

Dinuclear Rhodium Complexes Containing a Linear C₂RhC₄RhC₂ Chain¹

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Received December 9, 1997

The reaction of *trans*-[RhCl(=C=CHPh)(PiPr₃)₂] (**1**) and *trans*-[RhCl(=C=CMe₂)(PiPr₃)₂] (**3**) with 50% aqueous NaOH, in the presence of TEBA, afforded the hydroxorhodium complexes *trans*-[Rh(OH)(=C=CRR')(PiPr₃)₂] (**2**, **4**) in good to excellent yield. Compound **2** (R = H, R' = Ph) reacted with D₂O to give *trans*-[Rh(OD)(=C=CHPh)(PiPr₃)₂] (**2-d**) and with Brønsted acids HX (X = CF₃CO₂, OPh, C≡CPh) to yield the corresponding derivatives *trans*-[Rh(X)(=C=CHPh)(PiPr₃)₂] (**5–7**), respectively. Treatment of **2** and **4** with Ph₃SnC≡CC≡CSnPh₃ also led to the displacement of the hydroxo ligand and to the formation of the dinuclear complexes *trans,trans*-[{Rh(=C=CRR')(PiPr₃)₂]₂(μ-C₄)] (**8**, **9**) in 75–80% yield. The X-ray crystal structure analysis of **9** revealed the presence of a linear 10-atom C=C–RhC≡CC≡CRh=C=C chain with the midpoint of the central C–C bond as a crystallographic center of symmetry.

Introduction

In the search for highly reactive metallacumulenes of the general composition *trans*-[Rh(X)(=C=C=CRPh)(PiPr₃)₂], we recently reported that the hydroxorhodium(I) derivatives (X = OH) react with acetic acid and phenol at room temperature to give the corresponding acetato (X = O₂CMe) and phenolato (X = OPh) metal compounds almost quantitatively.² Moreover, these new allenylidenerhodium(I) complexes in the presence of CO undergo a migratory insertion of the C=C=CRPh unit into the Rh–OR' bond to generate γ-functionalized alkynyl ligands.

This result together with the similar course of the intramolecular C–C coupling reactions of vinylidene and allenylidene complexes *trans*-[Rh(R)(=C=CHR')(PiPr₃)₂]³ and *trans*-[Rh(R)(=C=C=CR'Ph)(PiPr₃)₂]⁴ enforced our interest to prepare also the hydroxovinylidenerhodium derivatives and to use them as starting materials for other vinylidenerhodium compounds. In this article we describe the synthesis of *trans*-[Rh(OH)(=C=CRR')(PiPr₃)₂] and illustrate that the hydroxo ligand of these compounds can be replaced by not only trifluoroacetate, phenolate, and phenylacetylide but also by the C₄²⁻ dianion. Despite the great achievements made by Sonogashira,⁵ Gladysz,⁶ Lapinte,⁷ and others^{8,9} in obtaining transition-metal complexes with bridging C₄ (and more general C_n) ligands, there is to the best of our knowledge no dinuclear compound known in which

vinylidene units are disposed *trans* to a naked C₄ (or C_n) bridge.

Results and Discussion

Treatment of the chloro compound **1**¹⁰ in benzene with 50% aqueous NaOH in the presence of [PhCH₂NEt₃]Cl (TEBA) gave the hydroxo complex **2** in about 60% yield (Scheme 1). It was possible to check the completion of the reaction by measuring the ³¹P NMR spectrum of the organic phase, in which the doublet resonance of **1** appears at 43.1 ppm and that of **2** is slightly shifted downfield at 44.1 ppm. The procedure for the preparation of **2** is somewhat similar to that for the synthesis of both [Rh(μ-OH)(PPh₃)₂]₂¹¹ and [Rh(μ-OH)(PiPr₃)₂]₂,¹² which also proceeds in benzene/water under biphasic

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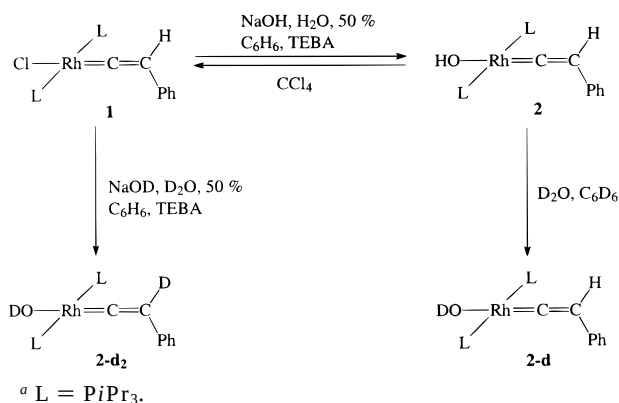
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Scheme 1^a

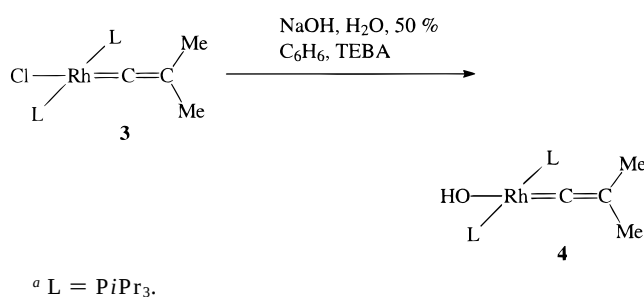
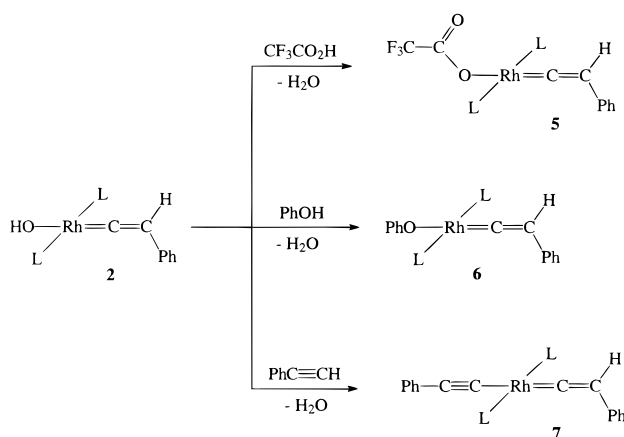
conditions. It is important to note, however, that the preparation of the hydroxovinylidene complex fails in the absence of TEBA as a phase-transfer reagent.

