

Coordination and Coupling of OH-Functionalized C₂ Units at a Single Metal Center: The Synthesis of Alkynyl(vinylidene), Alkynyl(enyne), Bis(alkynyl)hydrido, Enynyl, and Hexapentaene Rhodium Complexes from Propargylic Alcohols as Precursors

Helmut Werner,* Ralf Wiedemann, Norbert Mahr, Paul Steinert, and Justin Wolf

Dedicated to Professor Martin A. Bennett on the occasion of his 60th birthday

Abstract: The reaction of $[\text{Rh}(\eta^3\text{-C}_3\text{H}_5)(\text{P}i\text{Pr}_3)_2]$ (**1**) with $\text{HC}\equiv\text{C}-\text{CH}(\text{Ph})\text{OH}$ yields the alkynyl(vinylidene) complex $\text{trans}-[\text{Rh}\{\text{C}\equiv\text{C}-\text{CH}(\text{Ph})\text{OH}\}\{\text{C}=\text{CH}-\text{CH}(\text{Ph})\text{OH}\}(\text{P}i\text{Pr}_3)_2]$ (**2**), while from **1** and $\text{HC}\equiv\text{C}-\text{CPh}_2\text{OH}$ the alkynyl(enyne)metal derivative $\text{trans}-[\text{Rh}(\text{C}\equiv\text{C}-\text{CPh}_2\text{OH})\{\eta^2-(E)\text{-Ph}_2(\text{OH})\text{C}-\text{C}\equiv\text{C}-\text{CH}=\text{CH}-\text{CPh}_2\text{OH}\}(\text{P}i\text{Pr}_3)_2]$ (**3**) is obtained. On treatment with 1-alkyn-3-ols $\text{HC}\equiv\text{C}-\text{CR}_2\text{OH}$ ($\text{R} = \text{Me}, \text{Ph}, i\text{Pr}$), the highly reactive π -benzyl compound $[\text{Rh}(\eta^3\text{-CH}_2\text{Ph})(\text{P}i\text{Pr}_3)_2]$ (**4**) yields the five-coordinate complexes $[\text{RhH}(\text{C}\equiv\text{C}-\text{CR}_2\text{OH})_2(\text{P}i\text{Pr}_3)_2]$ (**5–7**) of which those with $\text{R} = \text{Me}$ and Ph can be converted to the alkynyl(vinylidene)metal isomers $\text{trans}-[\text{Rh}(\text{C}\equiv\text{C}-\text{CR}_2\text{OH})(\text{C}=\text{CH}-\text{CR}_2\text{OH})(\text{P}i\text{Pr}_3)_2]$ (**8, 9**). Compounds **8** and **9** react

with $\text{L}' = \text{CO}$ and isocyanides by migration of the alkynyl ligand to the vinylidene unit to give the enynylrhodium(I) complexes $\text{trans}-[\text{Rh}\{\eta^1-(Z)\text{-C}(\text{C}\equiv\text{C}-\text{CR}_2\text{OH})=\text{CH}-\text{CR}_2\text{OH}\}(\text{L}')(\text{P}i\text{Pr}_3)_2]$ (**10, 11**; $\text{L}' = \text{CO}$; **12–15**; $\text{L}' = \text{CNR}'$). Cleavage of the $\text{Rh}-\text{C}$ σ -bond of **10** with $\text{CF}_3\text{-CO}_2\text{H}$ affords $\text{trans}-[\text{Rh}(\eta^1\text{-O}_2\text{CCF}_3)(\text{CO})(\text{P}i\text{Pr}_3)_2]$ (**16**) and the enyne (E)- $\text{Me}_2(\text{OH})\text{C}-\text{C}\equiv\text{C}-\text{CH}=\text{CH}-\text{CMe}_2\text{OH}$ (**17**). Compounds **5–7** react with $\text{L}' = \text{CO}$ and isocyanides to give the octahedral 1:1 adducts $[\text{RhH}(\text{C}\equiv\text{C}-\text{CR}_2\text{OH})_2(\text{L}')(\text{P}$

$i\text{Pr}_3)_2]$ (**18–20** and **24–27**), of which the CO derivatives **18–20** readily eliminate $\text{HC}\equiv\text{C}-\text{CR}_2\text{OH}$ to yield $\text{trans}-[\text{Rh}(\text{C}\equiv\text{C}-\text{CR}_2\text{OH})(\text{CO})(\text{P}i\text{Pr}_3)_2]$ (**21–23**). On treatment of **6** or **9** ($\text{R} = \text{Ph}$) with Al_2O_3 in the presence of chloride ions, besides $\text{trans}-[\text{RhCl}(\text{C}\equiv\text{C}=\text{CPh}_2)(\text{P}i\text{Pr}_3)_2]$ (**28**) the hexapentaenerrhodium(I) complex $\text{trans}-[\text{RhCl}(\eta^2\text{-Ph}_2\text{C}=\text{C}=\text{C}=\text{C}=\text{C}=\text{CPh}_2)(\text{P}i\text{Pr}_3)_2]$ (**29**) is formed. The kinetically preferred isomer $\text{trans}-[\text{RhCl}(\eta^2\text{-Ph}_2\text{C}=\text{C}=\text{C}=\text{C}=\text{C}=\text{CPh}_2)(\text{P}i\text{Pr}_3)_2]$ (**33**) has been prepared from $[\text{RhCl}(\text{P}i\text{Pr}_3)_2]_2$ and $\text{Ph}_2\text{C}=\text{C}=\text{C}=\text{C}=\text{C}=\text{CPh}_2$; it rearranges smoothly at room temperature to the thermodynamically more stable isomer **29**. The molecular structures of **7** and **29** have been determined.

Keywords

alkyne complexes · carbon carbon coupling · pentaenes · rhodium complexes · vinylidene complexes

Introduction

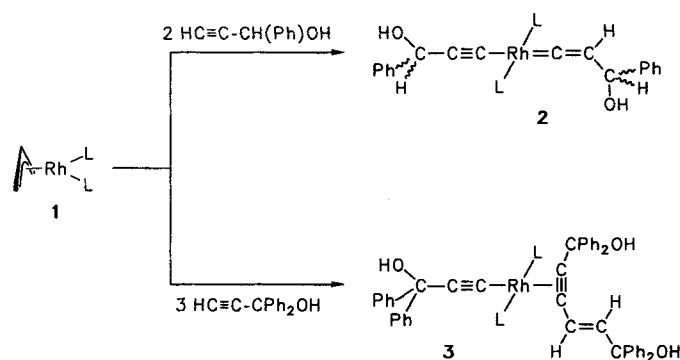
Derivatives of propargyl alcohol of the general composition $\text{HC}\equiv\text{C}-\text{CR}(\text{R}')\text{OH}$ are useful starting materials for the preparation of transition-metal complexes containing the metallacumulene $\text{M}=\text{C}=\text{C}=\text{CRR}'$ as a molecular unit.^[1] Following the synthetic route developed by Selegue^[2] for cationic cyclopentadienylruthenium compounds $[\text{C}_5\text{H}_5\text{Ru}(\text{C}=\text{C}=\text{CRR}')(\text{PMe}_3)_2]^+$, we have recently shown that from the γ -functionalized 1-alkynes $\text{HC}\equiv\text{C}-\text{CR}(\text{R}')\text{OH}$ ($\text{R} = \text{H}, \text{alkyl}, \text{aryl}$; $\text{R}' = \text{alkyl}, \text{aryl}$) the corresponding four-coordinate allenylidene-rhodium complexes $\text{trans}-[\text{RhCl}(\text{C}=\text{C}=\text{CRR}')(\text{P}i\text{Pr}_3)_2]$ can be obtained as well.^[3] With $[\text{RhCl}(\text{P}i\text{Pr}_3)_2]_2$ as starting material, a stepwise and almost quantitative conversion of the 1-alkyn-3-ol to the isomeric vinylidene $\text{C}=\text{CH}-\text{CR}(\text{R}')\text{OH}$ and, on treatment with Al_2O_3 or traces of acids, to the allenylidene $\text{C}=\text{C}=\text{CRR}'$ takes place.^[3]

In continuation of these studies we now describe a method to bind two OH-functionalized C₂ units such as an alkyne, an alkynyl, or a vinylidene ligand to rhodium as a metal center. The most challenging aspect of this work was to find out whether in the coordination sphere two of these units can be coupled together; this would provide a chance to generate a novel double OH-functionalized C₄ ligand. In this context, we were particularly interested in establishing a relationship with the reactivity of analogous vinylidenerhodium complexes $\text{trans}-[\text{Rh}(\text{R})(\text{C}=\text{CHR}')(\text{P}i\text{Pr}_3)_2]$ ($\text{R} = \text{Me}, \text{Ph}, \text{CH}=\text{CH}_2, \text{C}\equiv\text{CR}'$), which on treatment with CO or isocyanides undergo migratory insertion of the vinylidene moiety into the metal-carbon σ bond.^[4] Most recently, it was also observed that this coupling of two C-bonded ligands is even possible *without* the presence of a supporting substrate; this opens up a novel synthetic pathway to π -allyl- and π -butadienylrhodium compounds.^[5]

Results and Discussion

Reactions of $[\text{Rh}(\eta^3\text{-C}_3\text{H}_5)(\text{P}i\text{Pr}_3)_2]$ (1**) with 1-alkyn-3-ols:** The π -allyl rhodium complex **1**, which has already been used for the

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Scheme 1. L = $\text{P}i\text{Pr}_3$.

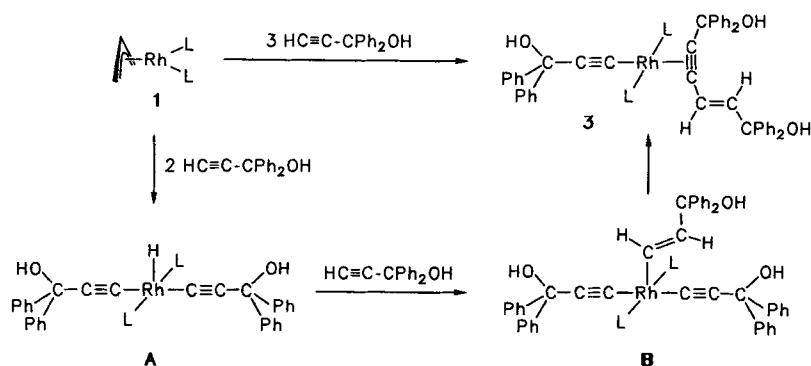
preparation of monomeric carboxylate and alkynyl rhodium(I) derivatives,^[6] reacted smoothly with the substituted propargylic alcohol $\text{HC}\equiv\text{C}-\text{CH}(\text{Ph})\text{OH}$ in neat triethylamine as solvent to give the four-coordinate alkynyl-(vinylidene)rhodium(I) compound **2** (Scheme 1) in about 80% yield. The dark-blue solid was only moderately air-sensitive and soluble in most organic solvents (except for hexane and diethyl ether). Solutions of **2** in chlorinated hydrocarbons such as CHCl_3 or CH_2Cl_2 were not stable and decomposed fairly rapidly at room temperature.

