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Substitution and Hydrogenation Reactions on Rhodium(I)−Ethylene Complexes of the Hydrotris(pyrazolyl)borate Ligands Tp′ (Tp′ = Tp, Tp^{Me2})[†]

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The bis(ethylene) Rh species $Tp^{Me2}Rh(C_2H_4)_2$ (**1***) (Tp^{Me2} = tris(3,5-dimethyl-1-pyrazol-1-yl)hydroborate) has been obtained from $[RhCl(C_2H_4)_2]_2$ and KTp^{Me2}. Complex **1*** easily decomposes in solution to give mainly the butadiene species $Tp^{Me2}Rh(\eta^4\text{-}C_4H_6)$. In the solid state its thermal decomposition follows a different course and the allyl $Tp^{Me2}RhH(\textit{syn}\text{-}C_3H_4Me)$ is cleanly obtained as a mixture of *exo* and *endo* isomers. The complexes $Tp'Rh(C_2H_4)_2$ (Tp′ = Tp, Tp^{Me2}) afford the monosubstituted species $Tp'Rh(C_2H_4)(PR_3)$ upon reaction with PR_3 but react differently with L = CO or CNR: the Tp compound gives dinuclear $[TpRh]_2(\mu\text{-L})_3$ complexes, while, in the case of **1***, $Tp^{Me2}Rh(C_2H_4)(L)$ species are obtained. The ethylene ligand of complexes $Tp^{Me2}Rh(C_2H_4)(PR_3)$ is labile, and several peroxo compounds of composition $Tp^{Me2}Rh(O_2)(PR_3)$ have been isolated by their reaction with O_2. All the mononuclear Rh(I) complexes are formulated as 18e$^-$ trigonal bipyramidal species on the basis of IR and NMR spectroscopic studies. A series of dihydride complexes of Rh(III) of formulation $Tp'RhH_2(PR_3)$ have been prepared by the hydrogenation of the corresponding ethylene derivatives. Complexes $[TpRh]_2(\mu\text{-CNCy})_3$, $Tp^{Me2}Rh(C_2H_4)(PEt_3)$, and $Tp^{Me2}Rh(O_2)(PEt_3)$ have been further characterized by X-ray diffraction studies.

Introduction

The hydrotris(pyrazolyl)borate anions, Tp′, have become very useful and versatile ligands in transition metal coordination and organometallic chemistry.[1−3] Despite their consideration as cyclopentadienyl analogues, their complexes with transition elements often exhibit unusual reactivity patterns, which in many instances find no precedent in the related Cp′ systems.

In recent years, a number of studies on complexes of these ligands with the G9 elements, particularly Rh and Ir, have become available.Whereas in the oxidation state III the κ^3 binding mode is the commonest by far, both bidentate and tridentate coordination can be encountered in Rh(I) and Ir(I) complexes. The propensity of Rh(I) to adopt a square-planar geometry explains the relative abundance of the κ^2-Tp′ coordination mode in compounds of composition $Tp'RhL_2$[4−15] and also the frequent observation of the $\kappa^2-\kappa^3$ isomerism of the ligand.[4,5,16,17] For Ir(I), tridentate coordination appears to prevail but the steric effects associated with the pyrazolyl substituents may have an important influence on the hapticity of the ligand.[14,18−21]

Another issue of interest in connection with this kind of complex concerns the relative stability of oxidation states I and III, notably in connection with the C−H bond activation of the ethylene ligand in $Tp'M^I-C_2H_4$ complexes.[22] In contrast with the Cp′ analogues, η^2-ethene derivatives of $Tp'Ir^I$ systems are

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[†] This paper is dedicated to Prof. René Poilblanc on the occasion of his retirement.

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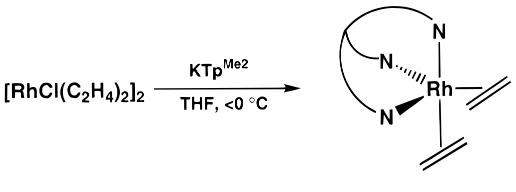
unstable with respect to the Ir(III) vinyl hydride isomers. Theoretical calculations[23] suggest that the increased relative stability of the latter depends on the steric bulk of the Tp′ ligand. For Tp′Rh(C_2H_4)(CO) systems these calculations indicate not only that κ^2-Tp′ η^2-ethene structures are more favorable than the analogous κ^3-Tp′ η^2-ethene but moreover that the Rh(III) hydrido vinyl compounds are thermally unstable with respect to the κ^2-Tp′ η^2-ethene complexes.

We have reported recently[18,19,24−26] the chemical properties of Tp′Ir(C_2H_4)(L) complexes (L = Tp, Tp^{Me2}). Herein we discuss the synthesis of the related compound $Tp^{Me2}Rh(C_2H_4)_2$ (**1***) and its reactivity (along with that of the analogous derivative $TpRh(C_2H_4)_2$ (**1**)) toward soft donors, dihydrogen and dioxygen. In a subsequent contribution we will describe the intermolecular C−H bond activation reactions induced by these complexes. Part of this work has been communicated in preliminary form.[27,28]

Results and Discussion

Synthesis and Characterization of Tp′Rh(C_2H_4)(L) Complexes and Related Derivatives. Equation 1 shows the reaction conditions that allow the synthesis and isolation of the bis(ethylene) complex **1***. The depicted procedure is similar to that used previously by Trofimenko for the preparation of $TpRh(C_2H_4)_2$ (**1**), the analogous complex of the unsubstituted Tp ligand.[29] Working temperatures below 0 °C are required because of the relatively low thermal stability of **1***. The lower thermal stability of the related $Tp^{Me2}Ir(C_2H_4)_2$ with respect to the Tp derivative has already been noticed.[18]



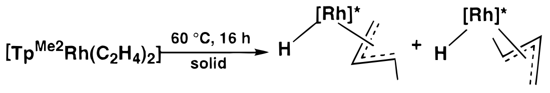
1*

(1)

Similarly to the Ir analogues[18,30,31] the two bis(ethene) complexes **1**[29] and **1*** are highly fluxional molecules; their room-temperature ^1H and $^{13}C\{^1H\}$ NMR spectra reveal equivalent environments for the three pyrazolyl rings and for the protio and carbon nuclei of the C_2H_4 ligands. For **1*** the C_2H_4 resonance is observed at 47.1 ppm (^1J(Rh,C) = 12 Hz), comparing well with the corresponding signal reported for **1** (49.0 ppm; ^1J(Rh,C) = 13 Hz).[14] It is therefore reasonable to assume that the two compounds have identical solution structures.

Establishing the denticity of the Tp′ ligands in usually fluxional Tp′RhL$_2$ complexes is not an easy task. Very recently, simple empirical criteria, that so far have proved very reliable, have been proposed. Akita, Moro-oka, and co-workers[4] have found that for complexes of the type Tp^{iPr2}Rh(diene), ν(B−H) bands around 2470 and 2540 cm^{-1} are suggestive of bidentate (κ^2) and tridentate (κ^3) coordination, respectively. Shortly afterward, Jones and co-workers have observed a relationship between the $^{11}B\{^1H\}$ chemical shift of the Tp^{Me2} moiety and its coordination mode,[5] these predictions being in excellent agreement with those based on the ν(B−H) values. According to the NMR criterium, chemical shifts in the range −5.9 to −7.0 ppm (relative to external $BF_3{\cdot}OEt_2$) are indicative of κ^2-Tp^{Me2} binding, whereas the tridentate Tp^{Me2} unit generates signals between −8.4 and −9.8 ppm. For complex **1*** these parameters have values of 2515 cm^{-1} (ν(B−H)) and −9.2 ppm (δ(^{11}B)); hence, a trigonal bipyramidal five-coordinate ground-state structure with κ^3-Tp^{Me2} can be proposed. This is similar to the structure found by X-ray crystallography for the iridium complex analog.[18] However, it is worth pointing out that the chemistry discussed in the following sections clearly indicates the ready accessibility for compounds **1** and **1*** of a four-coordinate, 16-electron state.

Complex **1*** decomposes cleanly in the solid state, and the allylic species $Tp^{Me2}RhH(\eta^3$-*syn*-$C_3H_4Me)$ (**2***) is obtained (eq 2) after heating at 60 °C for about 16 h. Compound **2*** has been characterized by NMR spectroscopy as a 1:1 mixture of *endo* and *exo* isomers,[32,33] but upon standing of the sample for 1 day at 20 °C in C_6D_6 solution, a thermodynamic *endo*:*exo* ratio of ca. 6:1 is achieved. The *endo-syn*-**2*** isomer exhibits a distinctively high-field ^1H NMR resonance at −23.03 ppm, which appears as a doublet due to coupling to the ^{103}Rh nucleus (7.5 Hz). The allyl moiety also gives characteristic signals, details of which are provided in the Experimental Section.



endo-syn-**2*** *exo-syn*-**2***

(2)

Even though no attempts have been made to elucidate the mechanism of this transformation, by similarity with the iridium system analog[18] it can be suggested that the C−C coupling involves the intermediacy of an undetected $Tp^{Me2}RhH(CH{=}CH_2)(C_2H_4)$ intermediate, resulting from the activation of an olefinic C−H bond. Evidence for the accessibility of such a hydrido vinyl species in solution has been given in a preliminary communication.[27] However, this decomposition route does not appear to play a relevant role in solution since, at room temperature, **1*** (C_6H_6 or C_6H_{12}) slowly gives the butadiene derivative **3a*** along with other products (Scheme 1). The formation of **3a*** is favored by the presence of an excess of C_2H_4; in fact a Rh-mediated disproportionation of ethylene ($3C_2H_4 \rightarrow C_4H_6 + C_2H_6$) is suggested to explain these observations. Although this transformation is catalyzed by some transition metal compounds,[34] in the present case it is stoichiometric. As shown also in Scheme 1, complex **3a*** is best obtained by action of butadiene on **1***, by the stepwise treatment

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(22) A complete list of references on this topic can be found in refs 18 and 19.