Compound **2** is a red-violet, very air-sensitive solid which is soluble in most organic solvents, including pentane, and decomposes at 40 °C. Typical spectroscopic features of **2** are the weak OH stretching band at 3650 cm^{-1} in the IR, the doublet-of-triplets resonance for the $=\text{CHPh}$ proton at 1.84 ppm in the ^1H NMR, and the low-field signals (both doublet-of-triplets) for the α -C and β -C vinylidene carbon atoms at 298.3 and 113.8 ppm in the ^{13}C NMR spectrum.

If the starting material **1** was treated instead of 50% aqueous NaOH with a 50% solution of NaOD in D_2O , the β -position of the vinylidene unit was 94% deuterated to give **2-d₂** as the main product. In the ^1H NMR spectrum of **2-d₂** the resonance corresponding to the $=\text{CHPh}$ proton had nearly disappeared and a broad singlet is observed in the ^2H NMR spectrum at 1.86 ppm. Compound **2** reacted with D_2O to yield instead of **2-d₂** the monodeuterated derivative **2-d**, indicating that the vinylidene proton is not acidic enough to undergo a H/D exchange in the absence of base.

The dimethylvinylidene complex **3**, which has recently been prepared in an unconventional way by using an olefin instead of an alkyne as the precursor for the C₂ ligand,¹³ also reacted with 50% aqueous NaOH in the presence of TEBA under biphasic conditions to give the Rh–OH derivative **4** in practically quantitative yield. The red-violet solid, which is quite air-sensitive, is thermally more stable than **2** and melts at 93 °C with decomposition. The IR and NMR spectroscopic data for **4** are in full agreement with the structural proposal shown in Scheme 2 and thus deserve no further comment.

Like the related allenylidenerhodium(I) derivatives *trans*- $[\text{Rh}(\text{OH})(=\text{C}=\text{C}=\text{CRPh})(\text{PiPr}_3)_2]$,² compound **2** afforded on treatment with equimolar amounts of $\text{CF}_3\text{CO}_2\text{H}$ and PhOH the trifluoroacetato and phenolato complexes **5** and **6** almost quantitatively (Scheme 3). An alternative route to **5** has already been described using $[\text{Rh}(\eta^2\text{-O}_2\text{CCF}_3)(\text{PiPr}_3)_2]$ and $\text{PhC}\equiv\text{CH}$ as the starting materials.¹⁴ The phenolato complex is a red-

Scheme 2^aScheme 3^a

violet solid which can be handled in air for a short period of time and has been characterized by both elemental analysis and spectroscopic means.

Phenylacetylene behaves similarly to phenol and upon addition to a solution of **2** in pentane at low temperature yields the alkynylvinylidenerhodium(I) compound **7** (Scheme 3). This was originally prepared from either **1**^{3a} or $[\text{Rh}(\eta^3\text{-CH}_2\text{Ph})(\text{PiPr}_3)_2]$ ¹⁵ and subsequently used for the preparation of the isomeric π -butadienyl complex $[\text{Rh}(2,3,4\text{-}\eta)\text{-PhCHCHC}=\text{CHPh})(\text{PiPr}_3)_2]$.^{3a}

Both the hydroxorhodium(I) derivatives **2** and **4**, on treatment with 0.5 molar equiv of $\text{Ph}_3\text{SnC}\equiv\text{CC}=\text{CSnPh}_3$, afforded the complexes **8** and **9** (Scheme 4) in 75–80% yield. Dinuclear rhodium compounds containing a “naked” C₄ bridge are not without precedent and have been prepared in our laboratory either from buta-1,4-diyne¹⁶ or from $\text{Me}_3\text{SiC}\equiv\text{CC}=\text{CSiMe}_3$ ¹² as precursors of the C₄ unit. The formation of Ph_3SnOH as a secondary product in the reaction of **2** and **4** with the bis-stannylated diyne has been substantiated by comparison of the IR and NMR data with those of an authentic sample.¹⁷ Compounds **8** and **9** are green, air-sensitive crystalline materials which in the solid state can be stored at 0 °C but slowly decompose in solution. The correct composition of **8** and **9** has been proved by elemental analysis as well as mass spectrometry.

Since it is possible that compounds of the general composition *trans*- $[\text{Rh}(\text{C}\equiv\text{CR})(=\text{C}=\text{CHR}')(\text{PiPr}_3)_2]$ are in equilibrium with the corresponding isomers *trans*-

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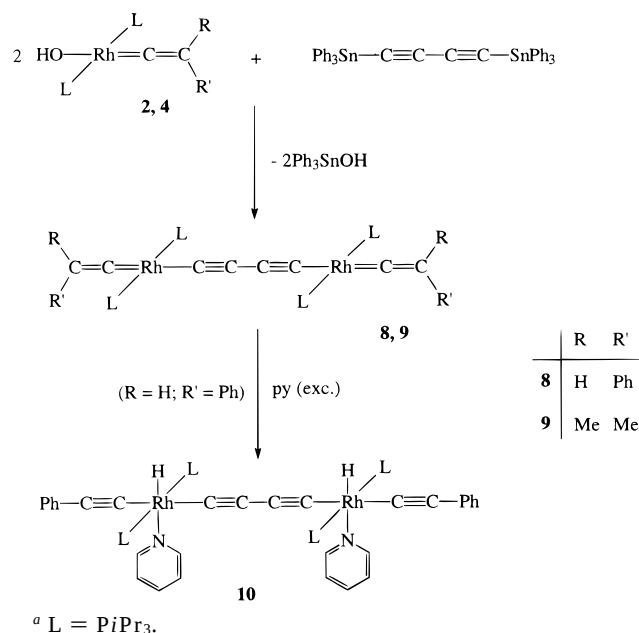
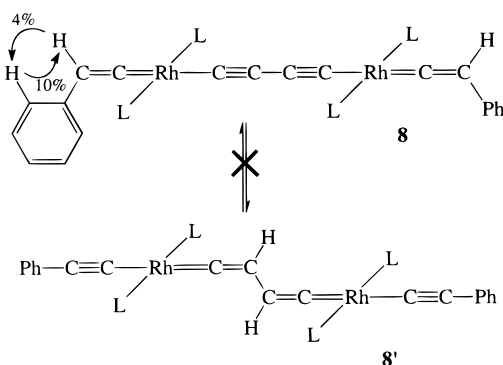
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Scheme 4^aScheme 5^a