Since the synthesis of complex **2** was carried out with a racemic mixture of the 1-alkyn-3-ol, the isolated product consisted of a mixture of two pairs of diastereoisomers. All attempts to separate these species by fractional crystallization or chromatographic techniques failed. Surprisingly, the existence of the mixture of isomers cannot be observed either in the ^{31}P NMR spectrum, which displays only one sharp doublet caused by Rh–P coupling, or in the ^1H NMR spectrum, in which instead of two sets of signals for the CH_3 protons of the isopropyl groups only two slightly broadened resonances at $\delta = 1.28$ and 1.27 are observed. However, the ^{13}C NMR spectrum of **2** shows two separated signals for most of the carbon atoms of the C_3 units, of which those at $\delta = 304.19$ and 304.10 are most typical for the α -carbon atom of the vinylidene ligand.^[7] The corresponding resonances of the metal-bound alkynyl carbon atom appear at $\delta = 121.93$ and 121.88 , respectively, and like the signals of the $\text{Rh}=\text{C}=\text{C}$ carbon are split into a doublet of triplets.

Under exactly the same conditions as those employed for the preparation of **2**, the reaction of **1** with $\text{HC}\equiv\text{C}-\text{CPh}_2\text{OH}$ did not lead to the formation of an alkynyl(vinylidene)rhodium(I) complex but instead gave the alkynyl(enyne) compound **3**. If three equivalents of the 1-alkyn-3-ol were used, the isolated yield of **3** was 55%. One of the most typical features of the NMR spectroscopic data of **3** (which forms orange, almost air-stable crystals) is the doublet for the vinylic proton $-\text{CH}=\text{CHR}$ at $\delta = 7.46$ in the ^1H NMR spectrum, which shows a H–H coupling of 15.1 Hz. This value is characteristic for *trans* proton–proton coupling in disubstituted olefins^[8] and thus supports the *E* configuration at the $\text{C}=\text{C}$ double bond of the enyne ligand. The IR spectrum of **3** displays two strong bands at 2075 and 1910 cm^{-1} , which are assigned to the $\text{C}\equiv\text{C}$ stretching frequencies of an alkynyl and an alkyne ligand, respectively.

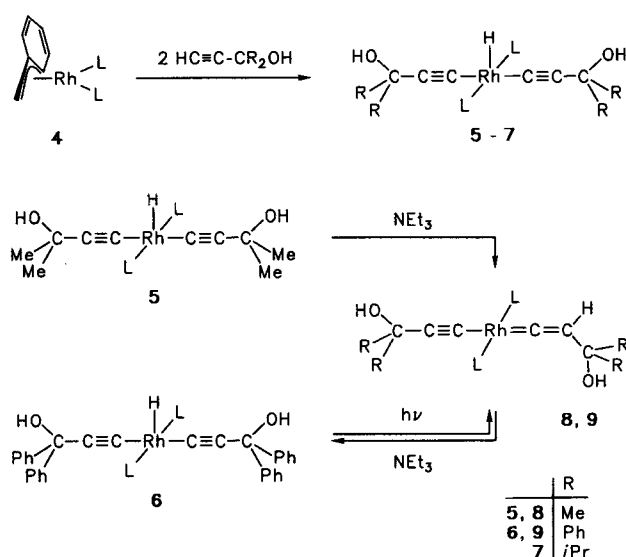
The proposed mechanism for the formation of the unusual alkynyl(enyne) complex **3** is outlined in Scheme 2. We assume

that the initial step, which possibly involves the generation of an alkynyl(allyl)hydridorhodium(III) species as an intermediate by oxidative addition of $\text{HC}\equiv\text{C}-\text{CPh}_2\text{OH}$ to **1**, is rather slow and that therefore compound **A** (which, as discussed below, has been prepared by a different route and is in fact an intermediate in the formation of **3**) reacts with a further molecule of the 1-alkyn-3-ol by insertion into the Rh–H bond to give **B**. For the final step, the metal-assisted coupling of an alkynyl and a vinyl ligand, there is precedent insofar as we have recently shown that on treatment of an octahedral acetato(alkynyl)vinylrhodium derivative with CO the corresponding enyne $\text{RC}\equiv\text{C}-\text{CH}=\text{CHR}$ is formed almost quantitatively along with an acetato(carbonyl)rhodium complex.^[9]

Scheme 2. Proposed mechanism for the formation of **3**; L = $\text{P}i\text{Pr}_3$.

The advantage of the complex $[\text{Rh}(\eta^3-\text{CH}_2\text{Ph})(\text{P}i\text{Pr}_3)_2]$ (4**) as starting material:** Since attempts to isolate the bis(alkynyl)hydridorhodium(III) compound **A** (Scheme 2) remained unsuccessful, and further experiments to prepare alkynylrhodium(I) complexes related in structure to **2** and **3** from **1** and $\text{HC}\equiv\text{C}-\text{CR}_2\text{OH}$ ($\text{R} = \text{Me}$ and $i\text{Pr}$) also failed, we turned our attention to the reactivity of the η^3 -benzyl compound $[\text{Rh}(\eta^3-\text{CH}_2\text{Ph})(\text{P}i\text{Pr}_3)_2]$ (**4**) toward 1-alkyn-3-ols. We had already observed that **4** reacts with phenylacetylene to yield *trans*- $[\text{Rh}(\text{C}\equiv\text{CPh})(=\text{C}=\text{CHPh})(\text{P}i\text{Pr}_3)_2]$ via the isomeric alkynyl(alkynyl)rhodium(I) and bis(alkynyl)hydridorhodium(III) species as intermediates.^[6a] With this in mind, it was not surprising that on treatment of compound **4** with two equivalents of $\text{HC}\equiv\text{C}-\text{CR}_2\text{OH}$ ($\text{R} = \text{Me}$, Ph , $i\text{Pr}$) a rapid reaction occurred that led to the formation of white (**5**), yellow (**6**), or orange (**7**) solids in 65–75% yield. The ^1H as well as the ^{13}C NMR spectra of the products (which are only slightly air-sensitive) leave no doubt that instead of the expected *trans*- $[\text{Rh}(\text{C}\equiv\text{CR}')(\text{C}=\text{CHR}')(\text{P}i\text{Pr}_3)_2]$ ($\text{R}' = \text{CR}_2\text{OH}$) vinylidenerhodium(I) complexes, the bis(alkynyl)hydridorhodium(III) isomers (Scheme 3) are formed. The ^1H NMR spectra of **5–7** display a doublet of triplets at around $\delta = -30$, which, together with the large Rh–H coupling of about 50 Hz, is most typical for a five-coordinate hydridorhodium(III) species.^[10] Moreover, in the ^{13}C NMR spectra, signals appear in the region for alkynyl ($\delta = 115$ – 118) but not for vinylidene carbon atoms. The ^1H and ^{13}C NMR spectra of **7** illustrate a special feature insofar as they show two sets of resonances for the protons and the carbon atoms of the isopropyl CH_3 groups of the $\text{C}i\text{Pr}_2\text{OH}$ substituents, which because of the symmetry of the molecule are diastereotopic. We note that this phenomenon is observed for all complexes containing the alkynyl unit $\text{C}\equiv\text{C}-\text{C}i\text{Pr}_2\text{OH}$ as ligand.

Compound **5** reacted slowly in benzene at room temperature to give the OH-functionalized alkynyl(vinylidene)rhodium(I) complex **8** in about 65% isolated yield. This rearrangement, which

Scheme 3. L = $\text{P}(\text{iPr})_3$.

was accompanied by a characteristic change of color from colorless to dark blue, could be significantly facilitated by addition of NEt_3 . In triethylamine as solvent, the vinylidene complex **8** could also be prepared directly from **4** and two equivalents of $\text{HC}\equiv\text{C}-\text{CMe}_2\text{OH}$. In this case, the yield was 73%. According to the IR and NMR spectroscopic data, the structure of **8** is completely analogous to that of **2**, with *trans* disposed phosphine and alkynyl/vinylidene ligands.

In contrast to **5**, the bis(alkynyl)hydrido complex **6** was rather inert in benzene solution. In neat triethylamine, a slow isomerization to the alkynyl(vinylidene)rhodium(I) derivative **9** occurred which, however, did not go to completion. After stirring for 2 hours, an equilibrium between **6** and **9** of 30:70 was established, which remained almost constant even upon slightly increasing the temperature. A nearly quantitative rearrangement of **6** to **9** took place on irradiation of a solution of the bis(alkynyl)hydrido complex in benzene for 30 minutes. After removal of the solvent and recrystallization from toluene/pentane, a dark-blue, only modestly air-sensitive solid was isolated, the IR and NMR spectroscopic data of which are very similar to those of **2** and **8**. It should be mentioned that compound **9** is not stable in benzene or toluene solution and partly rearranges to the isomer **6** until the equilibrium of **6**:**9** = 30:70 is reached. We furthermore note that in contrast to **5** and **6**, complex **7** is completely inert and does not react to give *trans*- $[\text{Rh}(\text{C}\equiv\text{CR}')(\text{C}=\text{CHR}')(\text{P}(\text{iPr})_3)_2]$ ($\text{R}' = \text{C}(\text{iPr})_2\text{OH}$) either thermally or photochemically.