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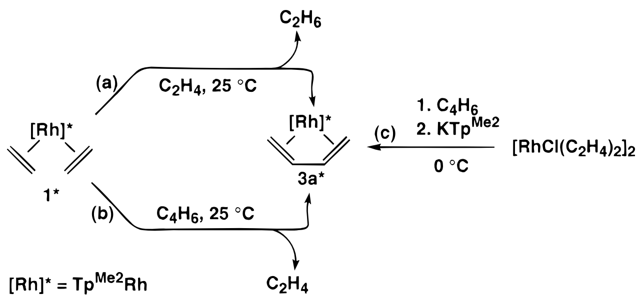
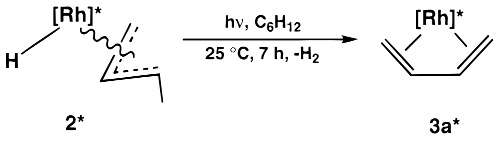
Scheme 1

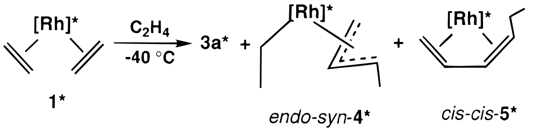


of $[RhCl(C_2H_4)_2]_2$ with C_4H_6 and KTp^{Me2} or, alternatively, by photolysis of the allylic species **2*** (eq 3).



(3)

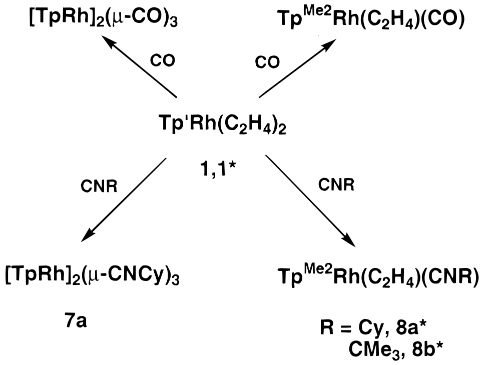
Interestingly, the **1*** to **3a*** transformation is strongly inhibited (to ca. 20% of the total turnover) when it is conducted at −40 °C in the presence of C_2H_4. Under these conditions a third molecule of C_2H_4 becomes incorporated into the products and complexes **4*** and **5*** are additionally produced (eq 4) in 35 and 45% yield, respectively. These two complexes have been purified by preparative thin-plate chromatography, and their formulation as the *endo-syn*-**4*** and *cis-cis*-**5*** isomers is supported by NMR spectroscopic data including 2D-NOESY experiments. For comparative purposes, the analogous derivative *cis-trans*-**5*** has been prepared quantitatively by the reaction of $[RhCl(C_2H_4)_2]_2$ with KTp^{Me2} in the presence of an excess of commercial *trans*-1,3-hexadiene. Obviously, complexes **4*** and **5*** are formed from **1*** through complicated, yet undisclosed, pathways and further experimentation is needed before a mechanistic proposal can be made.



(4)

A closely related Rh(I)−diene complex that contains the 2,3-dimethylbutadiene ligand, $Tp^{Me2}Rh(\eta^4\text{-}2,3\text{-}Me_2C_4H_4)$ (**3b***), can be readily prepared by either of routes b or c of Scheme 1. **3a***,**b*** display similar spectroscopic properties. In particular, the stretching of the B−H bond originates an IR absorption at 2515 (**3a***) or 2520 cm $^{-1}$ (**3b***), and the $^{11}B\{^1H\}$ signal of this functionality has an almost identical chemical shift in the two compounds at ca. −9.8 ppm. Once more these data are in agreement with tridentate coordination of the Tp^{Me2} ligand. For comparative purposes in connection with the structure of these compounds the somewhat analogous $Bp^{Me2}Rh(\eta^4\text{-}2,3\text{-}Me_2C_4H_4)$ derivative, **6b***, has also been obtained (using KBp^{Me2}, route c, Scheme 1).[35] **3b*** and **6b*** differ considerably in some spectroscopic characteristics, and for example while the terminal CH_2 resonance of the butadiene ligand appears at ca. 22 ppm (^1J(C, Rh) = 16 Hz) in the Tp^{Me2} complex, for the Bp^{Me2} species the corresponding value is ca. 44 ppm (^1J(C, Rh) = 12 Hz).

Scheme 2



The bis(ethene) complexes **1** and **1*** react very rapidly at 25 °C with soft Lewis bases such as CO and organic isocyanides, CNR (Scheme 2), to afford adducts of different nature. The steric bulkiness of the Tp′ ligands has an important effect in the course of these transformations. Thus, the interaction of **1** with CO gives the very insoluble binuclear complex $[TpRh]_2(\mu\text{-}CO)_3$[36] that contains only bridging CO ligands, whereas for **1*** the product of the carbonylation is first the mononuclear mixed adduct $Tp^{Me2}Rh(C_2H_4)(CO)$, reported by Ghosh and Graham in preliminary form,[13] and then $Tp^{Me2}Rh(CO)_2$.[12] The reactions of **1** and **1*** with isocyanides are similar and allow the isolation (Scheme 2) of the new compounds $[TpRh]_2(\mu\text{-}CNCy)_3$ (**7a**) (Cy = C_6H_{11}) and $Tp^{Me2}Rh(CNR)(C_2H_4)$ [R = Cy (**8a***), CMe_3 (**8b***)].

The IR spectrum of binuclear **7a** shows a very broad and intense band centered at ca. 1735 cm^{-1}, i.e., in the region expected for μ_2-CNR functionalities.[37−40] Also worth mentioning is a medium-intensity ν(B−H) stretching vibration at 2480 cm^{-1}. While in comparison with Tp^{Me2} compounds there are insufficient data available on ν(B−H) for complexes of the unsubstituted Tp ligand, in the structurally characterized $[(\kappa^3\text{-}Tp)Ru(CO)_2]_2$[41] this band appears at 2485 cm^{-1}. Very recently, Hill and co-workers[11] have found very similar frequencies (ca. 2480 cm^{-1}) in some TpRh compounds structurally characterized as containing a κ^3-Tp ligand. In addition, it has been noted that ν(B−H) shifts to higher energy as the substituents attached to the pyrazolyl rings become more electron-donating.[4] On this basis and if one takes into account that ν(B−H) changes from 2435 to 2390 cm^{-1} on going from KTp^{Me2} to KTp, the 2485 cm^{-1} value found for **7a**, albeit lower by ca. 20−40 cm^{-1} than those computed for the κ^3-Tp^{Me2} complexes already discussed, may be safely taken as indicative of tridentate Tp coordination. As discussed below, this has been confirmed by X-ray crystallography.

Figure 1 shows an ORTEP representation of the molecules of **7a**; important bond distances and angles are collected in Table 1, while Table 2 contains relevant structural data. Each of the two Rh atoms is in the center of a distorted octahedron that

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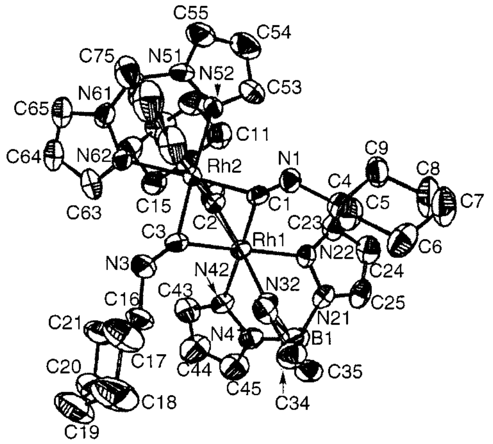


Figure 1. Molecular structure of complex **7a**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex **7a**

Rh(1)−Rh(2)	2.560(1)	N(1)−C(1)	1.21(1)
Rh(1)−C(1)	2.01(1)	N(1)−C(4)	1.48(1)
Rh(1)−C(2)	1.98(1)	N(2)−C(2)	1.21(1)
Rh(1)−C(3)	2.04(1)	N(2)−C(10)	1.467(1)
Rh(2)−C(1)	1.99(1)	N(3)−C(3)	1.23(2)
Rh(2)−C(2)	2.05(1)	N(3)−C(16)	1.47(2)
Rh(2)−C(3)	1.98(1)		
C(2)−Rh(1)−C(3)	84.3(4)	Rh(1)−C(1)−Rh(2)	79.5(4)
C(1)−Rh(1)−C(3)	80.8(4)	Rh(2)−C(2)−N(2)	139.4(9)
C(1)−Rh(1)−C(2)	85.6(4)	Rh(1)−C(2)−N(2)	141.7(9)
C(1)−N(1)−C(4)	125(1)	Rh(1)−C(2)−Rh(2)	78.9(4)
C(2)−N(2)−C(10)	128(1)	Rh(2)−C(3)−N(3)	140.1(9)
C(3)−N(3)−C(16)	128(1)	Rh(1)−C(3)−N(3)	140.7(9)
Rh(2)−C(1)−N(1)	138.9(8)	C(1)−Rh(2)−C(3)	82.8(4)
Rh(1)−C(1)−N(1)	141.5(8)	C(1)−Rh(2)−C(2)	84.4(4)

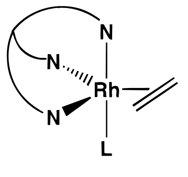
Table 2. Crystal and Structure Refinement Data for Complex **7a**

chem formula $C_{39}H_{35}B_2N_{15}Rh_2$	fw 941.2
$a = 29.302(9)$ Å	space group $C2/c$
$b = 16.761(3)$ Å	$T = 22$ °C
$c = 19.534(4)$ Å	$\lambda = 0.710\ 69$ Å
$\beta = 100.76(2)°$	$\rho_{calcd} = 1.33$ g cm^{-3}
$V = 9425(4)$ Å^3	μ(Mo Kα) = 7.3 cm^{-1}
$Z = 8$	$R^a = 5.6$
	$R_w{}^b = 7.8$

^{a} $R = \Sigma|\Delta F|/\Sigma|F_o|$. ^{b} $R_w = (\Sigma w\Delta^2F/\Sigma w|F_o|^2)^{1/2}$.