$[\text{Rh}(\text{C}\equiv\text{CR}')(\text{C}=\text{CHR})(\text{P}i\text{Pr}_3)_2]$,¹⁸ we checked by an NOE experiment that the product of the reaction of **2** with $\text{Ph}_3\text{SnC}\equiv\text{CC}\equiv\text{CSnPh}_3$ is **8** and not the isomeric species $[\{\text{Rh}(\text{C}\equiv\text{CPh})(\text{P}i\text{Pr}_3)_2\}_2(\mu\text{-C}\equiv\text{CHCH}=\text{C})]$ (**8'**). The results of the NOE experiment (Scheme 5) confirmed the vicinity of the phenyl group and the vinylidene hydrogen in the molecule and thus excluded isomer **8'**.

The result of the X-ray crystal structure analysis of **9** is shown in Figure 1. The two $\text{Rh}(\text{C}=\text{CMe}_2)(\text{P}i\text{Pr}_3)_2$ fragments are bridged by an almost perfectly linear C_4 unit, and since the $\text{Rh}=\text{C}=\text{C}$ moieties such as the $\text{C}=\text{C}=\text{C}$ backbone of allenes are also linear, the skeleton of **9** represents a linear 10-atom $\text{C}_2\text{RhC}_4\text{RhC}_2$ chain. The midpoint of the $\text{C}-\text{C}$ single bond of the C_4 bridge lies on a crystallographic center of symmetry, and therefore, only four halves of the molecule are found in the unit cell. As a consequence, both P_2RhC_2 planes lie parallel in the crystal and not perpendicular as one would expect due to the bulkiness of the phosphine ligands. Despite the steric demand of the methyl groups at C_4 , the $\text{P}1-\text{Rh}-\text{P}2$ axis is only slightly bent, the corresponding bond angle being $177.10(8)^\circ$. The distances $\text{Rh}-\text{C}3$ and $\text{C}3-$

$\text{C}4$ (see Table 1) are comparable to those of the mononuclear complex $\text{trans-}[\text{RhCl}(\text{C}=\text{CHMe})(\text{P}i\text{Pr}_3)_2]$ (1.775(6) and 1.32(1) Å),¹⁹ which illustrates that the C_4 unit like chloride is predominantly a σ -donor ligand. With regard to the bonding pattern in **9**, it should be mentioned that the $\text{Rh}-\text{C}3$ bond length is almost identical with the $\text{Rh}-\text{CO}$ distance in $[\{\text{Rh}(\text{CO})(\text{P}i\text{Pr}_3)_2\}_2(\mu\text{-C}_4)]$ (1.832(4) Å),¹² indicating that in agreement with theoretical calculations²⁰ the π -acceptor character of CO and vinylidenes is quite similar.

Since it has been shown by both experimental^{16,21} and theoretical studies²² that vinylidenerhodium complexes $\text{trans-}[\text{RhX}(\text{C}=\text{CHR})(\text{P}i\text{Pr}_3)_2]$ could rearrange, depending on the anionic ligand X and the substituent R, to the isomeric alkynylhydrido isomers $[\text{RhH}(\text{C}\equiv\text{CR})\text{X}(\text{P}i\text{Pr}_3)_2]$ and vice versa, the reaction of **8** toward pyridine was investigated. From previous work it was known²¹ that the sometimes very labile, five-coordinate alkynylhydridorhodium(III) species can be trapped by pyridine to give the more stable six-coordinate compounds $[\text{RhH}(\text{C}\equiv\text{CR})\text{X}(\text{py})(\text{P}i\text{Pr}_3)_2]$. The dinuclear complex reacted with pyridine very smoothly indeed to afford the 1:2 adduct **10** (Scheme 4) as a beige solid in 61% yield. The most characteristic spectroscopic features of **10** are the intense $\text{C}\equiv\text{C}$ stretching frequency at 2086 cm^{-1} in the IR, the high-field signal for the metal-bonded hydrogens at -17.94 ppm in the ^1H NMR, and the single resonance for the ^{31}P nuclei at 42.1 ppm in the ^{31}P NMR spectrum, the latter being split into a doublet due to $\text{Rh}-\text{P}$ coupling. In solution, the bis-(pyridine) adduct is rather labile and slowly decomposes to give $\text{trans-}[\text{Rh}(\text{C}\equiv\text{CPh})(\text{py})(\text{P}i\text{Pr}_3)_2]$.^{21a}

In summary, we have shown in this work that compounds such as **8** and **9** possessing a linear $\text{C}_2\text{RhC}_4\text{-RhC}_2$ chain are accessible, provided that instead of the well-known chlororhodium(I) derivatives **1** and **3** the corresponding hydroxo complexes **2** and **4** are used as starting materials. In contrast to the numerous compounds of the general composition $[\text{M}(\text{OR})_n\text{L}_m]$, where M is a d^0 , d^1 , or d^2 metal center, related species with electron-rich (d^6-d^{10}) transition metals are still relatively rare.^{23,24} We hope that the propensity of the allenylidene complexes $\text{trans-}[\text{Rh}(\text{OH})(\text{C}=\text{C}=\text{CRPh})(\text{P}i\text{Pr}_3)_2]$ to react with acidic substrates by forming new rhodium-element bonds^{2,18,25} as well as the first results on the reactivity of **2** and **4** reported here will spur further activities in this field.

