated dichloromethane (8 mL). The resulting solid was refluxed for 2 h and then heptane was added. This was filtered off, washed with heptane and diethyl ether, and dried in vacuum to afford 30 mg of microcrystalline [Rh{**7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$**}(py)$_2$]·$^1/_2$CH$_2$Cl$_2$ (87%). Anal. Calcd for $C_{36}H_{40}B_9P_2N_2Rh$·$^1/_3$CH$_2$Cl$_2$: C, 56.16; H, 5.18; N, 3.54. Found: C, 55.23; H, 4.76; N, 3.26. IR (KBr): υ_{max}(B–H) = 2575, 2522 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6, 25 °C, TMS): δ −2.0 (br, 1 H, B**H**B), 5.52 (s, C**H**$_2$Cl$_2$), 6.71, 7.41–7.90, 8.71 (m, 30 H, C$_{aryl}$–**H**). ^{11}B-NMR (128 MHz, DMSO, 25 °C, BF$_3$·Et$_2$O): δ = −9.9 (2 B), −15.4 (5 B), −28.9 (1 B), −35.3 (1 B). ^{31}P{^{1}H}-NMR (162 MHz, DMSO-d_6, 25 °C, H$_3$PO$_4$): δ = 72.20 (dd, ^2J(PP)$_c$ = 24 Hz, ^1J(RhP) = 146 Hz, PPh$_2$), 86.00 (dd, ^2J(PP)$_c$ = 24 Hz, ^1J(RhP) = 121 Hz, PPh$_2$).

X-ray Structure Determination of [Rh{7,8-(PPh$_2$)$_2$-7,8-C$_2$B$_9$H$_{10}$}(cod)]. Data were collected at room temperature on a CAD4-Enraf-Nonius diffractometer in *w*-scan mode using graphite-monochromated Mo Kα radiation. A total of 13 185 reflections were measured (2.17 ≤ θ ≤ 30.44°); 10 220 independent reflections with I≥3.0σ(I) were used in the refinement. Absorption corrections were not carried out due to the irregularity of the crystal and the low absorption coefficient ($\mu_{\text{Mo K}\alpha} = 5.20\ \text{cm}^{-1}$).

The structure was solved using the Patterson function and difference Fourier syntheses (XTAL3.2),[23] with neutral atomic form factors.[24] Attempted solutions in the space groups $P4_1$ and $P4_3$ indicated that $P4_3$ was the correct space group. The positions of the disordered C_8H_{12} ligand appeared initially as those labeled as C(51)−C(58). After partial refinement of these positions, neighboring difference density peaks were observed with geometry correct for this ligand. These secondary positions were assigned as C(61)−C(68) and an overall population parameter for C(51)−C(58) was refined to a value of 0.6852 (population C(61)−C(68) = 1 − 0.6852). C(51)−C(58) and C(61)−C(68) were refined with isotropic thermal parameters while the remaining 38 non-hydrogen atoms were refined with anisotropic thermal parameters. Phenyl ring hydrogen atoms were placed in ideal calculated positions, and carborane hydrogen positions were found from the difference Fourier map, except for one hydrogen which could not be found and was omitted from the calculations. C_8H_{12} hydrogen positions could not be found from the difference Fourier synthesis and were not included in the calculations. Hydrogen atom parameters were not refined. Isotropic thermal parameters for the hydrogen atoms were estimated as $1.25U(\text{C,B}_{\text{parent}})$. The total number of parameters refined was 407. This model refined to $R = 0.040$ and $R_w = 0.054$, while refinement of the model of opposite chirality did not achieve a significant improvement in the R-factor. R-factors are based on $|F|$, where $R = \sum|F_o - F_c|/\sum|F_o|$ and $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$. Weighting scheme $w = 1/\sigma^2(F)$, with modified σ: $\sigma^2(\text{I}) = \sigma^2(I)_{\text{diff}} + 0.0004\sigma^4(I)_{\text{diff}}$. Highest residual electron density in the final difference map was 1.5 e/Å^3, 0.72 Å from the Rh atom.

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Supporting Information Available: Tables including complete X-ray experimental details, hydrogen atom positional parameters, anisotropic thermal parameters, a complete list of bond lengths and angles, and intermolecular hydrogen contact distances, and positional parameters and B_{eq} (13 pages). Ordering information is given on any current masthead page.

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