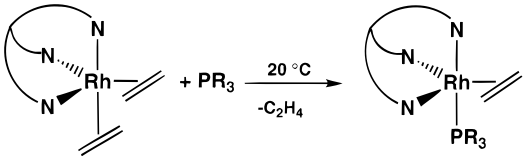
consists of the three pyrazolyl nitrogens and the carbon atoms of the isocyanide ligands. These act as almost symmetrical bridges. The close Rh−Rh contact at 2.560(1) Å is indicative of a single bond between them,[42] and it is probably the cause of the fairly acute Rh(1)−C−Rh(2) angles, which average 79.2(4)°. The Rh−N and Rh−C bonds have normal values; as expected, the latter are slightly longer than in mononuclear Rh(I)−CNR compounds (2.0 Å, average in **7a**, vs 1.88 Å, average value in $Tp^{Me2}Rh(CNCH_2CMe_3)_2$[7]). In accord with their bridging role, the CNR ligands are strongly bent, with C−N−C angles in the range 125−128° and with the cyclohexyl rings oriented in the less sterically congested manner. Interestingly, $Cp'_2Rh_2(L)_3$ complexes (Cp′ = C_5H_5, indenyl; L = CO, CNR) have usually only one bridging ligand and are therefore formulated as $[Cp'Rh(L)]_2(\mu\text{-}L)$.[43] Probably, the bigger cone angle of the Tp ligand as compared with Cp is responsible for the adoption of the $Rh_2(\mu\text{-}L)_3$ structures.

The mononuclear isocyanide derivatives **8a***,**b*** are characterized by ν(B−H) stretches of 2515 and 2520 cm^{-1}, respectively. The pyrazolyl rings of **8a*** appear as a 2:1 set of resonances, both in the ^{1}H and the $^{13}C\{^1H\}$ NMR spectra. The observation of two signals in a 1:1 ratio for the C_2H_4 protons indicates that the rotation around the Rh(I)−C_2H_4 bond is slow at room temperature relative to the NMR time scale. All these data support the κ^3-Tp^{Me2} structure **A**, in which the isocyanide ligand occupies the remaining axial site. Location of a molecule of C_2H_4 in an equatorial position optimizes the back-donation from the Rh(I) center.[18,19,44] In the two complexes the olefinic, ^{13}C nuclei resonate at ca. 19 ppm and are coupled to the ^{103}Rh nucleus (ca. 16 Hz).



A

Compounds **1** and **1*** react smoothly with stoichiometric amounts of tertiary phosphines (or bidentate phosphines such as $Me_2PCH_2CH_2PMe_2$, dmpe) to give (eq 5) the mixed ethene−phosphine adducts $Tp'Rh(C_2H_4)(L)$ [Tp′ = Tp, L = PMe_2Ph (**9b**), PEt_3 (**9c**); Tp′ = Tp^{Me2}, L = PMe_3 (**9a***),[15b] PMe_2Ph (**9b***), PEt_3 (**9c***), $^1/_2$ dmpe (**9d***)]. Very recently, Heinekey and coworkers have reported the formation of related $Tp'Rh(C_2H_4)(PR_3)$ derivatives.[14,15] For compounds **9b**,**c**, ν(B−H) appears around 2465 cm^{-1} whereas in complexes **9*** of the Tp^{Me2} ligand this absorption comes at 2520 cm^{-1}. These and other data supports a κ^3 binding of the Tp′ ligand with the specific configuration shown in eq 5.



1,1* **9, 9*** (5)

The structure derived for complexes **9** and **9*** from the spectroscopic data has been confirmed by X-ray studies carried out using a single crystal of the PEt_3 derivative **9c***. Figure 2 shows an ORTEP view of one of the two crystallographically independent molecules of this compound. Some pertinent bond distances and angles are summarized in Table 3, and Table 4 contains relevant structural data. As can be seen, the rhodium atom has a severely distorted trigonal bypiramidal environment made up of the three pyrazolyl nitrogens, the phosphine, and the ethylene ligands. The equatorial plane contains two of the N atoms of the Tp^{Me2} group as well as the olefinic carbon atoms C(1) and C(2), the latter at a distance of 2.070(7) Å (average) from the metal atom. The C(1)−C(2) bond length of 1.415(10) Å is intermediate between a single (1.54 Å) and a double (1.34 Å) carbon−carbon bond. The corresponding C(1)′−C(2)′ distance in the other independent molecule of the unit cell is longer (1.494(11) Å), but the large standard deviations prevents any additional comments or comparisons (e.g. with other Rh(I)−C_2H_4 complexes) to be made. Their mean value (ca. 1.45 Å)

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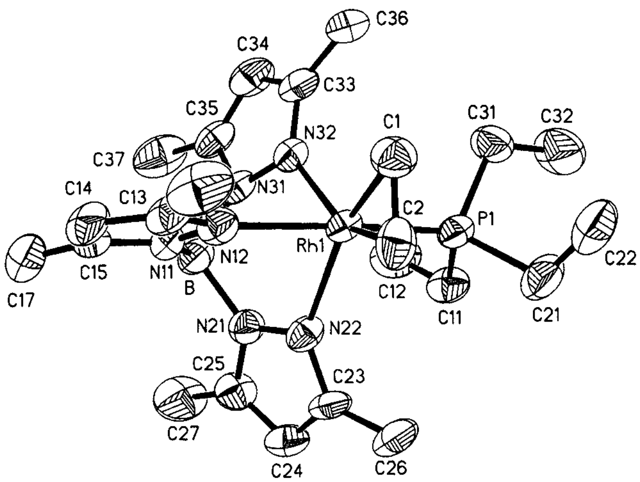


Figure 2. ORTEP view of one of the two independent molecules of complex **9c***.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex **9c***

Rh(1)−C(2)	2.053(7)	Rh(1′)−C(1′)	2.073(9)
Rh(1)−N(32)	2.206(6)	Rh(1′)−N(32′)	2.193(6)
Rh(1)−N(12)	2.227(6)	Rh(1′)−N(12′)	2.232(6)
Rh(1)−C(1)	2.087(7)	C(1′)−C(2′)	1.494(11)
Rh(1)−N(22)	2.219(6)	Rh(1′)−C(2′)	2.131(9)
Rh(1)−P(1)	2.245(2)	Rh(1′)−N(22′)	2.204(6)
C(1)−C(2)	1.415(10)	Rh(1′)−P(1′)	2.254(2)
C(2)−Rh(1)−C(1)	40.0(3)	C(1′)−Rh(1′)−C(2′)	41.6(3)
C(2)−Rh(1)−P(1)	93.2(2)	C(1′)−Rh(1′)−P(1′)	90.4(3)
C(1)−Rh(1)−P(1)	91.8(2)	C(2′)−Rh(1′)−P(1′)	91.5(2)
C(2)−C(1)−Rh(1)	68.7(4)	C(2′)−C(1′)−Rh(1′)	71.3(5)
C(1)−C(2)−Rh(1)	71.3(5)	C(1′)−C(2′)−Rh(1′)	67.1(5)

Table 4. Crystal and Structure Refinement Data for Complexes **9c*** and **10c***

	9c*	**10c***
chem formula	$C_{23}H_{41}BN_6PRh$	$C_{21}H_{37}BN_6O_2PRh$
fw	546.31	549.25
space group	$P2_{1/c}$	$P2_{1/c}$
a, Å	19.6385(12)	17.532(2)
b, Å	16.3298(10)	11.1955(11)
c, Å	19.3328(12)	13.7896(13)
β, deg	118.9080(10)	109.323(2)
Z	8	4
V, Å^3	5427.4(6)	2554.1(4)
ρ_{calcd}, g cm^{-3}	1.337	1.428
T, °C	20	25
λ, Å	0.710 73	(Mo Kα)
μ, cm^{-1}	7.1	7.6
R^a	0.1311	0.0767
$R_w{}^b$	0.1366	0.1258

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

compares well with the C═C bond of the analogous Tp^{Me2}Ir(C$_2$H$_4$)(PMe$_3$) derivative (1.44 Å).[19]

In accord with other authors,[14] we believe that the substitution reactions of Tp′Rh(C$_2$H$_4$)$_2$ complexes with soft Lewis bases are probably associative in nature, with easily accessible κ^2-Tp′ 16e$^-$ species as intermediates.