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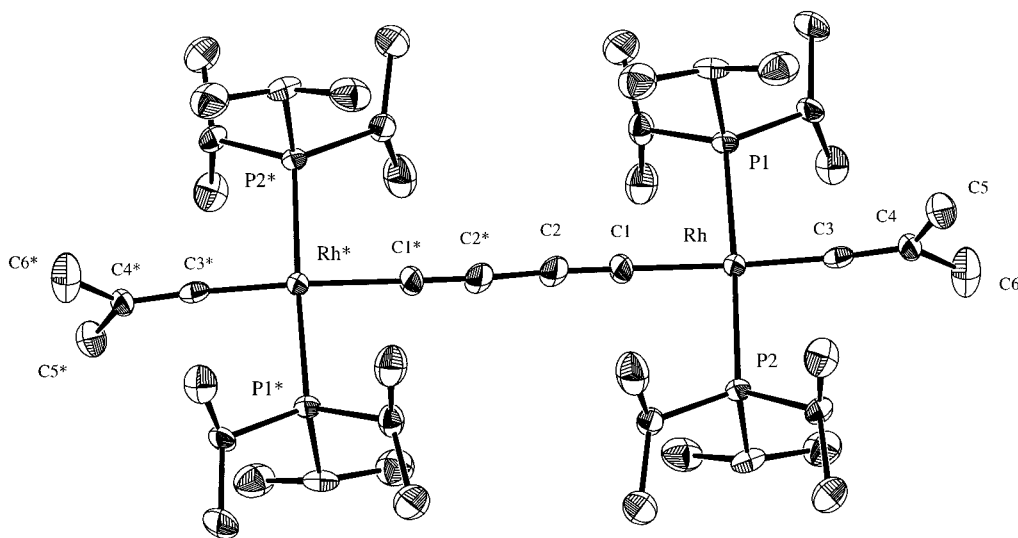
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**Figure 1.** Molecular structure (ORTEP plot) of compound **9**.**Table 1.** Selected Bond Distances and Angles with Esd's for Compound **9**^a

Bond Distances (Å)			
Rh–C3	1.857(7)	C2–C2*	1.38(1)
Rh–C1	2.023(7)	C3–C4	1.305(9)
Rh–P1	2.324(2)	C4–C6	1.51(1)
Rh–P2	2.333(2)	C4–C5	1.51(1)
C1–C2	1.221(9)		
Bond Angles (deg)			
C3–Rh–C1	172.1(3)	C2–C1–Rh	173.1(7)
C3–Rh–P1	91.5(2)	C1–C2–C2*	176(1)
C1–Rh–P1	88.7(2)	C4–C3–Rh	174.9(6)
C3–Rh–P2	91.2(2)	C3–C4–C6	121.6(7)
C1–Rh–P2	88.7(2)	C3–C4–C5	121.9(7)
P1–Rh–P2	177.10(8)	C6–C4–C5	116.5(6)

^a The midpoint of the bond C2–C2* is a center of symmetry; therefore, the corresponding bond distances Rh–C1/Rh*–C1* etc. and bond angles P1–Rh–P2/P1*–Rh*–P2* etc. are identical.

Experimental Section

All reactions were carried out under an inert atmosphere of argon by use of Schlenk techniques. The starting materials **1**,¹⁰ **3**,¹³ and $Ph_3SnC\equiv CC\equiv CSnPh_3$ ²⁶ were prepared as described in the literature. NMR spectra were recorded at room temperature on Bruker AC 200 and Bruker AMX 400 instruments (abbreviation: dvt = doublet of virtual triplets) and IR spectra on Perkin-Elmer 1420 and Bruker IFS 25 spectrometers. Melting points were determined by DTA. Electron impact mass spectra were obtained on Finnigan MAT 90 and MAT 8200 instruments; electrospray ionization mass spectra were obtained on a Finnigan MAT TSQ 7000 instrument operating in the positive-ion mode (m/z = relative abundance).

Preparation of *trans*-[Rh(OH)(=C=CHPh)(PiPr₃)₂] (2**).** A solution of **1** (198 mg, 0.35 mmol) in 10 mL of benzene was treated with 3 mL of 50% aqueous NaOH (saturated with argon) and TEBA (10 mg). The reaction mixture was vigorously stirred for 90 min at room temperature, and the completion of the reaction was checked by measuring the ³¹P NMR spectrum of the organic phase. The organic phase was then transferred to another Schlenk tube, and the aqueous phase was extracted with 5 mL of benzene. The combined benzene solutions were brought to dryness in vacuo, and the residue was extracted with 10 mL of pentane. The extract was concentrated to ca. 2 mL in vacuo and then stored for 4

days at –60 °C. Red-violet crystals precipitated, which were filtered, washed twice with 2 mL portions of pentane (–40 °C), and dried: yield 114 mg (60%); mp 40 °C dec; IR (C₆H₆) ν -(OH) 3650, ν (C=C), 1641, 1616, 1593, 1570 cm^{–1}; ¹H NMR (C₆D₆, 400 MHz) δ 7.29 (d, J (HH) = 7.2 Hz, 2H, *ortho* H of C₆H₅), 7.13 (t, J (HH) = 8.0 Hz, 2H, *meta* H of C₆H₅), 6.87 (t, J (HH) = 7.2 Hz, 1H, *para* H of C₆H₅), 2.50 (m, 6H, PCHCH₃), 1.84 (dt, J (RhH) = 1.6 Hz, J (PH) = 3.2 Hz, 1H, Rh=C=CH), 1.29 (dvt, N = 13.2 Hz, J (HH) = 6.8 Hz, 36H, PCHCH₃), 0.64 (br t, J (PH) = 5.2 Hz, 1H, OH); ¹³C{¹H} NMR (C₆D₆, 100.6 MHz) δ 298.3 (dt, J (RhC) = 47.2 Hz, J (PC) = 17.1 Hz, Rh=C), 128.4, 124.9, 124.1 (all s, CH of C₆H₅, the signal of *ipso* C overlaps with the signal of the solvent), 113.8 (dt, J (RhC) = 13.1 Hz, J (PC) = 6.0 Hz, Rh=C=C), 23.2 (vt, N = 18.9 Hz, PCHCH₃), 20.2 (s, PCHCH₃); ³¹P{¹H} NMR (C₆D₆, 162.0 MHz) δ 44.1 (d, J (RhP) = 146.1 Hz). Anal. Calcd for C₂₆H₄₉OP₂Rh: C, 57.56; H, 9.10. Found: C, 57.86; H, 9.13. EI MS (70 eV): m/z 542 (0.3, M⁺), 440 (1, M⁺ – PhC₂H), 422 (0.4, M⁺ – PhC₂H – H₂O), 160 (59, PiPr₃⁺), 118 (87, PiPr₂H⁺), 76 (100, PiPrH₂⁺).