The molecular structure of complex 7: Since it could not be unambiguously decided from the spectroscopic data of the bis(alkynyl)hydridorhodium(III) derivatives **5–7** whether these compounds possess a square pyramidal or a trigonal bipyramidal configuration, an X-ray crystal structure analysis of **7** was carried out. The result is shown in Figure 1 along with the principal bond lengths and angles. The position of the hydride ligand was located by a difference Fourier analysis and was found to be disordered in the ratio of 1:1 above and below the plane of the rhodium, the phosphorus, and the metal-bonded carbon atoms. The structure therefore corresponds to that of a square pyramid with an exactly linear P-Rh-P and an almost linear C-C-Rh-C-C arrangement. The Rh–C1 and Rh–C10 bond lengths

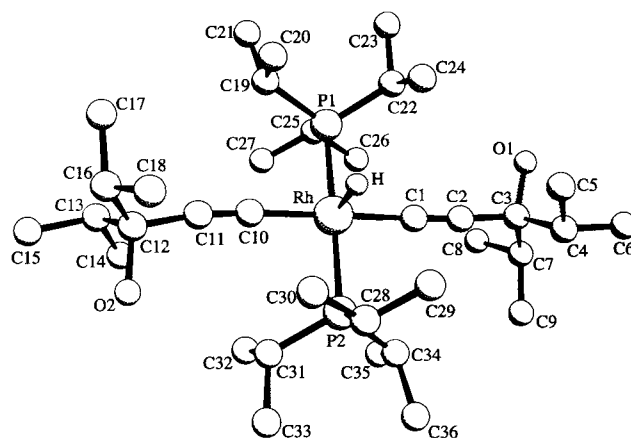
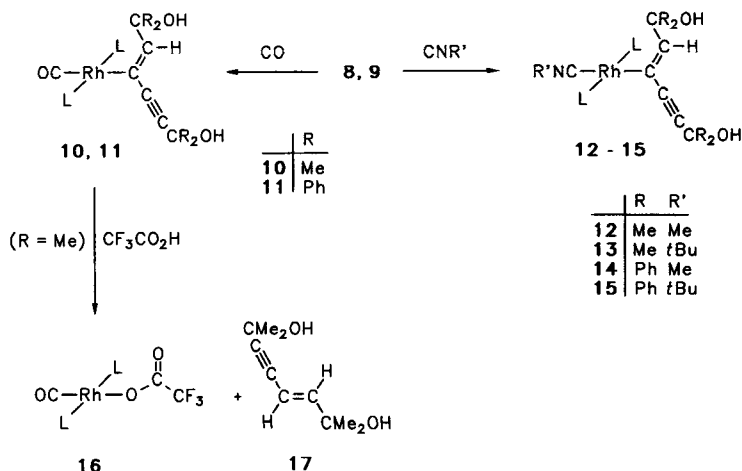


Fig. 1. Molecular structure of **7**. The diagram shows only one of the two sites for the hydrido hydrogen atom, which is disordered above and below the coordination plane. Principal bond lengths [Å] and angles [°], with estimated standard deviations in parentheses: Rh–P1 2.332(1), Rh–P2 2.338(1), Rh–C1 2.032(4), Rh–C10 2.022(4), Rh–H 1.46, Rh–H* 1.56, C1–C2 1.206(4), C2–C3 1.479(5), C10–C11 1.203(4), C11–C12 1.483(5), O1–C3 1.450(4), O2–C12 1.457(4); P1–Rh–P2 179.49(4), P1–Rh–C1 89.6(1), P1–Rh–C10 91.4(1), P2–Rh–C1 90.65(9), P2–Rh–C10 88.35(9), C1–Rh–C10 178.9(1), Rh–C1–C2 177.6(3), C1–C2–C3 176.6(4), Rh–C10–C11 176.3(3), C10–C11–C12 171.9(4).

[2.032(4) and 2.022(4) Å] are nearly identical to those of the octahedral bis(alkynyl)hydrido complex $[\text{RhH}(\text{C}\equiv\text{CPh})_2(\text{PMe}_3)_3]$ [2.019(4) Å],^[11] but significantly longer than in the related compound $[\text{RhHCl}\{\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)=\text{CH}_2\}(\text{py})(\text{P}(\text{iPr})_3)_2]$ [1.958(4) Å],^[7e] in which chloride is *trans* to the alkynyl ligand. The distances Rh–P1, Rh–P2 and C1–C2, C10–C11 are very similar to those in other mono- or bis(alkynyl) rhodium complexes containing $[\text{Rh}(\text{P}(\text{iPr})_3)_2]$ as a building block^[4, 7c, 9, 10b, 12] and thus deserve no further comments.

Reactions of the alkynyl(vinylidene)rhodium(I) and bis(alkynyl)hydridorhodium(III) complexes with CO and isocyanides—a smooth route for C–C coupling: Following the observation that σ -bonded alkyl, aryl, and vinyl groups as well as alkynyl ligands $\text{C}\equiv\text{CR}$ ^[4, 13] can migrate to the α -carbon atom of a metal-bonded vinylidene unit on reaction with carbon monoxide, the compounds **8** and **9** were likewise treated with CO. In benzene as solvent, a spontaneous reaction occurred that was indicated by a color change from dark blue to pale yellow. Removal of the solvent and recrystallization from pentane gave the products **10** and **11** (Scheme 4) in 80–85% yield. The

Scheme 4. L = $\text{P}(\text{iPr})_3$.

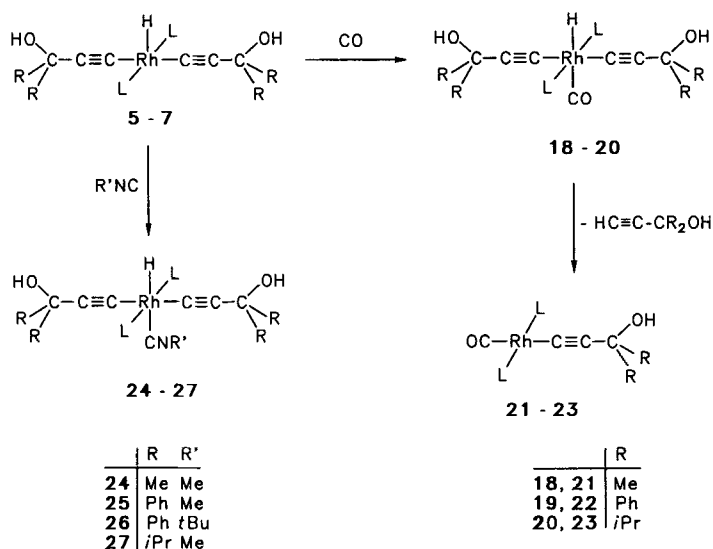
^1H and ^{13}C NMR spectroscopic data support the assumption that by coupling of the alkynyl and vinylidene moieties an enynyl ligand is formed. It is *trans* disposed to the CO group, since the ^1H and ^{31}P NMR spectra confirm that the PiPr_3 ligands are *trans* to each other. The most characteristic feature of the ^1H NMR spectra of **10** and **11** is the sharp doublet of triplets at $\delta = 6.94$ (**10**) or 8.03 (**11**), respectively, which is assigned to the vinylic proton $\text{C}=\text{CHCR}_2\text{OH}$. In view of the similarity of the chemical shift and the $\text{Rh}-\text{H}$ and $\text{P}-\text{H}$ coupling constants of this signal with the corresponding data of the related complex *trans*- $[\text{Rh}\{\eta^1-(Z)\text{-C}(\text{C}\equiv\text{CCO}_2\text{Me})=\text{CHCO}_2\text{Me}\}(\text{CO})(\text{PiPr}_3)_2]$, the structure of which has been determined by X-ray analysis,^[4a] we assume that in **10** and **11** the substituents CR_2OH and $\text{Rh}(\text{CO})(\text{PiPr}_3)_2$ at the $\text{C}=\text{C}$ double bond are also in the *cis* position. Owing to the steric requirements of the two bulky PiPr_3 groups, the rotation of the enynyl ligand around the $\text{Rh}-\text{C}$ bond is probably seriously hindered, as is indicated by the double set of signals for the PCHCH_3 protons in the ^1H NMR spectra. We furthermore note that the rate of the H/D exchange of the two hydroxy protons in **11** is remarkably different. While in the presence of D_2O , the signal at $\delta = 5.49$ disappears rather quickly (i.e., in less than 10 min), the second resonance at $\delta = 2.48$ loses only about 30% of its intensity in 12 hours; in this case, for the complete H/D exchange two days are necessary.

The reactions of **8** and **9** with CNMe and $\text{CN}t\text{Bu}$ took place selectively as well and afforded the corresponding enynylrhodium(I) complexes **12–15** in 70–75% yield. In contrast to the carbonyl derivatives **10** and **11**, the yellow crystalline isocyanide compounds **12–15**, which for a short period of time can be handled in air, are only sparingly soluble in benzene, toluene, and acetone. In solution, they are fairly unstable and decompose to a variety of products, which have as yet not been identified. The IR spectra of **12** and **14** show an intense $\text{C}\equiv\text{N}$ stretching frequency at about 2160 cm^{-1} , while those of **13** and **15** display three bands between 2050 and 2160 cm^{-1} , the assignment of which is not clear. This phenomenon has also been observed by Jones et al. in the case of other square planar isocyaniderhodium(I) complexes^[14] and still needs a convincing explanation.

With $\text{CF}_3\text{CO}_2\text{H}$, the cleavage of the enynyl–rhodium bond in **10** proceeded almost instantaneously and (as determined by NMR measurements) gave the trifluoroacetatorhodium complex **16**^[15] and the enyne **17** quantitatively. This result is noteworthy, since similar enynylrhodium compounds *trans*- $[\text{Rh}\{\eta^1-(Z)\text{-C}(\text{C}\equiv\text{CR})=\text{CHR}\}(\text{CO})(\text{PiPr}_3)_2]$ with phenyl or *tert*-butyl instead of CMe_2OH as substituents react with $\text{CF}_3\text{CO}_2\text{H}$ in benzene or acetone to give the corresponding butatrienes $\text{RCH}=\text{C}=\text{C}=\text{CHR}$ in 90–95% yield.^[4a] As a possible explanation for the difference in behavior, it is conceivable that in the case of **10** the acid initially interacts with the OH functionalities and not with the triple bond, which prevents the formation of a butatriene moiety.

In the presence of CO or isocyanides, the five-coordinate bis(alkynyl)hydridometal derivatives **5–7** added one more ligand and afforded the octahedral complexes **18–20** and **24–27**, respectively. As outlined in Scheme 5, the CO adducts **18–20** (which are colorless, only slightly air-sensitive solids) further reacted in benzene at room temperature by elimination of $\text{HC}\equiv\text{C}-\text{CR}_2\text{OH}$ to give the square planar rhodium(I) compounds **21–23**. This behavior of **18–20** is similar to that of the trimethylstannyl complex $[\text{Rh}(\text{SnMe}_3)(\text{C}\equiv\text{CPh})_2(\text{PPh}_3)_3]$, which on treatment with CO affords *trans*- $[\text{Rh}(\text{C}\equiv\text{CPh})(\text{CO})(\text{PPh}_3)_2]$ and $\text{PhC}\equiv\text{CSnMe}_3$ as well as triphenylphosphine.^[16]

In contrast to the CO adducts **18–20**, the analogous isocyanide compounds **24–27** were quite inert toward elimination

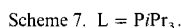
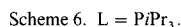


Scheme 5. L = PiPr_3 .