Before we close this section, and as further support of the applicability of the IR (ν(B−H)) critera for assigning the denticity of the Tp′ ligands, we consider worth noting that in the compounds Tp^{Me2}Rh(C$_2$H$_4$)(L) [L = C$_2$H$_4$ (**1***), PMe$_3$ (**9a***)] the chemical shift difference between the ^{13}C resonances of the olefinic ligands ($\Delta\delta_C$ = 47 − 16 = 31 ppm) is very similar to that encountered in the analogous but square planar complexes Bp^{Me2}Rh(C$_2$H$_4$)(L) (L = C$_2$H$_4$, PMe$_3$; $\Delta\delta_C$ = 61 − 33 = 28 ppm), where the auxiliary ligand has κ^2-binding mode.[35] Moreover, in the analogous iridium compounds Tp^{Me2}Ir(C$_2$H$_4$)(L) (L = C$_2$H$_4$,[18] PMe$_3$[19]) which contain κ^3-Tp^{Me2}, $\Delta\delta_C$ has also a very close value, 34 ppm. In our view, the similar $\Delta\delta_C$ values found for the three sets of complexes mean that the denticity of the auxiliary polydentate ligand is the same within this couple. Hence since **9a*** contains κ^3-Tp^{Me2}, the bis(ethene) complex **1*** must also contain a tridentate Tp^{Me2} ligand as inferred from the values of ν(B−H) and δ(^{11}B{^{1}H}).

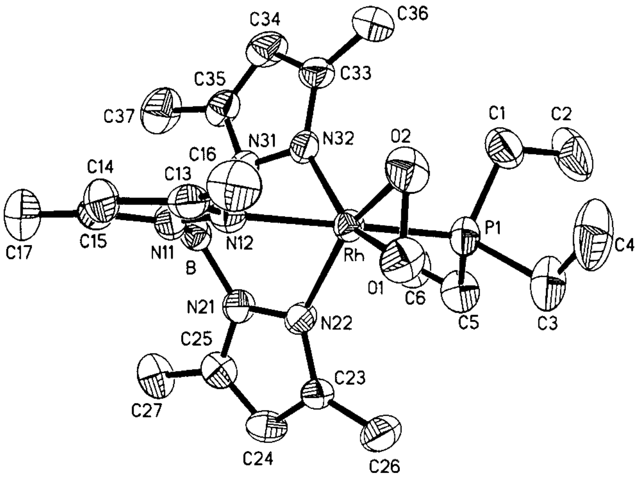
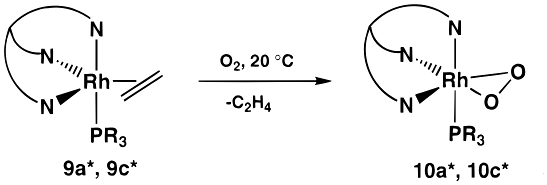


Figure 3. Molecular structure of complex **10c***.

Reactions with O$_2$ and H$_2$. Diethyl ether solutions of the phosphine adducts Tp^{Me2}Rh(C$_2$H$_4$)(PR$_3$) [PR$_3$ = PMe$_3$ (**9a***), PEt$_3$ (**9c***)] react with O$_2$, probably by an associative mechanism, at room temperature and pressure to give the η^2-dioxygen[45−51] derivatives Tp^{Me2}Rh(O$_2$)(PR$_3$), **10a***,**c***, respectively (eq 6), which are isolated as yellow crystalline materials.



(6)

In the higher energy region of the IR spectrum there is a medium-intensity band at ca. 2520 cm^{-1}, suggestive of κ^3-Tp^{Me2} binding. This assumption is further substantiated by the δ(^{11}B{^{1}H}) value of −9.1 ppm found for these compounds.

A single-crystal X-ray study carried out with the PEt$_3$ derivative **10c*** (see Figure 3 and Tables 4 and 5 for relevant information) confirms the proposed formulation. If the O$_2$ unit is view as occupying a single coordination site (the O(1)−Rh−O(2) angle is only of 42.5(2)°), then the coordination geometry approaches a distorted trigonal bipyramid. The axial N(12)−Rh bond form angles close to 90° with the two Rh−O vectors (ca. 95°, average) and approaches the ideal 180° value expected

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(45) For metal−dioxygen complexes see the following special issue: *Chem. Rev.* **1994**, *94*, 567−856. For some very recent compounds see, for instance, refs 11, 46, and 47.

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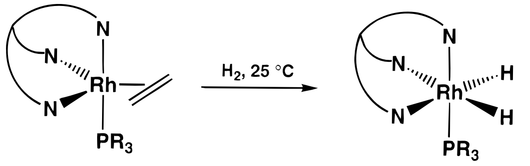
Table 5. Selected Bond Lengths (Å) and Angles (deg) for Complex **10c***

Rh−O(1)	1.997(4)	Rh−O(2)	1.997(4)
Rh−N(22)	2.084(4)	Rh−N(32)	2.092(4)
Rh−N(12)	2.143(5)	Rh−P(1)	2.271(2)
O(1)−O(2)	1.448(5)		
O(1)−Rh−O(2)	42.5(2)	O(2)−Rh−P(1)	87.59(12)
O(1)−Rh−P(1)	88.73(13)	O(2)−O(1)−Rh	68.8(2)

for a *trans*-N(12)−Rh−P(1) arrangement (176.21(13)°). To maximize π back-donation from the metal the molecule of O_2 occupies an equatorial site, the corresponding Rh−O bonds being almost perpendicular to the Rh−P(1). This arrangement of the O_2 ligand is very similar to that of the molecule of C_2H_4 in the precursor compounds **9***. The O−O separation at 1.448(5) Å is clearly in accord with the peroxo formulation, mean distances of about 1.48 Å being usually quoted for this functionality.[48−51]

Dihydrogen reacts also with Tp′Rh(C_2H_4)(PR_3) compounds to give dihydride complexes Tp′Rh(H)$_2$(PR_3) [Tp′ = Tp, PR_3 = PMe_2Ph (**11b**), PEt_3 (**11c**), Tp′ = Tp^{Me2}, PR_3 = PMe_3 (**11a***), PMe_2Ph (**11b***), PEt_3 (**11c***)] as shown in eq 7. Heinekey et al. have reported recently some other members of this series.[14] The reactions represented in eq 7 are facile and occur, probably through 16e$^-$ η^2-Tp′ intermediates, at room temperature under 2−3 atm of H_2. The formulation proposed for these compounds finds support in the spectroscopic data. For instance, in the IR spectrum of the PMe_3 compound **11a*** bands can be found at 2515, 2050, and 2030 cm^{-1}, which may be attributed to ν(B−H) of a tridentate Tp^{Me2} group (2515 cm^{-1}) and to the stretching vibrations of the two Rh−H bonds. In the ^1H and $^{13}C\{^1H\}$ NMR spectra, the pyrazolyl rings give rise to two sets of resonances in a 2:1 ratio. The two hydride ligands have equal environments and originate a high-field doublet of doublets due to coupling to the ^{103}Rh and the ^{31}P nuclei (δ −17.09; ^1J(H,Rh) = 21; ^2J(H,P) = 36 Hz). Finally, the $^{11}B\{^1H\}$ chemical shift of the ⋗B−H unit (δ −9.1) is in accord with the κ^3-Tp^{Me2} structure expected for the 18e$^-$ count of a Rh(III) complex.



(7)

9,9* **11,11***

Interestingly, the ^1J(P,Rh) values obtained for these hydrides (ca. 140 Hz) are quite similar to those of the Rh(I) complexes Tp′Rh(C_2H_4)(PR_3) (ca. 151 Hz). Therefore, there is very little dependence on this magnitude upon the oxidation state of the Rh center and this is in contrast with the experimental observations made on the Cp′ systems,[52] for which differences up to 150 Hz are found.

Conclusions

The bis(ethylene) complex $Tp^{Me2}Rh(C_2H_4)_2$ (**1***) has been synthesized and shown to possess an 18-electron trigonal bipyramidal structure, both in the solid state and in solution. This complex has poor thermal stability, but the nature of the decomposition products depends on the reaction conditions (solution or solid-state reaction; presence or absence of free ethylene). Complex **1*** reacts with soft bases such as CO and CNR to give Tp^{Me2}Rh(C_2H_4)(L) derivatives whereas the related TpRh(C_2H_4)$_2$ (**1**) gives binuclear [TpRh]$_2$(μ-L)$_3$ species. Both **1** and **1*** afford Tp′Rh(C_2H_4)(PR_3) on treatment with trialkylphosphines. These substitution reactions are believed to occur through associative pathways in which thermally accessible κ^2-Tp′, 16 e$^-$ species act as intermediates. All reported Tp′Rh(C_2H_4)(L) complexes have been shown to possess a trigonal bipyramidal ground-state structure in which the ethylene ligand occupies an equatorial position in order to maximize Rh → C_2H_4 electron back-donation. The easy accessibility of κ^2-Tp′ intermediates is also probably responsible for the smooth oxygenation and hydrogenation of the ethylene species Tp′Rh(C_2H_4)(PR_3) to Tp′Rh(O_2)(PR_3) and Tp′Rh(H)$_2$(PR_3) complexes, respectively.

Experimental Section

All preparations and manipulations were carried out under oxygen-free nitrogen following conventional Schlenk techniques. Solvents were rigorously dried and degassed before use. The complexes [RhCl(C_2H_4)$_2$]$_2$[53] and TpRh(C_2H_4)$_2$[29] and the salts KHB(pz)$_3$[54,55] (KTp) and KHB(3,5-Me_2-pz)$_3$[54,55] (KTp^{Me2}) were prepared according to literature procedures. Microanalysis were performed by the Microanalytical Service of the University of Sevilla. Infrared spectra were recorded on Perkin-Elmer model 683 and 883 and Bruker model Vector 22 spectrometers, and NMR spectra on Bruker AMX-300, DRX-400, and AMX-500 spectrometers. The ^1H and $^{13}C\{^1H\}$ resonances of the solvent were used as the internal standard, but chemical shifts are reported with respect to TMS. ^{31}P and ^{11}B NMR shifts are referenced to external 85% H_3PO_4 and BF_3·OEt_2, respectively. Most of the NMR assignments are based on extensive ^1H−^1H and ^1H−^{31}P decoupling experiments, NOEDIFF measurements, and homo- and heteronuclear two-dimensional spectra. All spectra were obtained at 25 °C unless otherwise indicated.