Reaction of **2 with CCl₄.** A solution of **2** (15 mg, 0.03 mmol) in C₆D₆ (0.6 mL) was treated with CCl₄ (4 μ L, 0.04 mmol) at room temperature. The reaction mixture was stirred at room temperature for 1.5 h. The ¹H and ³¹P NMR spectra of the blue-green solution showed a quantitative conversion of **2** into **1**.

Preparation of *trans*-[Rh(OD)(=C=CHPh)(PiPr₃)₂] (2-d**).** A solution of **2** (10 mg, 0.02 mmol) in 0.6 mL of C₆D₆ was treated with D₂O (0.4 mL) for 15 min at room temperature. After removal of the aqueous phase, ¹H and ³¹P NMR spectra were measured. A single compound was observed, whose NMR and IR data were very similar to those of **2**. The most significant differences between the spectra of **2** and **2-d** were the absence of the triplet of the OH proton in the ¹H NMR spectrum and the absence of the ν (OH) band in the IR spectrum of the C₆D₆ solution. IR: ν (C=C) 1641, 1616, 1593 cm^{–1}. ¹H NMR (C₆D₆, 200 MHz): δ 7.27 (d, J (HH) = 7.3 Hz, 2H, *ortho* H of C₆H₅), 7.13 (t, J (HH) = 7.3 Hz, 2H, *meta* H of C₆H₅), 6.87 (t, J (HH) = 7.3 Hz, 1H, *para* H of C₆H₅), 2.48 (m, 6H, PCHCH₃), 1.80 (dt, J (RhH) = 1.6 Hz, J (PH) = 3.1 Hz, 1H, Rh=C=CH), 1.27 (dvt, N = 13.4 Hz, J (HH) = 6.9 Hz, 36H, PCHCH₃). ³¹P{¹H} NMR (C₆D₆, 81.0 MHz): δ 44.6 (d, J (RhP) = 146.9 Hz).

Preparation of *trans*-[Rh(OD)(=C=CDPh)(PiPr₃)₂] (2-d₂**).** This was prepared analogously as described for **2**, using a solution of **1** (123 mg, 0.22 mmol) in 7 mL of C₆H₆, 1.5 mL of a 50% solution of NaOD in D₂O (saturated with argon), and TEBA (6 mg) as starting materials: red-violet solid; yield 33 mg (28%). By integration of the signals in the ¹H NMR

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spectrum (in C_6D_6), a D/H ratio of 17/1 (94% D) at the β -carbon position of the vinylidene ligand was determined. A triplet was observed at δ 0.68, indicating that a small amount of *trans*-[Rh(OH)(C $\equiv$ CDPh)(PiPr $_3$) $_2$] had also been formed by D/H exchange with solvent water; this triplet disappeared upon treatment with D_2O . Characteristic spectroscopic data for **2-d $_2$** : IR (C_6H_6) $\nu(C\equiv C)$ 1614, 1593, 1570 cm^{-1} ; 1H NMR (C_6D_6 , 200 MHz) δ 7.26 (d, $J(HH)$ = 6.9 Hz, 2H, *ortho* H of C_6H_5), 7.12 (t, $J(HH)$ = 7.7 Hz, 2H, *meta* H of C_6H_5), 6.87 (t, $J(HH)$ = 7.1 Hz, 1H, *para* H of C_6H_5), 2.48 (m, 6H, PCHCH $_3$), 1.26 (dvt, N = 13.5 Hz, $J(HH)$ = 6.9 Hz, 36H, PCHCH $_3$); 2H NMR (C_6H_6 , 61.4 MHz, $\delta[C_6D_6]$ 7.15 ppm was used as reference) δ 1.86 (br s, Rh=C=CDPh); $^{13}C\{^1H\}$ NMR (C_6D_6 , 100.6 MHz) δ 128.4, 124.9, 124.2 (all s, CH of C_6H_5 , the signal of *ipso* C overlaps with the signal of the solvent), 23.2 (vt, N = 18.9 Hz, PCHCH $_3$), 20.2 (s, PCHCH $_3$), the signals of the α and β vinylidene carbons are not observed; $^{31}P\{^1H\}$ NMR (C_6D_6 , 81.0 MHz) δ 44.4 (d, $J(RhP)$ = 145.0 Hz).

Preparation of *trans*-[Rh(OH)(C $\equiv$ CMe $_2$)(PiPr $_3$) $_2$] (4). A solution of **3** (118 mg, 0.23 mmol) in 5 mL of benzene was treated with 1.5 mL of aqueous NaOH (saturated with argon) and TEBA (5 mg). The reaction mixture was vigorously stirred for 2.5 h at room temperature, and the completion of the reaction was checked by measuring the ^{31}P NMR spectrum of the organic phase. The aqueous phase was removed, and the organic phase was washed four times with 7 mL portions of degassed water. The benzene solution was brought to dryness in vacuo. The residue was dissolved in 5 mL of benzene, and after the solvent was removed a red-violet solid was isolated. It was washed twice with 2 mL portions of pentane ($-40^\circ C$): yield 109 mg (96%); mp $93^\circ C$ dec; IR (C_6H_6) $\nu(C\equiv C)$ 1675 cm^{-1} ; 1H NMR (C_6D_6 , 200 MHz) δ 2.46 (m, 6H, PCHCH $_3$), 1.79 (t, $J(PH)$ = 2.0 Hz, 6H, Rh=C=C(CH $_3$) $_2$), 1.33 (dvt, N = 13.1 Hz, $J(HH)$ = 6.9 Hz, 36H, PCHCH $_3$), 0.63 (br t, 1H, OH); $^{13}C\{^1H\}$ NMR (C_6D_6 , 50.3 MHz) δ 296.6 (dt, $J(RhC)$ = 45.4 Hz, $J(PC)$ = 17.5 Hz, Rh=C), 107.1 (dt, $J(RhC)$ = 12.6 Hz, $J(PC)$ = 5.8 Hz, Rh=C=C), 22.9 (vt, N = 17.9 Hz, PCHCH $_3$), 20.2 (s, PCHCH $_3$), 7.5 (s, Rh=C=C(CH $_3$) $_2$); $^{31}P\{^1H\}$ NMR (C_6D_6 , 81.0 MHz) δ 45.0 (d, $J(RhP)$ = 148.2 Hz). Anal. Calcd for $C_{22}H_{49}OP_2Rh$: C, 53.44; H, 9.99. Found: C, 53.03; H, 9.75.