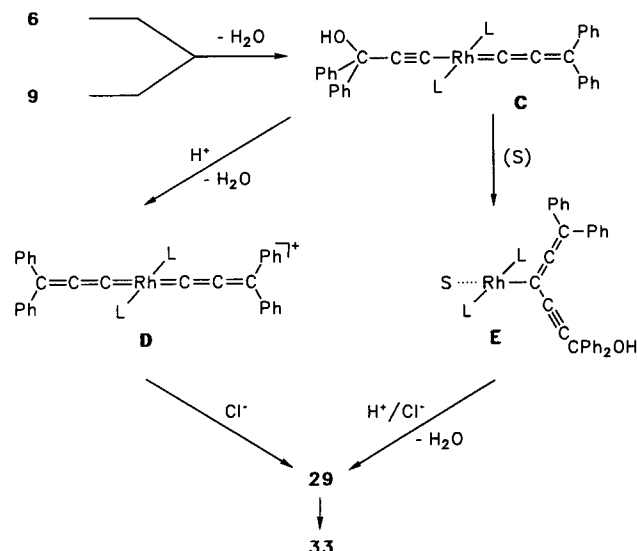
of $\text{HC}\equiv\text{C}-\text{CR}_2\text{OH}$ and could not be transformed into *trans*- $[\text{Rh}(\text{C}\equiv\text{C}-\text{CR}_2\text{OH})(\text{CNR}')(\text{PiPr}_3)_2]$. With regard to the NMR spectroscopic data, it is worth mentioning that in the ^1H NMR spectra of **24–27** the hydride signal appears at around $\delta = -10.8$, which means that in comparison with **5–7** it is shifted by about 20 ppm to lower fields. The difference from the chemical shift of the parent five-coordinate hydrido complexes **5–7** is even larger for the carbonyl derivatives **18–20**, the ^1H NMR spectra of which display a signal at around $\delta = -9.0$. A possible explanation of the remarkable difference is that in **5–7** the position *trans* to the hydride is free, whereas in **18–20** and **24–27** it is occupied by a CO or CNR ligand, which possesses a strong *trans* influence upon the chemical shift.

Coupling of two C_3 units to a C_6 ligand: Since it was known that the allenylidenerhodium complexes *trans*- $[\text{RhCl}(\text{C}\equiv\text{C}=\text{C}=\text{CPh})(\text{PiPr}_3)_2]$ can be prepared from propargylic alcohols $\text{HC}\equiv\text{C}-\text{CR}(\text{Ph})\text{OH}$ via intermediately formed alkyne, alkynyl(hydrido), and vinylidene metal derivatives,^[3] we attempted to use compounds **6** and **9** for the same purpose. On passing a solution of **6** or **9** in benzene through a column filled with acidic alumina (which from the commercial sources we use *always* contains chloride), a fairly quick change of color from blue to red took place. If chromatography was continued, two red fractions were separated, of which the second (with a longer retention time) contained the allenylidene complex **28**.^[3a] From the first fraction, a red solid was isolated that consisted of **29** (Scheme 6) as the major and **33** (Scheme 7) as the minor component. Upon stirring a solution of **29/33** in benzene for 2 h at room temperature, a quantitative conversion of **33** to the more stable isomer **29** occurred. The yield of **29**, the composition of which has been confirmed by elemental analysis and X-ray crystallography (see below), was 70%. The red air-stable compound is readily soluble in chloroform but only sparingly soluble in ether, benzene, toluene, and saturated hydrocarbons.

The assumption that **33** is the kinetically preferred and **29** the thermodynamically preferred isomer could be confirmed by independent synthesis of the two compounds from $[\text{RhCl}(\text{PiPr}_3)_2]_2$ (**32**)^[17] (see Scheme 7). The reaction of **32** with 1,1,6,6-tetraphenylhexapentaene $\text{Ph}_2\text{C}=\text{C}=\text{C}=\text{C}=\text{C}=\text{CPh}_2$ (**31**) in toluene at -30°C led exclusively to the formation of **33**, provided that the solution was worked up quickly at low temperature. In contrast to **29**, the more symmetrical compound **33**



With regard to the mechanism of formation of **33** (and **29**) from **6** or **9** we assume that, on analogy with the preparation of *trans*-[RhCl(=C=C=CPh₂)(PiPr₃)₂] from *trans*-[RhCl(=C=CH-CPh₂OH)(PiPr₃)₂] and Al₂O₃,^[3a] an alkynyl(allynylidene)rhodium(i) intermediate **C** is formed initially (Scheme 8). This can either be converted by proton attack (and elimination of water) to the bis(allynylidene)metal cation **D** or, alternatively, by migration of the alkynyl ligand to the α-carbon of the allynylidene unit to give **E**. The migratory insertion step could be assisted by the solvent or, as has been shown in a similar case,^[9] by chloride ions. Coupling of the two C₃ fragments of **D** or acid-initiated abstraction of OH⁻ from **E** could then generate the hexapentaene ligand and, on addition of Cl⁻, give complex **33**. We note that there is precedent for the linkage of two allynylidene moieties to give a tetrasubstituted hexapentaene as on heating of [C₅H₅Mn(CO)₂(=C=C=C*t*Bu₂)] small quantities of *t*Bu₂C=C=C=C=C=C=*t*Bu₂ are formed.^[21] A related rhodi-



Scheme 8. L = $\text{P}i\text{Pr}_3$, S = solvent.

um-assisted coupling of two vinylidene ligands to give a coordinated butatriene is also known.^[22]

The molecular structure of complex 29: To confirm the unsymmetrical coordination of the hexapentaene ligand, a single-crystal X-ray structural analysis of **29** was performed. The SCHAKAL diagram (Fig. 2) reveals that the coordination geometry around the rhodium center is square planar, with the phosphine ligands *trans* to each other and thus the chloride and the hexapentaene are also in a *trans* disposition. While the Rh–P bond lengths are almost identical (see legend to Fig. 2), the Rh–C2 and Rh–C3 distances differ slightly by about 0.015 Å. The P–Rh–P axis is not exactly linear, possibly because of the unsymmetrical bonding situation of the cumulene unit. In agreement with previous findings,^[23] the C₆ chain is bent, possessing C–C–C angles that are similar to those in the related

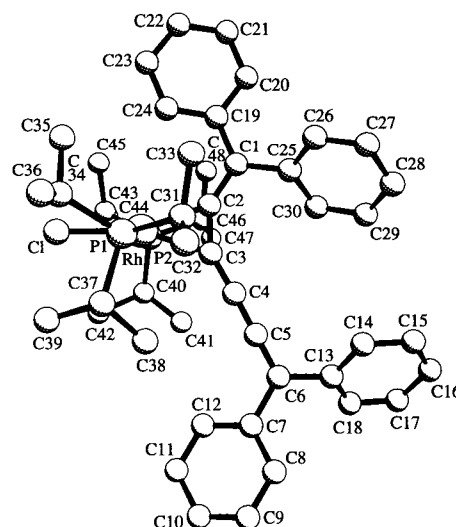


Fig. 2. Molecular structure of **29**. Principal bond lengths [Å] and angles [°], with estimated standard deviations in parentheses: Rh–P1 2.393(1), Rh–P2 2.389(1), Rh–C2 2.017(4), Rh–C3 2.031(4), Rh–Cl 2.366(1), C1–C2 1.352(6), C2–C3 1.347(6), C3–C4 1.304(7), C4–C5 1.283(7), C5–C6 1.321(7), P1–Rh–P2 171.58(5), P1–Rh–C2 94.1(1), P1–Rh–C3 90.6(1), P1–Rh–Cl 86.30(5), P2–Rh–C2 93.4(1), P2–Rh–C3 92.7(1), P2–Rh–Cl 88.11(5), Cl–Rh–C2 159.7(1), Cl–Rh–C3 161.4(2), C2–Rh–C3 38.9(2), Rh–C2–C3 71.1(3), Rh–C3–C2 70.0(3), Rh–C2–C1 144.6(4), Rh–C3–C4 138.9(4), C1–C2–C3 144.0(5), C2–C3–C4 151.1(5), C3–C4–C5 175.8(5), C4–C5–C6 179.7(7).

hexapentaene and butatriene rhodium(I) complexes.^[23, 24] The plane of the carbon atoms C1–C6 is nearly perpendicular to the plane containing the metal, the chloride, and the phosphorus atoms, the dihedral angle being 89.8(1)°. It should be mentioned that the distance C2–C3 is only slightly longer (by 0.05–0.06 Å) than the distances C3–C4 and C4–C5, and almost identical to the bond length C1–C2.

Conclusion

The present investigations have shown that not only allenylidene transition-metal complexes but also those having either two OH-functionalized alkynyl or one alkynyl and one vinylidene ligand coordinated to rhodium can be prepared from propargylic alcohols $\text{HC}\equiv\text{C}-\text{CR}(\text{R}')\text{OH}$ as starting materials. The substituents R and R' from the 1-alkyn-3-ol mainly determine which of the two types of compounds, the bis(alkynyl)-hydrido or the alkynyl(vinylidene) isomer, is the kinetically preferred product. In contrast to the alkynyl(chloro)hydrido-rhodium complexes $[\text{RhH}\{\text{C}\equiv\text{C}-\text{CR}(\text{R}')\text{OH}\}\text{Cl}(\text{P}(\text{Pr}_3)_2)]$, which quickly rearrange in toluene at room temperature to give the vinylidenemetal derivatives $\text{trans}[\text{RhCl}\{\text{C}=\text{CH}-\text{CR}(\text{R}')\text{OH}\}(\text{P}(\text{Pr}_3)_2)]$,^[3, 7e] the related complexes $[\text{RhH}\{\text{C}\equiv\text{C}-\text{CR}(\text{R}')\text{OH}\}]_2(\text{P}(\text{Pr}_3)_2)_2$ are quite inert under the same conditions. Only on photolysis or prolonged stirring in neat triethylamine can they be converted to the isomers $\text{trans}[\text{Rh}\{\text{C}\equiv\text{C}-\text{CR}(\text{R}')\text{OH}\}(\text{C}=\text{CH}-\text{CR}(\text{R}')\text{OH})](\text{P}(\text{Pr}_3)_2)_2$. These four-coordinate compounds react smoothly with CO or isocyanides by migration of the alkynyl group to the α -carbon of the vinylidene ligand to yield the corresponding σ -enynylrhodium(I) complexes. A particularly striking aspect is the exclusive formation of the (Z)-isomers; this sets them apart from the previously reported enynyl complexes.^[25] We assume that it is mainly for steric reasons that the attack of the alkynyl occurs only at the side of the $\text{Rh}=\text{C}=\text{CHX}$ fragment ($\text{X} = \text{CR}(\text{R}')\text{OH}$) opposite to the substituent X. The addition of CO or isocyanides to the metal center of the bis(alkynyl)hydrido compounds does not initiate C–C coupling of the two C_2 units as was observed in a similar case between an alkynyl and a vinyl ligand.^[9]

The most remarkable feature of this work, however, is the generation of the hexapentaene $\text{Ph}_2\text{C}=\text{C}=\text{C}=\text{C}=\text{C}=\text{CPh}_2$ by C–C coupling and acid-assisted elimination of OH^- and H_2O from either $[\text{RhH}(\text{C}\equiv\text{C}-\text{CPh}_2\text{OH})_2](\text{P}(\text{Pr}_3)_2)_2$ or $\text{trans}[\text{Rh}(\text{C}\equiv\text{C}-\text{CPh}_2\text{OH})(\text{C}=\text{CH}-\text{CPh}_2\text{OH})](\text{P}(\text{Pr}_3)_2)_2$. Although the synthesis of some tetraalkyl- and tetraarylhexapentaene transition-metal complexes has been reported in the literature,^[23, 26] to the best of our knowledge the formation of such a compound by coupling of two C_3 units in the coordination sphere of a metal is without precedent. Studies in progress are aimed to find out whether starting materials such as $[\text{RhH}(\text{C}\equiv\text{C}-\text{CR}_2\text{OH})(\text{C}\equiv\text{C}-\text{CR}'_2\text{OH})\text{L}_2]$ or $\text{trans}[\text{Rh}(\text{C}\equiv\text{C}-\text{CR}_2\text{OH})(\text{C}=\text{CH}-\text{CR}'_2\text{OH})\text{L}_2]$ are accessible and can be used both for the preparation of metal complexes with *unsymmetrical* hexapentaenes $\text{R}_2\text{C}=\text{C}=\text{C}=\text{C}=\text{C}=\text{CR}'_2$ as ligands and of butenynylrhodium derivatives $\text{trans}[\text{Rh}\{\eta^1\text{-C}(\text{C}\equiv\text{C}-\text{CR}_2\text{OH})=\text{CH}-\text{CR}'_2\text{OH}\}(\text{CO})\text{L}_2]$ with two different substituents R, R' attached to the C_4 unit.