$Tp^{Me2}Rh(C_2H_4)_2$ (1*). A solution of [RhCl(C_2H_4)$_2$]$_2$ (0.79 g, 2 mmol) in THF (50 mL) was cooled to −30 °C and treated with KTp^{Me2} (1.35 g, 4 mmol). The mixture was stirred for 4 h, and the volatiles were then removed under reduced pressure at −20 °C (higher temperature must be avoided up to this stage). The residue was dissolved in CH_2Cl_2−Et_2O (1:1, 40 mL) and filtered through Celite. The resulting yellow-orange solution was evaporated to dryness to give 1.5 g of complex **1*** (80% yield). This product must be stored below 0 °C. ^1H NMR (C_6D_6): δ 5.61 (s, 3 H, 3 CH_{pz}), 2.59 (d, 8 H, 2 C_2H_4, ^2J(H,Rh) = 2 Hz), 2.43, 2.16 (s, 9 H each, 6 Me_{pz}). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 150.4, 143.4 (1:1 ratio, C_{qpz}), 107.1 (CH_{pz}), 47.1 (d, C_2H_4, ^1J(C,Rh) = 12 Hz), 14.4, 12.5 (1:1 ratio, Me_{pz}). Anal. Calcd for $C_{19}H_{30}BN_6Rh$: C, 50.0; H, 6.6; N, 18.4. Found: C, 50.2; H, 6.6; N, 18.7.

$Tp^{Me2}RhH(\eta^3$-*syn*-$C_3H_4Me)$ (2*). A solid sample of **1*** (0.05 g, 0.1 mmol) was heated, under N_2, at 60 °C for 16 h. The ^1H NMR spectra of the white powder thus obtained revealed quantitative formation of **2*** as a 6:1 mixture of *exo* and *endo* isomers. After the sample was standing at 25 °C in C_6D_6 for 24 h, a 6:1 thermodynamic mixture, favoring the *endo* isomer, was reached. Data for *endo*-*syn*-**2*** are as follows: ^1H NMR (C_6D_6) δ 5.59, 5.61, 5.56 (s, 1 H each, 3 CH_{pz}), 5.08 (br q, 1 H, H_C, J(C,A) ≈ J(C,D) = 10.5, J(C,B) = 7.4 Hz), 3.92 (dq, 1 H, H_D, J(H,Me) = 6.3 Hz), 3.17 (d, 1 H, H_B), 2.73 (d,1 H, H_A), 2.32, 2.27, 2.22, 2.14, 2.12, 1.85 (s, 3 H each, 6 Me_{pz}), 1.39 (d, 3 H, Me_{al}), −23.03 (d, 1 H, RhH, ^1J(H,Rh) = 7.5 Hz); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 150.6, 150.3, 149.9, 143.7, 143.2, 142.8 (C_{qpz}), 107.9, 105.6, 105.3 (CH_{pz}), 93.2 (d, CH_C, ^1J(C,Rh) = 5 Hz), 56.7 (d, *C*HMe, ^1J(C,Rh) = 10 Hz), 34.0 (d, CH_2, ^1J(C,Rh) = 13 Hz), 21.3 (CH*Me*), 15.2, 15.2, 13.8, 12.7, 12.6, 12.4 (Me_{pz}); IR (Nujol) 2072 (RhH) cm^{-1}. Anal. Calcd for $C_{19}H_{30}BN_6Rh$: C, 50.0; H, 6.6; N, 18.4. Found: C, 49.4; H, 6.8; N, 18.2.

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(52) See for example: Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1991**, *113*, 559.

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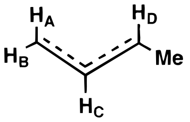


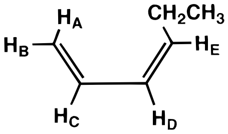
$Tp^{Me2}Rh(\eta^4-C_4H_6)$ (3a*). Complex **1*** (0.25 g, 0.5 mmol) was dissolved in THF (20 mL) and cooled to −20 °C. Butadiene was bubbled for 5 min and the cooling bath removed. After being stirred at room temperature for 1 h, the solution was taken to dryness. ^1H NMR analysis of the residue revealed a mixture of species with **3a*** predominating. Pure **3a*** can be obtained by crystallization from CH_2Cl_2−petroleum ether in 70% yield. Alternatively, this compound was prepared as follows: A stirred suspension of the dimer $[RhCl(C_2H_4)_2]_2$ (0.21 g, 0.54 mmol) in THF (20 mL) at 0 °C, was pressurized with butadiene (0.7 bar) and the mixture stirred for 10 min at this temperature, when the color of the suspension changed from orange to beige. The mixture was tranferred into a solution of KTp^{Me2} (0.37 g, 1.1 mmol) in THF (15 mL) at 0 °C, and the resulting suspension was stirred for 4 h at the same temperature. The solvent was evaporated under vacuo and the residue extracted with a mixture of CH_2Cl_2 (20 mL) and Et_2O (10 mL). The resulting suspension was filtered through Celite and the solvent evaporated in vacuo to yield pale yellow **3a*** (90%). ^1H NMR (CD_2Cl_2): δ 5.94, 5.71 (s, 1:2 ratio, 3 CH_{pz}), 5.65 (m, 2 H, 2 CH_2CH), 2.41, 2.34, 2.31, 2.19 (s, 1:1:2:2 ratio, 6 Me_{pz}), 2.25, 0.28 (m, 2 H each, 2 CH_2CH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 153.0, 151.0, 143.9, 143.8 (1:2:1:2 ratio, C_{qpz}), 107.1, 106.4 (2:1 ratio, CH_{pz}), 81.3 (d, $CHCH_2$, ^1J(C,Rh) = 7 Hz), 21.5 (d, $CHCH_2$, ^1J(C,Rh) = 16 Hz), 14.1, 13.7, 12.7, 12.4, (1:2:2:1 ratio, Me_{pz}). Anal. Calcd for $C_{19}H_{28}BN_6Rh$: C, 50.2; H, 6.2; N, 18.5. Found: C, 50.4; H, 6.2; N, 18.4.

$Tp^{Me2}Rh(\eta^4-2,3-Me_2C_4H_4)$ (3b*). To a stirred suspension of the dimer $[RhCl(C_2H_4)_2]_2$ (0.80 g, 2.05 mmol) in THF (40 mL) at 0 °C was added 2,3-dimethylbutadiene (2 mL, 17.7 mmol). The mixture was stirred for 1.5 h at room temperature, a solution of KTp^{Me2} (1.38 g, 4.1 mmol) in THF (30 mL) added, and the resulting suspension stirred for 3 h at the same temperature. The solvent was evaporated under vacuo and the residue extracted with a mixture of CH_2Cl_2 (60 mL) and Et_2O (30 mL). The resulting suspension was filtered through Celite and the solvent evaporated in vacuo to yield pale yellow **3b*** (85%). ^1H NMR (C_6D_6): δ 5.63 (s, 3 H, 3 CH_{pz}), 2.34, 0.66 (br d, 2 H each, 2 CH_2, ^1J(H,H) = 3.2 Hz), 2.24, 2.22 (s, 1:1 ratio, 6 Me_{pz}), 1.93 (s, 6 H, 2 Me). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 150.9, 142.4 (1:1 ratio, C_{qpz}), 106.7 (CH_{pz}), 99.3 (d, CCH_2, ^1J(C,Rh) = 6 Hz), 22.5 (d, CCH_2, ^1J(C,Rh) = 16 Hz, ^1J(C,H) = 151 Hz), 21.0 (C*Me*), 15.1, 12.7 (1:1 ratio, Me_{pz}). Anal. Calcd for $C_{21}H_{32}BN_6Rh$: C, 52.3; H, 6.7; N, 17.4. Found: C, 52.0; H, 6.7; N, 17.8.

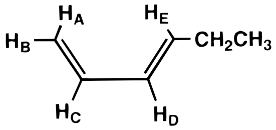
Reaction of Complex 1* with C_2H_4 at Low Temperature. As stated in the text, when complex **1*** is stirred in ethylene-saturated THF at −40 °C and the solution very slowly allowed to reach room temperature (Deward flask), the new complexes $Tp^{Me2}RhEt(\eta^3$-*syn*-$C_3H_4Me)$ (*endo-syn*-**4***) and $Tp^{Me2}Rh(\eta^4-C_4H_3Et)$ (*cis-cis*-**5***) are obtained in 35 and 45% yield, respectively. Complex **3a*** is also formed in 20% yield (NMR evidence). The three complexes can be separated in a spinning alumina plate using a mixture of petroleum ether−CH_2Cl_2−CH_3CN (100:50:1) as the mobile phase.