Preparation of *trans*-[Rh(η^1 -O $_2$ CCF $_3$)(C $\equiv$ CHPh)(PiPr $_3$) $_2$] (5). A solution of **2** (29 mg, 0.05 mmol) in 1.5 mL of C_6D_6 was treated with an equimolar amount of CF $_3$ CO $_2$ H and stirred for 5 min at room temperature. According to the 1H and $^{31}P\{^1H\}$ NMR spectra, a quantitative conversion of **2** to **5** occurred. The solvent was removed in vacuo; the green-blue residue was washed twice with 1 mL portions of pentane ($-40^\circ C$) and dried in vacuo: yield 30 mg (88%). The NMR data of the compound were identical with those of **5** reported in the literature.¹⁴

Preparation of *trans*-[Rh(OPh)(C $\equiv$ CHPh)(PiPr $_3$) $_2$] (6). A solution of **2** (119 mg, 0.22 mmol) in 5 mL of pentane was treated with phenol (17 mg, 0.18 mmol) at $-78^\circ C$. The reaction mixture was slowly warmed to room temperature, stirred for 1 h, and brought to dryness in vacuo. The residue was dissolved in 2 mL of acetone and the solution stored for 4 days at $-20^\circ C$. Red-violet crystals precipitated, which were washed three times with 2 mL portions of acetone ($-20^\circ C$) and dried in vacuo: yield 90 mg (67%); mp $85^\circ C$ dec; IR (C_6H_6) $\nu(C\equiv C)$ 1645, 1625, 1575 cm^{-1} ; 1H NMR (C_6D_6 , 200 MHz) δ 7.32–7.09 (m, 6H, *ortho* and *meta* H of C_6H_5 + *meta* H of C_6H_5O), 6.87 (t, $J(HH)$ = 7.3 Hz, 1H, *para* H of C_6H_5), 6.70 (t, $J(HH)$ = 7.2 Hz, 1H, *para* H of C_6H_5O), 6.67 (d, $J(HH)$ = 7.8 Hz, 2H, *ortho* H of C_6H_5O), 2.30 (m, 6H, PCHCH $_3$), 1.76 (dt, $J(RhH)$ = 1.5 Hz, $J(PH)$ = 3.3 Hz, 1H, Rh=C=CH), 1.22 (dvt, N = 13.6 Hz, $J(HH)$ = 7.0 Hz, 36H, PCHCH $_3$); $^{13}C\{^1H\}$ NMR (C_6D_6 , 100.6 MHz) δ 298.8 (dt, $J(RhC)$ = 53.3 Hz, $J(PC)$ = 18.1 Hz, Rh=C), 168.5 (s, *ipso* C of C_6H_5O), 129.1, 128.6 (both s, CH of C_6H_5), 126.9 (s, *ipso* C of C_6H_5), 125.2, 124.8, 120.3 (all s, CH of C_6H_5O and C_6H_5), 114.0–113.7 (m, Rh=C=CH and CH of C_6H_5), 23.9 (vt, N = 17.9 Hz, PCHCH $_3$), 20.3 (s,

PCHCH $_3$); $^{31}P\{^1H\}$ NMR (C_6D_6 , 162.0 MHz) δ 42.6 (d, $J(RhP)$ = 141.5 Hz); EI MS (70 eV) m/z 618 (0.4, M^+), 525 (2, [Rh(C $_2$ -HPh)(PiPr $_3$) $_2$] $^+$), 423 (2, [Rh(PiPr $_3$) $_2$] $^+$), 160 (31, PiPr $_3^+$), 118 (64, PiPr $_2$ H $^+$), 76 (100, PiPrH $_2^+$). Anal. Calcd for $C_{32}H_{53}OP_2Rh$: C, 62.13; H, 8.64. Found: C, 61.89; H, 8.73.

Preparation of *trans*-[Rh(C $\equiv$ CPh)(C $\equiv$ CHPh)(PiPr $_3$) $_2$] (7). This compound was prepared analogously to **6**, using **2** (52 mg, 0.10 mmol) and phenylacetylene (11 μ L, 0.10 mmol) as starting materials. The green solid was washed twice with 1.5 mL portions of pentane ($-40^\circ C$) and dried: yield 58 mg (97%). The NMR data of the compound were identical with those reported for **7** in the literature.¹⁴