Experimental Section

All experiments were carried out under an atmosphere of argon by Schlenk tube techniques. The starting materials **1** [6b], **4** [6b], **31** [20], and **32** [17] were prepared as described in the literature. The 1-alkyn-3-ols were commercial products from Aldrich and ABCR. NMR spectra were recorded at room temperature on Jeol FX90Q, Bruker AC200, and Bruker AMX400 instruments, IR spectra on a

Perkin–Elmer 1420 spectrophotometer. Abbreviations used: s, singlet; d, doublet; t, triplet; vt, virtual triplet; spt, septet; m, multiplet; br, broadened signal. Melting points were measured by DTA.

trans-[Rh(C≡C–CH(Ph)OH){C≡C=CH–CH(Ph)OH}(PiPr₃)₂] **(2): A solution of **1** (150 mg, 0.32 mmol) in 3 mL of triethylamine was treated at 10 °C with $\text{HC}\equiv\text{C}-\text{CH}(\text{Ph})\text{OH}$ (85 mg, 0.64 mmol) and stirred for 4 h. A slow change of color from orange to dark blue occurred. After the solvent had been removed in vacuo, the residue was extracted with 8 mL of toluene/pentane (1:4), and the extract was stored for 20 h at –30 °C. Dark-blue crystals precipitated, which were washed three times with 3 mL of pentane (0 °C) each and dried; yield 158 mg (78 %); m.p. 95 °C (decomp.); IR (KBr): $\tilde{\nu} = 3600$ (O–H), 2090 ($\text{C}\equiv\text{C}$), 1635 ($\text{C}=\text{C}$) cm^{-1} ; ¹H NMR (C_6D_6 , 200 MHz): $\delta = 7.53$ and 7.14 (both m, 10H, C_6H_5), 5.66 [d, $J(\text{H},\text{H}) = 9.6$ Hz, 1H, $=\text{CH}-\text{CH}(\text{Ph})\text{OH}$], 5.66 [s, 1H, $=\text{C}-\text{CH}(\text{Ph})\text{OH}$], 2.70 (m, 6H, PCHCH_3), 1.28 and 1.27 [both dvt, $N = 13.3$, $J(\text{H},\text{H}) = 6.6$ Hz, 18H each, PCHCH_3], signal of $=\text{CHR}$ proton probably covered by signal of PCHCH_3 , signal of OH protons not observed; ¹³C NMR (C_6D_6 , 100.6 MHz): $\delta = 304.19$ [dt, $J(\text{Rh},\text{C}) = 54.1$, $J(\text{P},\text{C}) = 20.6$ Hz, $\text{Rh}=\text{C}=\text{CHR}$], 304.10 [dt, $J(\text{Rh},\text{C}) = 54.1$, $J(\text{P},\text{C}) = 20.6$ Hz, $\text{Rh}=\text{C}=\text{CHR}$], 145.93 and 144.84 (both s, *ipso*- C_6H_5), 135.21 (m, $\text{Rh}-\text{C}\equiv\text{CR}$), 128.43, 128.16, 127.47, 127.11, 126.82, 126.02 (all s, C_6H_5), 121.93 [dt, $J(\text{Rh},\text{C}) = 38.2$, $J(\text{P},\text{C}) = 19.1$ Hz, $\text{Rh}-\text{C}\equiv\text{CR}$], 121.88 [dt, $J(\text{Rh},\text{C}) = 38.2$, $J(\text{P},\text{C}) = 19.1$ Hz, $\text{Rh}-\text{C}\equiv\text{CR}$], 114.52 [brdt, $J(\text{Rh},\text{C}) = 12.9$, $J(\text{P},\text{C}) = 6.4$ Hz, $\text{Rh}=\text{C}=\text{CHR}$], 66.46 [s, $=\text{CH}-\text{CH}(\text{Ph})\text{OH}$], 60.89 [s, $=\text{C}-\text{CH}(\text{Ph})\text{OH}$], 25.13 (vt, $N = 20.5$ Hz, PCHCH_3), 20.47 and 20.39 (both s, PCHCH_3); ³¹P NMR (C_6D_6 , 162.0 MHz): $\delta = 47.21$ [d, $J(\text{RhP}) = 134.9$ Hz]; $\text{C}_{36}\text{H}_{35}\text{O}_2\text{P}_2\text{Rh}$ (686.7): calcd C 62.97, H 8.37; found C 63.17, H 8.42.**

trans-[Rh(C≡C–CPh₂OH){η²-(E)-Ph₂(OH)C–C≡C–CH=CH–CPh₂OH}(PiPr₃)₂] **(3):**

Method a: A solution of **1** (55 mg, 0.12 mmol) in 3 mL of triethylamine was treated at 10 °C with $\text{HC}\equiv\text{C}-\text{CPh}_2\text{OH}$ (74 mg, 0.36 mmol). After the reaction mixture had been stirred for 2 h at room temperature, an orange air-stable solid precipitated. The mother liquor was decanted off, the precipitate was washed with 3 × 3 mL of pentane (0 °C) and dried; yield 69 mg (55 %).

Method b: A solution of **6** (60 mg, 0.07 mmol) in 2 mL of benzene was treated at room temperature with $\text{HC}\equiv\text{C}-\text{CPh}_2\text{OH}$ (15 mg, 0.07 mmol) and stirred for 2 h. The solvent was removed, the residue was washed with 3 × 1 mL of pentane (0 °C) and dried; yield 55 mg (75 %); m.p. 86 °C (decomp.); IR (KBr): $\tilde{\nu} = 3580$ (O–H), 2075 ($\text{C}\equiv\text{C}$), 1595 ($\text{C}=\text{C}$) cm^{-1} ; ¹H NMR (C_6D_6 , 400 MHz): $\delta = 7.99$, 7.79, 7.63 (all m, 4H each, *o*- C_6H_5), 7.46 [d, $J(\text{H},\text{H}) = 15.1$ Hz, 1H, $=\text{C}-\text{CH}=\text{CHR}$], 7.07 (m, 18H, C_6H_5), 4.37, 2.53, 2.22 (all s, 1H each, OH), 2.02 (m, 6H, PCHCH_3), 1.11 [dvt, $N = 13.6$, $J(\text{H},\text{H}) = 6.9$ Hz, 18H, PCHCH_3], 0.96 [dvt, $N = 12.5$, $J(\text{H},\text{H}) = 6.3$ Hz, 18H, PCHCH_3]; signal of $=\text{C}-\text{CH}=\text{CHR}$ proton is probably covered by signals of C_6H_5 ; ³¹P NMR (C_6D_6 , 162.0 MHz): $\delta = 39.29$ [d, $J(\text{RhP}) = 119.5$ Hz]; $\text{C}_{63}\text{H}_{57}\text{O}_3\text{P}_2\text{Rh}$ (1047.2); calcd C 72.26, H 7.41; found C 71.48, H 7.40. Compound **3** can also be prepared from **6** (60 mg, 0.07 mmol) and $\text{HC}\equiv\text{C}-\text{CPh}_2\text{OH}$ (15 mg, 0.07 mmol) in 3 mL of benzene; yield 55 mg (75 %).

[RhH(C≡C–CMe₂OH)₂(PiPr₃)₂] **(5): A solution of **4** (80 mg, 0.16 mmol) in 3 mL of benzene was treated at 10 °C with $\text{HC}\equiv\text{C}-\text{CMe}_2\text{OH}$ (30 μL, 0.31 mmol). After the reaction mixture had been stirred for 5 min, the solution was layered with 5 mL of pentane and stored at 0 °C. A white microcrystalline solid precipitated, which was separated from the solution, washed with 3 × 3 mL of pentane (0 °C), and dried; yield 61 mg (65 %); m.p. 91 °C (decomp.); IR (KBr): $\tilde{\nu} = 3600$ (O–H), 2140 ($\text{Rh}-\text{H}$), 2000, 1995 ($\text{C}\equiv\text{C}$) cm^{-1} ; ¹H NMR (C_6D_6 , 90 MHz): $\delta = 2.85$ (m, 6H, PCHCH_3), 1.61 [dvt, $N = 14.0$, $J(\text{H},\text{H}) = 7.3$ Hz, 36H, PCHCH_3], 1.25 [s, 12H, $-\text{C}(\text{CH}_3)_2\text{OH}$], –30.29 [dt, $J(\text{Rh},\text{H}) = 50.0$, $J(\text{P},\text{H}) = 13.4$ Hz, 1H, RhH], signal of OH protons not observed; ³¹P NMR (C_6D_6 , 36.2 MHz): $\delta = 53.25$ [d, $J(\text{Rh},\text{P}) = 99.9$ Hz]; $\text{C}_{28}\text{H}_{37}\text{O}_2\text{P}_2\text{Rh}$ (590.6); calcd C 56.94, H 9.73; found C 56.66, H 9.96.**