$Tp^{Me2}RhEt(\eta^3$-*syn*-$C_3H_4Me)$ (*endo-syn*-4*): ^1H NMR (C_6D_6) δ 5.80, 5.70, 5.44 (s, 1 H each, 3 CH_{pz}), 4.31 (dq, 1 H, H_D, *J*(D,C) = 12.2, *J*(H,Me) = 6.2 Hz), 3.71 (m, 1 H, H_C), 3.30 (d, 1 H, H_B, *J*(B,C) = 7.2 Hz), 3.13 (d, 1 H, H_A, *J*(A,C) = 11.6 Hz), 2.28, 2.28, 2.27, 2.23, 2.21, 1.75 (s, 3 H each, 6 Me_{pz}), 1.87, 1.43 (m, 1 H each, CH_2CH_3), 1.42 (d, 3 H, CH*Me*), 0.33 (t, 3 H, CH_2CH_3, ^3J(H,H) = 7.4 Hz); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 151.5, 151.1, 148.7, 143.3, 142.2 (1:1:1:2:1 ratio, C_{qpz}), 107.7, 106.8, 106.7 (CH_{pz}), 107.4 (d, CH_C, ^1J(C,Rh) = 6 Hz), 60.5 (d, *C*HMe, ^1J(C,Rh) = 10 Hz), 37.1 (d, CH_AH_B, ^1J(C,Rh) = 13 Hz), 19.1 (CH*Me*), 16.2 (CH_2CH_3), 14.3, 13.8, 13.4, 12.9, 12.8, 12.6 (Me_{pz}), 7.4 (d, CH_2CH_3, ^1J(C,Rh) = 21 Hz).

$Tp^{Me2}Rh(\eta^4-C_4H_3Et)$ (*cis-cis*-5*): ^1H NMR (C_6D_6) δ 5.82, 5.56, 5.47 (br, 1 H each, 3 CH_{pz}), 5.64 (m, 1 H, H_C, *J*(C,A) = 6.8, *J*(C,B) = *J*(C,D) = 5.2 Hz), 5.14 (t, 1 H, H_D, *J*(D,E) = 6.6 Hz), 3.25 (m, 1 H, H_E), 2.60 (dd, 1 H, H_B, *J*(B,A) = 4.5 Hz), 1.53 (dm, 1 H, H_A), 2.5−2.0 (br, 6 Me_{pz}), 1.5−0.9 (ABC_3 spin system, 5 H, CH_2CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 152.3, 150.2, 149.6, 143.7, 143.5, 143.2 (br, C_{qpz}), 107.6, 106.6, 106.4 (br, CH_{pz}), 86.1 (d, CH_C, ^1J(C,Rh) = 5, ^1J(C,H) = 162 Hz), 78.4 (d, CH_D, ^1J(C,Rh) = 6, ^1J(C,H) = 168 Hz), 39.4 (d, CH_E, ^1J(C,Rh) = 17, ^1J(C,H) = 166 Hz), 24.5 (d, CH_AH_B, ^1J(C,Rh) = 16, ^1J(C,H) = 166 Hz), 22.6 (CH_2CH_3, ^1J(C,H) = 128 Hz), 17.0 (CH_2CH_3), 15.1−12.5 (br, Me_{pz}).



$Tp^{Me2}Rh(\eta^4-C_4H_3Et)$ (*cis-trans*-5*). This compound is obtained as described above for complexes **3*** but using comercial *trans*-1,3-hexadiene. Yield: almost quantitative (NMR evidence). ^1H NMR (C_6D_6): δ 5.86, 5.60, 5.45 (s, 1 H each, 3 CH_{pz}), 5.48 (dd, 1 H, H_D, *J*(D,E) = 7.5, *J*(D,C) = 4.4 Hz), 5.38 (m, 1 H, H_C), 2.41, 2.29, 2.16, 2.15, 2.13, 2.02 (s, 3 H each, 6 Me_{pz}), 2.33 (dd, 1 H, H_B, *J*(B,C) = 5.7, *J*(B,A) = 2.6 Hz), 1.37 (m, 2 H, CH_2CH_3), 1.18 (q, H_E, *J*(E,CH_2) = 7.4 Hz), 0.25 (ddd, *J*(A,C) = 7.0, *J*(A,Rh) = 1.5 Hz); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 152.2, 149.9, 149.9, 143.4, 142.5 (1:1:1:1:2 ratio, C_{qpz}), 107.0, 106.4 (1:2 ratio, CH_{pz}), 85.5 (d, CH_C, ^1J(C,Rh) = 6 Hz), 74.2 (d, CH_D, ^1J(C,Rh) = 8 Hz), 46.0 (d, CH_E, ^1J(C,Rh) = 15 Hz), 24.7 (CH_2CH_3), 20.1 (d, CH_AH_B, ^1J(C,Rh) = 16 Hz), 16.5 (CH_2CH_3), 14.6, 14.3, 13.7, 12.7, 12.6, 12.3 (Me_{pz}).



$Bp^{Me2}Rh(\eta^4-2,3-Me_2C_4H_4)$ (6b*). To a suspension of $[RhCl(C_2H_4)_2)]_2$ (0.2 g, 0.5 mmol) in THF (20 mL)was added an excess of 2,3-dimethylbutadiene (0.6 mL, 5 mmol) and the resulting mixture stirred for 2 h at room temperature. A solution of KBp^{Me2} (0.25 g, 1 mmol) in THF (10 mL) was then added at −10 °C and stirring continued at this temperature for 3 h. The volatiles were removed in vacuo at 25 °C, and the residue was extracted with a mixture of CH_2Cl_2−Et_2O (2:1, 30 mL). After filtration through Celite and evaporation of the filtrate to dryness, crude red **6b*** was obtained in quantitative yield. Further purification can be achieved by crystallization from Et_2O−petroleum ether mixtures. ^1H NMR (C_6D_6): δ 5.62 (s, 2 H, 2 CH_{pz}), 2.59, 0.75 (br s, 2 H each, 2 CH_2), 2.36, 2.20, 1.84 (s, 6 H each, 4 Me_{pz} and 2 Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −15 °C): δ 149.2, 144.6 (1:1 ratio, C_{qpz}), 105.1 (CH_{pz}), 97.6 (d, CCH_2, ^1J(C,Rh) = 9 Hz), 44.6 (d, CCH_2, ^1J(C,Rh) = 12 Hz), 19.9 (C*Me*), 15.4, 13.0 (1:1 ratio, Me_{pz}). Anal. Calcd for $C_{16}H_{26}BN_4Rh$: C, 49.5; H, 6.7; N, 14.4. Found: C: 49.4; H, 6.9; N, 14.8.

$[TpRh]_2(\mu-CNCy)_3$ (7a). Complex **1** (0.044 g, 0.12 mmol) was reacted with a slight excess of CNCy in 6 mL of C_6H_{12}. After being stirred at 25 °C for 3 h, the mixture was taken to dryness. The residue was crystallized from Et_2O−petroleum ether, at −20 °C, in the form of a yellow microcrystalline powder. ^1H NMR (C_6D_6): δ 7.77, 7.56, 6.04 (m, 6 H each, 18 CH_{pz}), 2.56−0.74 (m, 33 H, 3 C_6H_{11}). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 193.7 (t, *C*NR, ^1J(C,Rh) = 28 Hz), 141.5, 134.3, 104.3 (CH_{pz}), 62.9, 36.2, 25.4, 23.8 (1:2:1:2 ratio, C_6H_{11}). IR (Nujol): 1735 (CN) cm^{-1}. Anal. Calcd for $C_{39}H_{50}B_2N_{15}Rh_2\cdot{}^1/_2Et_2O$: C, 49.4; H, 5.8; N, 21.1. Found: C, 49.2; H, 5.6; N, 20.4.

$Tp^{Me2}Rh(C_2H_4)(CNR)$ [R = C_6H_{11} (8a*), CMe_3 (8b*)]. These complexes were obtained as described above for complex **7a**. Data for **8a***: ^1H NMR (C_6D_6) δ 5.90, 5.31 (s, 2:1 ratio, 3 CH_{pz}), 3.39, 2.47 (br d, 2 H each, C_2H_4, J_{app} = 8.5 Hz), 2.62, 2.33, 2.18, 2.17 (s, 2:2:1:1 ratio, 6 Me_{pz}), 1.3−0.7 (m, 11 H, C_6H_{11}); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 151.7, 149.2, 142.7, 142.5 (1:2:1:2 ratio, C_{qpz}), 146.3 (d, *C*NR, ^1J(C,Rh) = 62 Hz), 107.9, 104.9 (1:2 ratio, CH_{pz}), 53.6, 32.6, 24.5, 22.7 (1:2:1:2 ratio, C_6H_{11}), 19.3 (d, C_2H_4, ^1J(C,Rh) = 16 Hz), 15.1, 13.3, 12.1, 12.1 (2:1:2:1 ratio, Me_{pz}); IR (Nujol) 2155 (CN) cm^{-1}. Data for **8b***: ^1H NMR (C_6D_6) δ 5.89, 5.30 (s, 2:1 ratio, 3 CH_{pz}), 3.37, 2.38 (br d, 2 H each, C_2H_4, J_{app} = 8 Hz), 2.61, 2.30, 2.17, 2.16 (s, 2:2:1:1 ratio, 6 Me_{pz}), 0.74 (s, 9 H, CMe$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 151.6, 149.2, 142.7, 142.5 (1:2:1:2 ratio, C$_{qpz}$), 145.8 (d, *C*NR,^1J(C,Rh) = 61 Hz), 107.9, 104.9 (1:2 ratio, CH$_{pz}$), 55.7 (*C*Me$_3$), 26.9 (C*Me*$_3$), 19.4 (d, C$_2$H$_4$, ^1J(C,Rh) = 16 Hz), 15.1, 13.3, 12.1, (2:1:3 ratio, Me$_{pz}$); IR (Nujol) (CN) 2135 cm^{-1}. Anal. Calcd for $C_{22}H_{35}BN_7Rh$: C, 51.7; H, 6.9; N, 19.2. Found: C, 52.2; H, 7.1; N, 17.5.