Preparation of *trans,trans*-[Rh(C $\equiv$ CHPh)(PiPr $_3$) $_2$] $_2$ -(μ -C $_4$) (8). A solution of **2**, prepared from **1** (180 mg, 0.32 mmol) as described above, in 15 mL of pentane was treated with Ph $_3$ SnC $\equiv$ CC $\equiv$ CSnPh $_3$ (109 mg, 0.15 mmol) at $-78^\circ C$. With continuous stirring, the mixture was slowly warmed to $0^\circ C$ and stirred at this temperature for 20 min; during that time, a change of color from red-violet to green occurred. The solution was concentrated to ca. 4 mL in vacuo, and ether was added (2 mL); then, the solution was chromatographed on Al $_2$ O $_3$ (neutral, activity grade V, column length 13 cm, column diameter 2 cm) at $0^\circ C$. With diethyl ether/pentane (1:4), a green fraction was eluted, which was brought to dryness in vacuo. A second brownish fraction was eluted with acetone, which after removal of the solvent gave a light-brown solid. This was identified by comparison of the spectroscopic data with those of an authentic sample of Ph $_3$ SnOH.¹⁷ The green fraction was brought to dryness in vacuo; the residue was washed three times with 2 mL portions of pentane ($-40^\circ C$) and dried in vacuo to afford a green solid which was pure by NMR spectroscopy: yield 132 mg (75%). Analytically pure **8** was obtained by recrystallization of the green solid from pentane: mp $84^\circ C$ dec; IR (C_6H_6) $\nu(C\equiv C)$ 1630, 1610, 1590, 1565 cm^{-1} , $\nu(C\equiv C)$ not located; 1H NMR (C_6D_6 , 200 MHz) δ 7.25 (d, $J(HH)$ = 7.4 Hz, 4H, *ortho* H of C_6H_5), 7.10 (t, $J(HH)$ = 7.4 Hz, 4H, *meta* H of C_6H_5), 6.87 (t, $J(HH)$ = 7.4 Hz, 2H, *para* H of C_6H_5), 2.68 (m, 12H, PCHCH $_3$), 1.63 (t, $J(PH)$ = 3.6 Hz, 2H, Rh=C=CH), 1.36 (dvt, N = 13.4 Hz, $J(HH)$ = 6.8 Hz, 72H, PCHCH $_3$); $^{13}C\{^1H\}$ NMR (C_6D_6 , 100.6 MHz) δ 310.0 (dt, $J(RhC)$ = 49.3 Hz, $J(PC)$ = 16.1 Hz, Rh=C), 128.5 (s, CH of C_6H_5), 126.4 (s, *ipso* C of C_6H_5), 125.7, 124.6 (both s, CH of C_6H_5), 123.1 (dt, $J(RhC)$ = 37.2 Hz, $J(PC)$ = 21.3 Hz, RhC $\equiv$ C, the signal of Rh–C $\equiv$ C overlaps with the signal of the solvent), 116.0 (dt, $J(RhC)$ = 12.1 Hz, $J(PC)$ = 6.0 Hz, Rh=C=CH), 25.7 (vt, N = 20.6 Hz, PCHCH $_3$), 20.7 (s, PCHCH $_3$); $^{31}P\{^1H\}$ NMR (C_6D_6 , 162.0 MHz) δ 47.6 (d, $J(RhP)$ = 135.8 Hz); ESI MS (acetonitrile/acetone) m/z 1099 (8, MH^+ and $M[^{13}C]^+$), 1098 (11, M^+), 997 (16, MH^+ – PhC $_2$ H), 996 (13, M^+ – PhC $_2$ H), 525 (69, [Rh(C $_2$ HPh)(PiPr $_3$) $_2$] $^+$), 423 (100, [Rh(PiPr $_3$) $_2$] $^+$). Anal. Calcd for $C_{56}H_{96}P_4Rh_2$: C, 61.20; H, 8.80. Found: C, 60.86; H, 8.66.

Preparation of *trans,trans*-[Rh(C $\equiv$ CMe $_2$)(PiPr $_3$) $_2$] $_2$ -(μ -C $_4$) (9). A solution of **4** (85 mg, 0.17 mmol) in 5 mL of pentane was treated with Ph $_3$ SnC $\equiv$ CC $\equiv$ CSnPh $_3$ (64 mg, 0.09 mmol) at $-78^\circ C$. With continuous stirring, the mixture was slowly warmed to room temperature and stirred at this temperature for 20 min. A change of color from red-violet to green occurred. The solvent was removed in vacuo, and 15 mL of pentane ($-78^\circ C$) was added to the residue. The cold green solution was filtered through a cotton pad, and the filtrate was brought to dryness in vacuo. The residue was dissolved in 4 mL of acetone, and after the solution was stored for 2 days at $-20^\circ C$ green crystals precipitated. They were washed with 3 mL portions of acetone ($-40^\circ C$) and dried: yield 68 mg (79%); mp $90^\circ C$ dec; IR (hexane) $\nu(C\equiv C)$ 1675 cm^{-1} , $\nu(C\equiv C)$ not located; 1H NMR (C_6D_6 , 400 MHz) δ 2.65 (m, 12H, PCHCH $_3$), 1.74 (t, $J(PH)$ = 2.4 Hz, 12H, Rh=C=C(CH $_3$) $_2$), 1.38 (dvt, N = 13.6 Hz, $J(HH)$ = 7.2 Hz, 72H, PCHCH $_3$); $^{13}C\{^1H\}$ NMR (C_6D_6 , 100.6 MHz) δ 308.6 (dt, $J(RhC)$ = 46.3 Hz, $J(PC)$ = 17.1 Hz, Rh=C), 127.4 (d, $J(RhC)$ = 10.1 Hz, RhC $\equiv$ C), 123.8 (dt, $J(RhC)$ = 38.2 Hz, $J(PC)$ = 19.1 Hz, RhC $\equiv$ C), 109.2

(dt, $J(\text{RhC}) = 12.1$ Hz, $J(\text{PC}) = 6.0$ Hz, $\text{Rh}=\text{C}=\text{C}(\text{CH}_3)_2$), 25.3 (vt, $N = 19.9$ Hz, PCHCH_3), 20.7 (s, PCHCH_3), 6.4 (s, $\text{C}=\text{C}(\text{CH}_3)_2$); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162.0 MHz) δ 47.9 (d, $J(\text{RhP}) = 138.0$ Hz); ESI MS (methanol/acetone) m/z 1001 ($[\text{M} - \text{H}]^+$), 477 (100, $[\text{Rh}(\text{C}_2\text{Me}_2)(\text{PiPr}_3)_2]^+$). Anal. Calcd for $\text{C}_{48}\text{H}_{96}\text{P}_4\text{Rh}_2$: C, 57.48; H, 9.65. Found: C, 57.28; H, 9.67.