[RhH(C≡C–CPh₂OH)₂(PiPr₃)₂] **(6): This was prepared as described for **5**, from **4** (110 mg, 0.21 mmol) and $\text{HC}\equiv\text{C}-\text{CPh}_2\text{OH}$ (89 mg, 0.42 mmol) as starting materials. Yellow, only moderately air-sensitive crystals; yield 125 mg (71 %); m.p. 101 °C (decomp.); IR (KBr): $\tilde{\nu} = 3600$ (O–H), 2090, 2080 ($\text{C}\equiv\text{C}$) cm^{-1} ; ¹H NMR (C_6D_6 , 200 MHz): $\delta = 7.84$ and 7.12 (both m, 20H, C_6H_5), 2.72 (m, 6H, PCHCH_3), 2.49 (s, 2H, OH), 1.10 [dvt, $N = 14.5$, $J(\text{H},\text{H}) = 7.3$ Hz, 36H, PCHCH_3], –30.15 [dt, $J(\text{Rh},\text{H}) = 50.9$, $J(\text{P},\text{H}) = 13.1$ Hz, 1H, RhH]; ¹³C NMR (C_6D_6 , 100.6 MHz): $\delta = 148.32$, 127.48, 127.16, 125.88 (all s, C_6H_5), 118.60 [d, $J(\text{Rh},\text{C}) = 8.9$ Hz, $\text{Rh}-\text{C}\equiv\text{CR}$], 118.40 [dt, $J(\text{Rh},\text{C}) = 38.1$, $J(\text{P},\text{C}) = 15.3$ Hz, $\text{Rh}-\text{C}\equiv\text{CR}$], 75.94 (s, $-\text{CPh}_2\text{OH}$), 24.75 (vt, $N = 22.8$ Hz, PCHCH_3), 20.12 (s, PCHCH_3); ³¹P NMR (C_6D_6 , 81.0 MHz): $\delta = 54.47$ [d, $J(\text{Rh},\text{P}) = 97.4$ Hz]; $\text{C}_{48}\text{H}_{55}\text{O}_2\text{P}_2\text{Rh}$ (838.9): calcd C 68.72, H 7.81; found C 68.91, H 8.16.**

[RhH(C≡C–C*i*Pr₂OH)₂(PiPr₃)₂] **(7): This was prepared as described for **5**, from **4** (120 mg, 0.23 mmol) and $\text{HC}\equiv\text{C}-\text{C*i*Pr}_2\text{OH}$ (65 mg, 0.47 mmol) as starting materials. Orange solid; yield 121 mg (75 %); m.p. 108 °C (decomp.); IR (KBr): $\tilde{\nu} = 3620$ (O–H), 2070 ($\text{C}\equiv\text{C}$) cm^{-1} ; ¹H NMR (C_6D_6 , 400 MHz): $\delta = 2.72$ (m, 6H, PCHCH_3), 2.01 [spt, $J(\text{H},\text{H}) = 7.1$ Hz, 4H, $-\text{C}(\text{CH}(\text{CH}_3)_2)_2\text{OH}$], 1.46 (s, 2H, OH), 1.25 [dvt, $N = 13.8$, $J(\text{H},\text{H}) = 6.7$ Hz, 36H, PCHCH_3], 1.20 [d, $J(\text{H},\text{H}) = 6.7$ Hz, 12H, $-\text{C}(\text{CH}(\text{CH}_3)_2)_2\text{OH}$], 1.16 [d, $J(\text{H},\text{H}) = 6.8$ Hz, 12H,**

$-C(CH_3)_2OH$, -30.45 [dt, $J(Rh,H) = 49.6$, $J(P,H) = 13.6$ Hz, 1H, RhH]; ^{13}C NMR (C_6D_6 , 100.6 MHz): $\delta = 118.04$ [d, $J(Rh,C) = 8.8$ Hz, $Rh-C\equiv CR$], 114.80 [dt, $J(Rh,C) = 38.1$, $J(P,C) = 15.2$ Hz, $Rh-C\equiv CR$], 78.66 (s, $-CPr_2OH$), 35.36 [s, $-C(CH_3)_2OH$], 24.95 (vt, $N = 22.8$ Hz, $PCHCH_3$), 20.36 (s, $PCHCH_3$), 18.70 and 17.29 [both s, $-C(CH_3)_2OH$]; ^{31}P NMR (C_6D_6 , 162.0 MHz): $\delta = 53.16$ [d, $J(Rh,P) = 100.2$ Hz]; $C_{30}H_{70}O_2P_2Rh$ (702.8): calcd C 61.52, H 10.47; found C 61.48, H 10.79.

trans-[Rh(η^1 -Z)-C($\equiv C$ -CMe₂OH)=CH-CMe₂OH](P*i*Pr₃)₂] (8):

Method a: A solution of **5** (80 mg, 0.14 mmol) in 3 mL of NEt_3 was stirred for 2 h at room temperature. The solvent was removed in vacuo, the residue was extracted with 5 mL of pentane and the extract was stored at $-30^\circ C$ for 10 h. A dark-blue microcrystalline solid precipitated, which was separated from the solution, washed with 3×3 mL of pentane ($0^\circ C$), and dried; yield 71 mg (89%).

Method b: A solution of **4** (100 mg, 0.19 mmol) in 3 mL of NEt_3 was treated at $10^\circ C$ with $H\equiv C-CMe_2OH$ (38 μL , 0.39 mmol) and stirred for 2 h. The color changed from orange to dark blue. The solvent was removed and the residue was worked up as described for method a; yield 82 mg (73%); m.p. $86^\circ C$ (decomp.); IR (KBr): $\tilde{\nu} = 3600$ (O-H), 2060 ($C\equiv C$), 1650, 1625 ($C=C$) cm^{-1} ; 1H NMR (C_6D_6 , 400 MHz): $\delta = 2.81$ (m, 6H, $PCHCH_3$), 1.59 (s, 1H, OH), 1.53 [s, 6H, $=CH-C(CH_3)_2OH$], 1.34 [dvt, $N = 13.4$, $J(H,H) = 7.1$ Hz, 36H, $PCHCH_3$], 1.30 [s, 6H, $\equiv C-C(CH_3)_2OH$], 0.14 [t, $J(P,H) = 3.7$ Hz, 1H, $=CHR$], signal of second OH proton not observed; ^{13}C NMR (C_6D_6 , 100.6 MHz): $\delta = 304.51$ [dt, $J(Rh,C) = 49.6$, $J(P,C) = 15.3$ Hz, $Rh-C\equiv CR$], 141.00 [d, $J(Rh,C) = 10.8$ Hz, $Rh-C\equiv CR$], 121.08 [dt, $J(Rh,C) = 17.7$, $J(P,C) = 5.1$ Hz, $Rh-C\equiv CR$], 113.57 [dt, $J(Rh,C) = 36.9$, $J(P,C) = 19.1$ Hz, $Rh-C\equiv CR$], 65.87 [s, $=CH-C(CH_3)_2OH$], 61.90 [s, $\equiv C-C(CH_3)_2OH$], 32.54 [s, $=CH-C(CH_3)_2OH$], 32.31 [s, $\equiv C-C(CH_3)_2OH$], 25.24 (vt, $N = 20.4$ Hz, $PCHCH_3$), 20.56 (s, $PCHCH_3$); ^{31}P NMR (C_6D_6 , 162.0 MHz): $\delta = 46.03$ [d, $J(Rh,P) = 135.8$ Hz]; $C_{28}H_{57}O_2P_2Rh$ (590.6): calcd C 56.94, H 9.73; found C 56.54, H 10.04.

trans-[Rh(η^1 -Z)-C($\equiv C$ -CPh₂OH)=CH-CPh₂OH](P*i*Pr₃)₂] (9): A solution of **6** (100 mg, 0.12 mmol) in 15 mL of benzene was irradiated at $5^\circ C$ for 35 min with a mercury lamp (Osram HBO 500 W). The color changed from yellow to dark blue. The solvent was removed, the residue was extracted with 5 mL of toluene/pentane (1:4), and the extract was stored at $-30^\circ C$ for 20 h. A dark-blue solid precipitated, which was separated from the solution, washed with 3×3 mL of pentane ($0^\circ C$), and dried; yield 77 mg (77%); m.p. $108^\circ C$ (decomp.); IR (KBr): $\tilde{\nu} = 3580$ (O-H), 2065 ($C\equiv C$), 1635 ($C=C$) cm^{-1} ; 1H NMR (C_6D_6 , 200 MHz): $\delta = 7.77$, 7.46, 7.08 (all m, 20H, C_6H_5), 2.90 (s, 1H, OH), 2.63 (m, 6H, $PCHCH_3$), 2.42 (brs, 1H, OH), 1.20 [dvt, $N = 13.5$, $J(H,H) = 6.9$ Hz, 36H, $PCHCH_3$], 0.94 [t, $J(P,H) = 3.6$ Hz, 1H, $=CHR$]; ^{13}C NMR (C_6D_6 , 100.6 MHz): $\delta = 301.77$ [dt, $J(Rh,C) = 50.3$, $J(P,C) = 15.1$ Hz, $Rh-C\equiv CR$], 138.33 [d, $J(Rh,C) = 9.1$ Hz, $Rh-C\equiv CR$], 127.85, 127.13, 127.09, 126.82, 126.77, 125.84 (all s, C_6H_5), 121.82 [dt, $J(Rh,C) = 12.1$, $J(P,C) = 6.0$ Hz, $Rh-C\equiv CR$], 75.96 (s, $=CH-CPh_2OH$), 67.50 (s, $\equiv C-CPh_2OH$), 25.25 (vt, $N = 20.4$ Hz, $PCHCH_3$), 20.30 (s, $PCHCH_3$); signal of $Rh-C\equiv CR$ probably covered by signal of C_6D_6 ; ^{31}P NMR (C_6D_6 , 81.0 MHz): $\delta = 46.94$ [d, $J(Rh,P) = 133.7$ Hz]; $C_{48}H_{65}O_2P_2Rh$ (838.9): calcd C 68.72, H 7.81; found C 68.48, H 7.80.