Tp′Rh(C$_2$H$_4$)(PR$_3$) Derivatives. All these complexes were prepared by following the procedure exemplified here for complex **9a***: A solution of complex **1*** (0.81 g, 1.75 mmol) in THF (40 mL) was cooled at −30 °C, and 1.75 mmol of PMe$_3$ (1.75 mL of a 1 M solution in THF) was added via syringe. After 15 min of stirring at this temperature the cold bath was removed and the solution further stirred for 1 h at room temperature. The volatiles were removed under vacuum, and 20 mL of Et$_2$O was added. The mixture was taken to dryness to afford complex **9a***, as a yellow microcrystaline powder, in almost quantitative yield. All these complexes can be recrystallized, albeit with considerable losses, from Et$_2$O or acetone at −20 °C.

TpRh(C$_2$H$_4$)(PMe$_2$Ph) (9b): ^{1}H NMR (C$_6$D$_6$) δ 7.8−5.8 (m, 14 H, C$_6$H$_5$ and CH$_{pz}$), 2.39, 1.98 (m, 2 H each, C$_2$H$_4$), 1.07 (d, 6 H, PMe$_2$, ^2J(H,P) = 9.3 Hz); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 143−104 (C$_6$H$_5$ and CH$_{pz}$), 23.9 (dd, C$_2$H$_4$, ^1J(C,Rh) = 17, ^2J(C,P) = 4 Hz), 14.4 (d, PMe$_2$, ^1J(C,P) = 30 Hz); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 24.4 (d, ^1J(P,Rh) = 154 Hz. Anal. Calcd for $C_{19}H_{25}BN_6PRh$: C, 47.3; H, 5.2; N, 17.4. Found: C, 46.6; H, 5.3; N, 17.1.

TpRh(C$_2$H$_4$)(PEt$_3$) (9c): ^{1}H NMR (C$_6$D$_6$) δ 7.85, 7.68, 7.40, 7.17, 6.07, 5.76 (m, 2:2:1:1:2:1 ratio, 9 CH$_{pz}$), 2.30, 1.92 (m, 2 H each, C$_2$H$_4$), 1.25 (m, 6 H, 3 PC*H*$_2$CH$_3$), 0.65 (m, 9 H, 3 PCH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 143.0, 134.6, 134.4, 104.5, 104.3 (s, 2:1:3:2:1 ratio, CH$_{pz}$), 22.1 (dd, C$_2$H$_4$, ^1J(C,Rh) = 17, ^2J(C,P) = 5 Hz), 16.0 (d, PCH$_2$, ^1J(C,P) = 27 Hz), 7.5 (s, PCH$_2$*C*H$_3$); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 36.7 (d, ^1J(P,Rh) = 149 Hz). Anal. Calcd for $C_{17}H_{29}BN_6PRh$: C, 44.2; H, 6.3; N, 18.2. Found: C, 43.9; H, 6.3; N, 17.6.

Tp^{Me2}Rh(C$_2$H$_4$)(PMe$_3$) (9a*): ^{1}H NMR (C$_6$D$_6$) δ 5.83, 5.19 (s, 2:1 ratio, 3 CH$_{pz}$), 3.29, 1.87 (br, 2 H each, C$_2$H$_4$), 2.45, 2.41, 2.17, 2.08 (s, 2:2:1:1 ratio, 6 Me$_{pz}$), 0.60 (d, 9 H, PMe$_3$, ^2J(H,P) = 9.6 Hz); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 150.7, 150.6, 144.3, 142.1 (2:1:2:1 ratio, C$_{qpz}$), 106.9, 105.6 (1:2 ratio, CH$_{pz}$), 16.3 (dd, C$_2$H$_4$, ^1J(C,Rh) = 17, ^2J(C,P) = 5 Hz), 14.7 (d, PMe$_3$, ^1J(C,P) = 31 Hz), 13.2, 12.6, 11.8 (2:3:1 ratio, Me$_{pz}$); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 14.6 (d, ^1J(P,Rh) = 152 Hz). Attempts to recrystalize this compound to get a sample of analytical purity were unsuccessful due to its high sensitivity to oxygen in solution.

Tp^{Me2}Rh(C$_2$H$_4$)(PMe$_2$Ph) (9b*): ^{1}H NMR (C$_6$D$_6$) δ 7.2−6.8 (m, 5 H, C$_6$H$_5$), 5.70, 5.17 (s, 2:1 ratio, 3 CH$_{pz}$), 2.43, 2.20, 2.19, 2.07 (s, 2:2:1:1 ratio, 6 Me$_{pz}$), 2.33, 2.20 (m, 2 H each, C$_2$H$_4$), 0.94 (d, 6 H, PMe$_2$, ^2J(H,P) = 9.5 Hz); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 151.2, 150.6, 144.4, 142.9 (2:1:2:1 ratio, C$_{qpz}$), 143−129 (C$_6$H$_5$), 107.1, 105.6 (1:2 ratio, CH$_{pz}$), 16.9 (dd, C$_2$H$_4$, ^1J(C,Rh) = 17, ^2J(C,Rh) = 5 Hz), 15.6, 13.2, 12.5, 11.9, (2:1:2:1 ratio, Me$_{pz}$), 13.1 (d, PMe$_2$, ^1J(C,P) = 31 Hz); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 19.4 (d, ^1J(P,Rh) = 151 Hz). Anal. Calcd for $C_{25}H_{37}BN_6PRh$: C, 53.0; H, 6.5; N, 14.8. Found: C, 52.4; H, 6.4; N, 14.6.

Tp^{Me2}Rh(C$_2$H$_4$)(PEt$_3$) (9c*): ^{1}H NMR (C$_6$D$_6$) δ 5.84, 5.18 (s, 2:1 ratio, 3 CH$_{pz}$), 2.50, 2.42, 2.24, 2.07 (s, 2:2:1:1 ratio, 6 Me$_{pz}$), 2.32, 2.22 (m, 2 H each, C$_2$H$_4$), 1.24 (m, 6 H, 3 PC*H*$_2$CH$_3$), 0.52 (m, 9 H, 3 PCH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 151−142(C$_{qpz}$), 107.3, 105.8 (1:2 ratio, CH$_{pz}$), 16.4 (d, PCH$_2$, ^1J(C,P) = 7 Hz), 16.0, 13.2, 12.6, 11.9 (2:1:2:1 ratio, Me$_{pz}$), 14.7 (d, C$_2$H$_4$, ^1J(C,Rh) = 17, ^2J(C,P) = 6 Hz); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 28.8 (d, ^1J(P,Rh) = 151 Hz). Anal. Calcd for $C_{23}H_{41}B N_6PRh$: C, 50.5; H, 7.5; N, 15.4. Found: C, 50.3; H, 7.4; N, 15.5.

[Tp^{Me2}Rh(C$_2$H$_4$)]$_2$dmpe (9d*): ^{1}H NMR (CDCl$_3$) δ 5.76, 5.27 (s, 2:1 ratio, CH$_{pz}$), 2.37, 1.36 (br, 2 H each, C$_2$H$_4$), 2.34, 2.24, 2.07, 1.36 (s, 2:2:1:1 ratio, 6 Me$_{pz}$), 0.56 (filled in d, 6 H, PMe$_2$, J(H,P)$_{app}$ = 8.4 Hz), −0.02 (d, 2 H, PCH$_2$, J(H,P) = 3 Hz); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 150.8, 150.5, 144.1, 142.5 (2:1:2:1 ratio, C$_{qpz}$), 106.9, 105.8 (1:2 ratio, CH$_{pz}$), 22.2 (filled in d, PCH$_2$, J(C,P)$_{app}$ = 30 Hz), 16.3, 13.4, 12.7, 11.9 (2:1:2:1 ratio, Me$_{pz}$), 15.8 (dd, C$_2$H$_4$, ^1J(C,Rh) = 17, ^2J(C,P) = 3 Hz), 12.9 (filled in d, PMe, J(C,P)$_{app}$ = 32 Hz); ^{31}P{^{1}H} NMR (CDCl$_3$) AA′ part of an AA′XX′ spin system, $\delta_A = \delta_{A'}$ = 21.6 (pseudo dt, ^1J(P,Rh) = 151 Hz). Anal. Calcd for $C_{40}H_{68}B_2N_{12}P_2Rh_2$: C, 47.7; H, 6.8; N, 16.7. Found: C, 47.1; H, 6.8; N, 16.2.