Preparation of *trans,trans*-[$\{\text{Rh}(\text{H})(\text{C}\equiv\text{CPh})(\text{py})-(\text{PiPr}_3)_2\}_2(\mu\text{-C}_4)$] (10). A solution of **8** (95 mg, 0.087 mmol) in 10 mL of pentane was treated with pyridine (1 mL), and the mixture was stirred at 40 °C for 1 h. The brownish yellow solution was then filtered through a cotton pad and brought to dryness in vacuo. The residue was dissolved in 1 mL of diethyl ether, and upon addition of pentane at room temperature, a beige solid precipitated. After the suspension was stored at −20 °C for 2 h, the mother liquor was separated and the solid washed twice with 2 mL portions of cold pentane (−20 °C) and dried in vacuo. A second portion of the beige solid was obtained from the mother liquor when it was concentrated and stored at −20 °C: yield 66 mg (61%); mp 58 °C dec; IR (Nujol–polyethylene) $\nu(\text{C}\equiv\text{C})$ 2086, $\nu(\text{C}=\text{C})$ 1594, 1569 cm^{-1} ; ^1H NMR (C_6D_6 , 400 MHz) δ 9.41 (br s, 4H, *ortho* H of $\text{C}_5\text{H}_5\text{N}$), 7.72 (d, $J(\text{HH}) = 7.5$ Hz, 4H, *ortho* H of C_6H_5), 7.19 (t, $J(\text{HH}) = 7.6$ Hz, 4H, *meta* H of C_6H_5), 6.98 (t, $J(\text{HH}) = 7.3$ Hz, 2H, *para* H of C_6H_5), 6.95 (t, $J(\text{HH}) = 7.1$ Hz, 2H, *para* H of $\text{C}_5\text{H}_5\text{N}$), 6.63 (br t, 4H, *meta* H of $\text{C}_5\text{H}_5\text{N}$), 2.98 (m, 12H, PCHCH_3), 1.32 (dvt, $N = 13.2$ Hz, $J(\text{HH}) = 6.7$ Hz, 72H, PCHCH_3), −17.94 (dt, $J(\text{RhH}) = 17.0$ Hz, $J(\text{PH}) = 14.0$ Hz, 2H, RhH); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100.6 MHz) δ 153.1 (br s, *ortho* C of $\text{C}_5\text{H}_5\text{N}$), 135.6 (s, CH of C_6H_5 or $\text{C}_5\text{H}_5\text{N}$), 131.3 (s, *ipso* C of C_6H_5), 130.7, 128.4 (both s, CH of C_6H_5 or $\text{C}_5\text{H}_5\text{N}$), 124.5 (m, $\text{RhC}\equiv\text{C}$), 124.1, 123.4 (both s, CH of C_6H_5 or $\text{C}_5\text{H}_5\text{N}$), 110.8, 99.3 (both d, $J(\text{RhC}) = 7.0$ Hz, $\text{RhC}\equiv\text{C}$), 96.9 (m, $\text{RhC}\equiv\text{C}$), 25.7 (vt, $N = 21.5$ Hz, PCHCH_3), 19.9 (s, PCHCH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162.0 MHz) δ 42.1 (d, $J(\text{RhP}) = 98.3$ Hz). Anal. Calcd for $\text{C}_{66}\text{H}_{106}\text{N}_2\text{P}_4\text{Rh}_2$: C, 63.04; H, 8.50; N, 2.24. Found: C, 62.66; H, 8.73; N, 2.24.

X-ray Structural Analysis of 9. Single crystals were grown from Et_2O at −20 °C; the crystal size was $0.08 \times 0.12 \times 0.16$ mm. Crystal data (from 24 reflections, $6^\circ < \theta < 13^\circ$): triclinic, space group $P\bar{1}$ (No. 2); $a = 7.900(1)$ Å, $b = 10.948(1)$ Å, $c = 16.541(2)$ Å, $\alpha = 109.33(1)^\circ$, $\beta = 91.70(1)^\circ$, $\gamma = 93.62(1)^\circ$, $V = 1345.3(3)$ Å³, $d_{\text{calcd}} = 1.238$ g cm^{-3} ; $\mu(\text{Mo K}\alpha) =$

0.753 mm^{−1} (Mo K α , $\lambda = 0.71073$ Å), maximum $2\theta = 46^\circ$, ω/θ scan, graphite monochromator, Zr filter (factor 16.4), $T = 293(2)$ K; 3923 reflections scanned, 3605 unique ($R(\text{int}) = 0.0415$), 2591 observed ($I > 2\sigma(I)$), LP and empirical absorption correction (ψ -scans, minimum transmission 87.30%); direct methods (SHELXS-86²⁷), 258 parameters, reflex/parameter ratio 13.97; $R1 = 0.0486$, $wR2 = 0.0834$ for 2591 observed reflections and $R1 = 0.0826$, $wR2 = 0.1023$ for all 3603 data reflections; residual electron density $+0.484/-0.486$ e Å^{−3}. The asymmetric unit contains only half of the molecule; the second half was generated by the symmetry instruction $-x, -y, -z$. Atoms generated by symmetry in Figure 1 are marked with asterisks. The positions of all hydrogen atoms were calculated according to ideal geometry and refined by full-matrix least squares on F^2 using the riding method (weighting scheme applied in the last cycle $w^{-1} = \sigma^2 F_o^2 + (0.0119P)^2 + 4.0625P$, where $P = (F_o^2 + 2F_c^2)/3$, SHELXL-93²⁷).

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (Grant No. SFB 347) and the Fonds der Chemischen Industrie. J.G.-R. is grateful to the Spanish Ministerio de Educación y Cultura and to the European Commission (Contract No. ERBFMBICT-960698) for a postdoctoral grant. We also gratefully acknowledge support by Mrs. Schedl and C. P. Kneis (DTA and elemental analysis), Mrs. M. L. Schäfer and Dr. W. Buchner (NMR measurements), Dr. G. Lange and Mr. F. Dadrich (EI mass spectra), and Dr. M. Herderich (ESI mass spectra) and Degussa AG for various gifts of chemicals.

Supporting Information Available: Tables of crystal data and refinement parameters, bond lengths and angles, and positional and thermal parameters for **9** (5 pages). Ordering information is given on any current masthead page.

OM9710780

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