trans-[Rh(η^1 -Z)-C($\equiv C$ -CMe₂OH)=CH-CMe₂OH](CO)(P*i*Pr₃)₂] (10): A slow stream of CO was passed through a solution of **8** (70 mg, 0.12 mmol) in 3 mL of benzene for 30 s at $10^\circ C$. The color changed from dark blue to bright yellow. After the solvent was removed in vacuo, the residue was worked up as described for **8**. Yellow, only moderately air-sensitive crystals; yield 62 mg (85%); m.p. $105^\circ C$; IR (KBr): $\tilde{\nu} = 3600$ (O-H), 2170 ($C\equiv C$), 1940 ($C\equiv O$), 1470 ($C=C$) cm^{-1} ; 1H NMR (C_6D_6 , 400 MHz): $\delta = 6.94$ [dt, $J(Rh,H) = 2.9$, $J(P,H) = 2.9$ Hz, 1H, $=CHR$], 4.38 (s, 1H, OH), 2.44 (m, 6H, $PCHCH_3$), 1.59 [s, 6H, $=CH-C(CH_3)_2OH$], 1.39 [s, 6H, $\equiv C-C(CH_3)_2OH$], 1.36 [dvt, $N = 13.8$, $J(H,H) = 7.2$ Hz, 18H, $PCHCH_3$], 1.27 [dvt, $N = 13.3$, $J(H,H) = 7.1$ Hz, 18H, $PCHCH_3$], signal of second OH proton not observed; ^{13}C NMR (C_6D_6 , 50.3 MHz): $\delta = 195.46$ [dt, $J(Rh,C) = 56.3$, $J(P,C) = 15.9$ Hz, $Rh-CO$], 151.34 [t, $J(P,C) = 4.1$ Hz, $Rh-C(R)=CHR$], 140.62 [dt, $J(Rh,C) = 25.7$, $J(P,C) = 14.0$ Hz, $Rh-C(R)=CHR$], 106.71 (s, $-C\equiv CR$), 88.75 [dt, $J(Rh,C) = 1.9$, $J(P,C) = 1.6$ Hz, $-C\equiv CR$], 70.28 [dt, $J(Rh,C) = 1.3$, $J(P,C) = 1.3$ Hz, $=CH-CMe_2OH$], 66.13 (s, $\equiv C-CMe_2OH$), 32.14 (s, $=CH-C(CH_3)_2OH$), 31.53 [t, $J(P,C) = 1.9$ Hz, $\equiv C-C(CH_3)_2OH$], 26.42 [dvt, $N = 20.1$, $J(Rh,C) = 1.3$ Hz, $PCHCH_3$], 20.86 and 19.95 (both s, $PCHCH_3$); ^{31}P NMR (C_6D_6 , 162.0 MHz): $\delta = 42.13$ [d, $J(Rh,P) = 134.85$ Hz]; $C_{30}H_{57}O_3P_2Rh$ (618.6): calcd C 56.31, H 9.29; found C 56.61, H 9.53.

trans-[Rh(η^1 -Z)-C($\equiv C$ -CPh₂OH)=CH-CPh₂OH](CO)(P*i*Pr₃)₂] (11): This was prepared as described for **10**, from **9** (110 mg, 0.13 mmol) as starting material. Yellow crystals; yield 87 mg (87%); m.p. $84^\circ C$ (decomp.); IR (KBr): $\tilde{\nu} = 3595$ (O-H), 2100 ($C\equiv C$), 1940 ($C\equiv O$) cm^{-1} ; 1H NMR (C_6D_6 , 200 MHz): $\delta = 8.03$ [dt, $J(Rh,H) = 2.9$, $J(P,H) = 2.9$ Hz, 1H, $=CHR$], 7.82 and 7.00 (both m, 20H, C_6H_5), 5.49 and 2.48 (both s, 1H each, OH), 2.11 (m, 6H, $PCHCH_3$), 1.07 [dvt, $N = 13.7$, $J(H,H) = 7.1$ Hz, 18H, $PCHCH_3$], 1.05 [dvt, $N = 13.3$, $J(H,H) = 6.9$ Hz, 18H, $PCHCH_3$]; ^{13}C NMR (C_6D_6 , 50.3 MHz): $\delta = 195.81$ [dt, $J(Rh,C) = 56.8$, $J(P,C) = 15.9$ Hz, $Rh-CO$], 150.79 and 147.01 (both s, *ipso*- C_6H_5), 147.76 [t, $J(P,C) = 4.3$ Hz, $Rh-C(R)=CHR$], 143.74 [dt, $J(Rh,C) = 26.2$, $J(P,C) = 13.1$ Hz, $Rh-C(R)=CHR$], 128.15, 127.96, 127.32, 126.97, 125.93, 125.87 (all s, C_6H_5),

102.57 (s, $-C\equiv CR$), 93.41 [dt, $J(Rh,C) = 1.8$, $J(P,C) = 1.8$ Hz, $-C\equiv CR$], 76.14 (s, $=CH-CPh_2OH$), 76.04 (s, $\equiv C-CPh_2OH$), 26.12 [dvt, $N = 20.1$, $J(Rh,C) = 1.2$ Hz, $PCHCH_3$], 20.54 and 19.86 (both s, $PCHCH_3$); ^{31}P NMR (C_6D_6 , 162.0 MHz): $\delta = 43.29$ [d, $J(Rh,P) = 132.2$ Hz]; $C_{49}H_{65}O_3P_2Rh$ (866.9): calcd C 67.89, H 7.56; found C 68.26, H 7.62.

trans-[Rh(η^1 -Z)-C($\equiv C$ -CMe₂OH)=CH-CMe₂OH](CNMe)(P*i*Pr₃)₂] (12): A solution of **8** (120 mg, 0.20 mmol) in 3 mL of benzene was treated at $10^\circ C$ with methylisocyanide (10 μL , 0.22 mmol). Immediately, a color change from dark blue to light yellow occurred. After the reaction mixture had been stirred for 1 min, the solvent was removed in vacuo, the residue was extracted with 5 mL of hexane, and the extract was stored at $-30^\circ C$ for 20 h. Yellow crystals precipitated, which were washed with 3×1 mL of pentane ($0^\circ C$) and dried; yield 93 mg (74%); m.p. $113^\circ C$ (decomp.); IR (KBr): $\tilde{\nu} = 3600$ (O-H), 2190 ($C\equiv N$), 2105 ($C\equiv C$) cm^{-1} ; 1H NMR (C_6D_6 , 400 MHz): $\delta = 7.02$ [dt, $J(Rh,H) = 2.5$, $J(P,H) = 2.4$ Hz, 1H, $=CHR$], 5.37 (s, 1H, OH), 2.40 (m, 6H, $PCHCH_3$), 2.14 (brs, 3H, $CNCH_3$), 1.88 (brs, 1H, OH), 1.66 [s, 6H, $=CH-C(CH_3)_2OH$], 1.46 [s, 6H, $\equiv C-C(CH_3)_2OH$], 1.41 [dvt, $N = 13.7$, $J(H,H) = 7.5$ Hz, 18H, $PCHCH_3$], 1.31 [dvt, $N = 12.6$, $J(H,H) = 7.1$ Hz, 18H, $PCHCH_3$]; ^{13}C NMR (C_6D_6 , 50.3 MHz): $\delta = 162.34$ [dt, $J(Rh,C) = 50.0$, $J(P,C) = 18.3$ Hz, $Rh-CNR$], 149.44 [t, $J(P,C) = 2.7$ Hz, $Rh-C(R)=CHR$], 142.32 [dt, $J(Rh,C) = 25.6$, $J(P,C) = 13.4$ Hz, $Rh-C(R)=CHR$], 106.69 (s, $-C\equiv CR$), 90.83 [dt, $J(Rh,C) = 1.8$, $J(P,C) = 1.8$ Hz, $-C\equiv CR$], 70.18 [dt, $J(Rh,C) = 1.2$, $J(P,C) = 1.2$ Hz, $=CH-CMe_2OH$], 66.29 (s, $\equiv C-CMe_2OH$), 32.35 [s, $=CH-C(CH_3)_2OH$], 31.89 [t, $J(P,C) = 1.8$ Hz, $=CH-C(CH_3)_2OH$], 26.17 [dvt, $N = 18.3$, $J(Rh,C) = 1.2$ Hz, $PCHCH_3$], 28.21 (brs, $CNCH_3$), 21.01 and 20.10 (both s, $PCHCH_3$); ^{31}P NMR (C_6D_6 , 81.0 MHz): $\delta = 42.08$ [d, $J(Rh,P) = 142.4$ Hz]; $C_{30}H_{60}NO_2P_2Rh$ (631.7): calcd C 57.05, H 9.58, N 2.22; found C 57.37, H 9.85, N 2.05.

trans-[Rh(η^1 -Z)-C($\equiv C$ -CMe₂OH)=CH-CMe₂OH](CN*n*Bu)(P*i*Pr₃)₂] (13):

This was prepared as described for **12**, from **8** (180 mg, 0.30 mmol) and $CN*n*Bu$ (35 μL , 0.31 mmol) as starting materials. Yellow crystals; yield 150 mg (73%); m.p. $96^\circ C$ (decomp.); IR (KBr): $\tilde{\nu} = 2160$, 2080, 2050 [$(C\equiv N) + (C\equiv C)$] cm^{-1} ; 1H NMR (C_6D_6 , 400 MHz): $\delta = 7.01$ [dt, $J(Rh,H) = 2.8$, $J(P,H) = 2.5$ Hz, 1H, $=CHR$], 5.35 (s, 1H, OH), 2.46 (m, 6H, $PCHCH_3$), 1.95 (brs, 1H, OH), 1.67 [s, 6H, $=CH-C(CH_3)_2OH$], 1.43 [s, 6H, $\equiv C-C(CH_3)_2OH$], 1.43 [dvt, $N = 13.4$, $J(H,H) = 7.0$ Hz, 18H, $PCHCH_3$], 1.33 [dvt, $N = 12.7$, $J(H,H) = 6.9$ Hz, 18H, $PCHCH_3$], 0.95 [s, 9H, $CNC(CH_3)_3$]; ^{13}C NMR (C_6D_6 , 100.6 MHz): $\delta = 155.45$ [dt, $J(Rh,C) = 51.0$, $J(P,C) = 17.3$ Hz, $Rh-CNR$], 148.77 [t, $J(P,C) = 3.5$ Hz, $Rh-C(R)=CHR$], 142.77 [dt, $J(Rh,C) = 25.6$, $J(P,C) = 13.3$ Hz, $Rh-C(R)=CHR$], 102.38 (s, $-C\equiv CR$), 90.49 (brs, $-C\equiv CR$), 70.10 (s, $=CH-CMe_2OH$), 66.34 (s, $\equiv C-CMe_2OH$), 55.04 [s, $CNC(CH_3)_3$], 32.37 [s, $\equiv C-C(CH_3)_2OH$], 31.91 [s, $=CH-C(CH_3)_2OH$], 29.78 [s, $CNC(CH_3)_3$], 26.18 (vt, $N = 18.3$ Hz, $PCHCH_3$), 21.70 and 20.06 (both s, $PCHCH_3$); ^{31}P NMR (C_6D_6 , 162.0 MHz): $\delta = 41.26$ [d, $J(Rh,P) = 142.9$ Hz]; $C_{33}H_{66}NO_2P_2Rh$ (673.8): calcd C 58.83, H 9.87, N 2.08; found C 59.12, H 10.07, N 1.91.

trans-[Rh(η^1 -Z)-C($\equiv C$ -CPh₂OH)=CH-CPh₂OH](CNMe)(P*i*Pr₃)₂] (14):