Tp^{Me2}Rh(O$_2$)(PR$_3$) [R = Me (10a*), Et (10c*)]. Complex **9c*** (0.27 g, 0.5 mmol) was dissolved in Et$_2$O (15 mL), and pure O$_2$ was bubbled for 5 min. The resulting solution was stirred for 18 h, under O$_2$, at 25 °C and the volatiles pumped off in vacuo. The residue was crystallized from acetone at −20 °C to produce yellow crystals in 70% yield. The same procedure was used in the synthesis of **10a***. Data for **10a***: ^{1}H NMR (C$_6$D$_6$) δ 5.68, 5.32 (s, 2:1 ratio, 3 CH$_{pz}$), 2.86, 2.29, 2.27, 2.03 (s, 1:2:2:1 ratio, 6 Me$_{pz}$), 0.87 (d, 9 H, PMe$_3$, ^2J(H,P) = 11.2 Hz); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 9.7 (d, ^1J(P,Rh) = 131 Hz). Anal. Calcd for $C_{18}H_{31}BN_6O_2PRh$: C, 42.5; H, 6.1; N, 16.5. Found C, 42.1; H, 6.3; N, 15.7. Data for **10c***: ^{1}H NMR (C$_6$D$_6$) δ 5.68, 5.30 (s, 2:1 ratio, 3 CH$_{pz}$), 2.87, 2.35, 2.28, 2.02 (s, 1:2:2:1 ratio, 6 Me$_{pz}$), 1.53 (m, 6 H, 3 PC*H*$_2$CH$_3$), 0.68 (m, 9 H, 3 PCH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 153.6, 153.2, 146.9, 141.9 (s, d, s, s, 2:1:2:1 ratio, C$_{qpz}$, J(C,P) = 5 Hz), 107.2, 106.5 (s, d, 2:1 ratio, CH$_{pz}$, J(C,P) = 4 Hz), 16.6, 12.5, 12.3, 10.9 (2:2:1:1 ratio, Me$_{pz}$), 14.6 (d, PCH$_2$, ^1J(C,P) = 28 Hz), 6.55 (d, PCH$_2$*C*H$_3$, ^2J(C,P) = 5 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 24.5 (d, ^1J(P,Rh) = 130 Hz). Anal. Calcd for $C_{21}H_{37}BN_6O_2PRh$: C, 45.9; H, 6.7; N, 15.3. Found: C, 45.8; H, 6.5; N, 15.3.

Tp′RhH$_2$(PR$_3$) [Tp′ = Tp, PR$_3$ = PMe$_2$Ph (11b), PEt$_3$ (11c); Tp′ = Tp^{Me2}, PR$_3$ = PMe$_3$ (11a*), PMe$_2$Ph (11b*), PEt$_3$ (11c*)]. All these complexes were obtained by reaction of the corresponding ethylene-Rh(I) derivative with H$_2$ (THF, 3 atm, 12−48 h). Only one member of this series has been subjected to microanalysis. Data for **11b**: ^{1}H NMR (C$_6$D$_6$) δ 7.9−5.7 (m, 14 H, C$_6$H$_5$ and CH$_{pz}$), 1.46 (dd, 6 H, PMe$_2$, ^2J(H,P) = 9.7, ^3J(H,Rh) = 1 Hz), −16.41 (dd, 2 H, 2RhH, ^1J(H,Rh) = 21, ^2J(H,P) = 33 Hz); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 146−104 (C$_6$H$_5$ and CH$_{pz}$), 20.3 (d, PMe$_2$, ^1J(C,P) = 34 Hz); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 21.7 (d, ^1J(P,Rh) = 140 Hz); IR (Nujol) 2041 (RhH) cm^{-1}. Data for **11c**: ^{1}H NMR (C$_6$D$_6$) δ 7.80, 7.61, 7.52, 7.43, 6.00, 5.77 (m, 1:2:2:1:2:1 ratio, 9 CH$_{pz}$), 1.42 (m, 6 H, 3 PC*H*$_2$CH3$_,$), 0.83 (m, 9 H, 3 PCH$_2$C*H*$_3$), −16.91 (dd, 2 H, 2 RhH, ^1J(H,Rh) = 21, ^2J(H,P) = 31 Hz); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ = 145.1, 142.8, 134.3, 133.3, 104.6, 104.5 (1:2:2:1:1:2 ratio, CH$_{pz}$), 20.9 (d, PCH$_2$, ^1J(C,P) = 30 Hz), 7.6 (PCH$_2$*C*H$_3$); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 46.8 (d, ^1J(P,Rh) = 141 Hz); IR (Nujol) 2080, 2058 (RhH) cm^{-1}. Data for **11a***: ^{1}H NMR (C$_6$D$_6$) δ 5.77, 5.52 (s, 2:1 ratio, 3 CH$_{pz}$), 2.44, 2.33, 2.27, 2.16 (s, 1:2:2:1 ratio, 6 Me$_{pz}$), 1.21 (d, 9 H, PMe$_3$, ^2J(H,P) = 9.2 Hz), −17.09 (dd, 2 H, 2 RhH, ^1J(H,Rh) = 21, ^2J(H,P) = 36 Hz); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 149.4, 149.0, 143.8, 142.4 (2:1:2:1 ratio, C$_{qpz}$), 105.6, 104.7 (2:1 ratio, CH$_{pz}$), 22.8 (d, PMe$_3$, ^1J(C,P) = 32 Hz), 16.5, 16.5, 12.7, 12.4 (2:1:2:1 ratio, Me$_{pz}$); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 1.88 (d, ^1J(P,Rh) = 138 Hz); IR (Nujol) 2052, 2028 (RhH) cm^{-1}. Data for **11b***: ^{1}H NMR (C$_6$D$_6$) δ 7.6−6.8 (m, 5 H, C$_6$H$_5$), 5.69, 5.60 (s, 2:1 ratio, 3 CH$_{pz}$), 2.51, 2.34, 2.20, 1.96 (s, 1:2:1:2 ratio, 6 Me$_{pz}$), 1.66 (dd, 6 H, PMe$_2$, ^2J(H,P) = 8.8, ^3J(H,Rh) = 1.2 Hz), −16.94 (dd, 2 H, 2 RhH, ^1J(H,Rh) = 20, ^2J(H,P) = 36 Hz); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 149.9, 149.2, 143.6, 142.4 (2:1:2:1 ratio, C$_{qpz}$), 139.2 (d, PC$_{ipso}$, ^1J(C,P) = 36 Hz), 135−129 (5 CH$_{ph}$), 105.6, 104.8 (2:1 ratio, CH$_{pz}$), 24.7 (d, PMe$_2$, ^1J(C,P) = 35 Hz), 16.8, 16.0, 12.8, 12.4 (1:2:2:1 ratio, Me$_{pz}$). ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 12.6 (d, ^1J(P,Rh) = 143 Hz); IR (Nujol) 2085, 2051 (RhH) cm^{-1}. Anal. Calcd for $C_{23}H_{22}BN_6PRh$: C, 51.1; H, 6.5; N, 15.6. Found: C, 51.1; H, 6.6; N, 15.1. Data for **11c***: ^{1}H NMR (C$_6$D$_6$) δ 5.76, 5.52 (s, 2:1 ratio, 3 CH$_{pz}$), 2.47, 2.37, 2.24, 2.15 (s, 1:2:1:2 ratio, 6 Me$_{pz}$), 1.55 (m, 6 H, 3 PC*H*$_2$CH$_3$), 0.84 (m, 9 H, 3 PCH$_2$C*H*$_3$), −17.37 (dd, 2 H, 2 RhH, ^1J(H,Rh) = 21, ^2J(H,P) = 33 Hz); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 149.6, 148.9, 144.0, 142.4 (2:1:2:1 ratio, C$_{qpz}$), 105.7, 104.5 (2:1 ratio, CH$_{pz}$), 21.3 (d, PCH$_2$, ^1J(C,P) = 29 Hz), 16.5, 16.2, 12.8, 12.5 (1:2:2:1 ratio, Me$_{pz}$), 7.8 (PCH$_2$*C*H$_3$); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 41.2 (d, ^1J(P,Rh) = 140 Hz); IR (Nujol) 2027 (RhH) cm^{-1}.

Crystal Structure Determinations of 7a, 9c*, and 10c*. The fundamental crystal data are given in Tables 2 and 4. Single crystals of the complexes **9c*** and **10c*** were coated with an epoxy resin and mounted in a CCD detector diffractometer. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Rh and P were taken ref 56. The structure was solved by direct and Fourier methods. Refinement was on F^2 for all reflections. Weighted R factors (R_w) and

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(56) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4, pp 72−98.

all goodnesses of fits are based on F^2; conventional R factors (R) are based on F, with F set to zero for negative F^2. The observed criterion of $F^2 > 2\sigma(F^2)$ is used only for calculating the R factor and is of no relevance to the choice of reflections for refinement. R factors based on F^2 are statistically about twice as large as those based on F, and R factors based on all data will be even larger. All esds are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles, and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. Hydrogen atoms were included as fixed contributions at their calculated positions.

For **7a**, a yellow crystal of prismatic shape was coated with an epoxy resin and mounted in a κ diffractometer. The cell dimensions were refined by least-squares fitting the θ values of the 25 reflections with a 2θ range of 18−28°. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Rh were taken from ref 56. The structure was solved by Patterson and Fourier methods. An empirical absorption correction[57,58] was applied at the end of the isotropic refinement. A final mixed refinement was undertaken. Hydrogen atoms were included with fixed isotropic contributions at their calculated positions. To prevent bias on ΔF vs F_0 or $\sin\,\theta/\lambda$, the last steps of the refinement were calculated with weights $w = w_1 w_2$, where $w_1 = 1/(a + b|F_0|)^2$ and $w_2 = 1/(c + d(\sin\,\theta/\lambda))$, with the following coefficients: for $|F_0| < 95$, $a = 17.83$, $b = -0.15$; for $1060 > |F_0| > 95$, $a = 0.44$, $b = 0.03$. Final difference synthesis showed some rest of electron density. The highest peak ($1.93e^-$) is at the special position (3/4.1/4.0). That means that if one is looking at the Et_2O molecule, the spatial group should not be $C2/c$ but Cc. The low proportion of solvent in the unit cell makes it imposible to create a disorder model. Most of the calculations were carried out with the *X-Ray80 System*.[59]

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determinations of complexes **9c*** and **10c*** and tables of atomic coordinates, anisotropic thermal parameters, and bonds lengths and angles for complex **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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