This was prepared as described for **12**, from **9** (176 mg, 0.21 mmol) and methylisocyanide (10 μL , 0.22 mmol) as starting materials. Yellow solid; yield 137 mg (74%); m.p. $119^\circ C$ (decomp.); IR (C_6H_6): $\tilde{\nu} = 3595$ (O-H), 2100 ($C\equiv C$), 2190 ($C\equiv N$) cm^{-1} ; 1H NMR (C_6D_6 , 200 MHz): $\delta = 8.11$ [dt, $J(Rh,H) = 2.9$, $J(P,H) = 2.5$ Hz, 1H, $=CHR$], 7.90 and 7.87 (both m, 4H each, *o*- C_6H_5), 7.03 (m, 12H, C_6H_5), 6.53 and 2.67 (both s, 1H each, OH), 2.07 (m, 6H, $PCHCH_3$), 1.17 [dvt, $N = 13.3$, $J(H,H) = 6.9$ Hz, 18H, $PCHCH_3$], 1.10 [dvt, $N = 13.0$, $J(H,H) = 6.9$ Hz, 18H, $PCHCH_3$]; ^{31}P NMR (C_6D_6 , 162.0 MHz): $\delta = 42.53$ [d, $J(Rh,P) = 139.5$ Hz].

trans-[Rh(η^1 -Z)-C($\equiv C$ -CPh₂OH)=CH-CPh₂OH](CN*n*Bu)(P*i*Pr₃)₂] (15):

This was prepared as described for **12**, from **9** (111 mg, 0.13 mmol) and $CN*n*Bu$ (16 μL , 0.14 mmol) as starting materials. Yellow crystals; yield 84 mg (69%); m.p. $113^\circ C$ (decomp.); IR (C_6H_6): $\tilde{\nu} = 3620$ (O-H), 2160, 2090, 2060 [$(C\equiv N) + (C\equiv C)$] cm^{-1} ; 1H NMR (C_6D_6 , 200 MHz): $\delta = 8.11$ [dt, $J(Rh,H) = 3.1$, $J(P,H) = 2.9$ Hz, 1H, $=CHR$], 7.92 and 7.82 (both m, 4H each, *o*- C_6H_5), 6.98 (m, 12H, C_6H_5), 6.48 [d, $J(Rh,H) = 1.1$ Hz, 1H, OH], 2.66 (s, 1H, OH), 2.12 (m, 6H, $PCHCH_3$), 1.22 [dvt, $N = 13.5$, $J(H,H) = 6.9$ Hz, 18H, $PCHCH_3$], 1.12 [dvt, $N = 12.6$, $J(H,H) = 6.9$ Hz, 18H, $PCHCH_3$], 0.87 [s, 9H, $CNC(CH_3)_3$]; ^{31}P NMR (C_6D_6 , 162.0 MHz): $\delta = 42.45$ [d, $J(Rh,P) = 141.0$ Hz]; $C_{33}H_{74}N_2O_2P_2Rh$ (922.0): calcd C 69.04, H 8.09, N 1.52; found C 69.06, H 8.00, N 1.43.

Reaction of 10 with CF_3CO_2H :

A solution of **10** (40 mg, 0.06 mmol) in 0.5 mL of [D_6]acetone was treated in an NMR tube at $10^\circ C$ with CF_3CO_2H (5 μL , 0.06 mmol). A quick change of color from bright yellow to pale yellow occurred. The resulting compounds were characterized by 1H NMR, ^{13}C NMR, and ^{31}P NMR spectroscopy as *trans*-[Rh(η^1 -O₂CCF₃)(CO)(P*i*Pr₃)₂] (**16**) [16] and (*E*)-Me₂(OH)C-C \equiv C-CH=CH-CMe₂OH (**17**) [27].

[RhH(η^1 -CMe₂OH)₂(CO)(P*i*Pr₃)₂] (18):

A slow stream of CO was passed through a solution of **5** (90 mg, 0.15 mmol) in 3 mL of benzene for 30 s at $10^\circ C$. After the reaction mixture had been stirred for 1 min, the solvent was removed in vacuo, and the residue was washed with 3×1 mL of pentane ($0^\circ C$) and dried. White microcrystalline solid; yield 85 mg (90%); m.p. $109^\circ C$ (decomp.); IR (KBr): $\tilde{\nu} = 3600$ (O-H), 2100, 2090, 2010, 1990 [$(C\equiv C) + (C\equiv O)$] cm^{-1} ; 1H NMR

(C_6D_6 , 200 MHz): δ = 2.79 (m, 6H, $PCHCH_3$), 1.57 (s, 2H, OH), 1.49 [s, 12H, $C(CH_3)_2OH$], 1.28 [dvt, N = 13.8, $J(H,H)$ = 7.3 Hz, 36H, $PCHCH_3$], -9.02 [dt, $J(Rh,H)$ = 9.4, $J(P,H)$ = 9.4 Hz, 1H, RhH]; ^{31}P NMR (C_6D_6 , 81.0 MHz): δ = 56.74 [d, $J(Rh,P)$ = 90.1 Hz]; $C_{29}H_{57}O_3P_2Rh$ (618.1): calcd C 56.31, H 9.30; found C 55.99, H 9.61.

[$RhH(C\equiv C-CPh_2OH)_2(CO)(P^iPr_3)_2$] (19): This was prepared as described for **18**, from **6** (80 mg, 0.10 mmol) as starting material. White, fairly air-stable crystals; yield 69 mg (84%); m.p. 94 °C (decomp.); IR (KBr): $\tilde{\nu}$ = 3580 (O-H), 2100, 2010, 2000 [$(C\equiv C) + (C\equiv O)$ cm^{-1}]; 1H NMR (C_6D_6 , 200 MHz): δ = 7.73 and 7.23 (both m, 20H, C_6H_5), 2.56 (m, 6H, $PCHCH_3$), 2.37 (s, 2H, OH), 1.13 [dvt, N = 14.3, $J(H,H)$ = 7.3 Hz, 36H, $PCHCH_3$], -8.91 [dt, $J(Rh,H)$ = 8.8, $J(P,H)$ = 8.8 Hz, 1H, RhH]; ^{31}P NMR (C_6D_6 , 81.0 MHz): δ = 57.62 [d, $J(Rh,P)$ = 87.2 Hz]; $C_{49}H_{65}O_3P_2Rh$ (866.9): calcd C 67.89, H 7.56; found C 67.85, H 7.60.

[$RhH(C\equiv C-CiPr_2OH)_2(CO)(P^iPr_3)_2$] (20): This was prepared as described for **18**, from **7** (80 mg, 0.11 mmol) as starting material. White microcrystalline solid; yield 77 mg (92%); m.p. 114 °C (decomp.); IR (KBr): $\tilde{\nu}$ = 3610 (O-H), 2100, 2010, 2000 [$(C\equiv C) + (C\equiv O)$ cm^{-1}]; 1H NMR (C_6D_6 , 200 MHz): δ = 2.77 (m, 6H, $PCHCH_3$), 1.92 [m, 4H, $-C(CH(CH_3)_2)_2OH$], 1.27 [dvt, N = 14.3, $J(H,H)$ = 7.3 Hz, 36H, $PCHCH_3$], 1.15 and 1.11 [both d, $J(H,H)$ = 6.4 Hz, 12H each, $-C(CH(CH_3)_2)_2OH$], -9.12 [dt, $J(Rh,H)$ = 8.5, $J(P,H)$ = 8.5 Hz, 1H, RhH], signal of OH protons not observed; ^{31}P NMR (C_6D_6 , 81.0 MHz): δ = 57.80 [d, $J(Rh,P)$ = 90.1 Hz]; $C_{37}H_{73}O_3P_2Rh$ (730.8): calcd C 60.81, H 10.07; found C 61.12, H 9.84.

trans-[$Rh(C\equiv C-CMe_2OH)(CO)(P^iPr_3)_2$] (21): A solution of **18** (85 mg, 0.14 mmol) in 3 mL of benzene was stirred for 15 h at room temperature. The solvent was removed in vacuo, the residue was extracted with 4 mL of pentane, and the extract was stored for 20 h at -30 °C. A yellow solid precipitated, which was separated from the solution, washed with 3 \times 1 mL of pentane (0 °C) and dried; yield 67 mg (91%); m.p. 125 °C; IR (KBr): $\tilde{\nu}$ = 3600 (O-H), 2095 ($C\equiv C$), 1940 ($C\equiv O$) cm^{-1} ; 1H NMR (C_6D_6 , 200 MHz): δ = 2.49 (m, 6H, $PCHCH_3$), 1.61 (s, 1H, OH), 1.55 [s, 6H, $C(CH_3)_2OH$], 1.29 [dvt, N = 13.9, $J(H,H)$ = 7.1 Hz, 36H, $PCHCH_3$]; ^{13}C NMR (C_6D_6 , 100.6 MHz): δ = 193.03 [dt, $J(Rh,C)$ = 58.8, $J(P,C)$ = 13.5 Hz, Rh-CO], 123.56 [dt, $J(Rh,C)$ = 11.5, $J(P,C)$ = 2.7 Hz, Rh-C \equiv CR], 111.72 [dt, $J(Rh,C)$ = 41.4, $J(P,C)$ = 21.7 Hz, Rh-C \equiv CR], 65.97 (s, $\equiv C-CMe_2OH$), 32.60 [s, $C(CH_3)_2OH$], 26.00 (vt, N = 21.4 Hz, $PCHCH_3$), 20.44 (s, $PCHCH_3$); ^{31}P NMR (C_6D_6 , 81.0 MHz): δ = 53.90 [d, $J(Rh,P)$ = 127.9 Hz]; $C_{24}H_{40}O_2P_2Rh$ (534.5): calcd C 53.93, H 9.24; found C 54.32, H 9.10.

trans-[$Rh(C\equiv C-CPh_2OH)(CO)(P^iPr_3)_2$] (22): This was prepared as described for **21**, from **19** (95 mg, 0.11 mmol) as starting material. Yellow air-stable crystals; yield 64 mg (88%); m.p. 121 °C; IR (KBr): $\tilde{\nu}$ = 3595 (O-H), 2100 ($C\equiv C$), 1935 ($C\equiv O$) cm^{-1} ; 1H NMR (C_6D_6 , 400 MHz): δ = 7.82, 7.18, 7.06 (all m, 10H, C_6H_5), 2.47 (m, 6H, $PCHCH_3$), 2.40 (s, 1H, OH), 1.23 [dvt, N = 13.9, $J(H,H)$ = 7.1 Hz, 36H, $PCHCH_3$]; ^{13}C NMR (C_6D_6 , 100.6 MHz): δ = 196.02 [dt, $J(Rh,C)$ = 58.8, $J(P,C)$ = 13.0 Hz, Rh-CO], 148.18, 127.81, 127.15, 126.76 (all s, C_6H_5), 121.00 [dt, $J(Rh,C)$ = 42.4, $J(P,C)$ = 21.2 Hz, Rh-C \equiv CR], 119.53 [dt, $J(Rh,C)$ = 11.8, $J(P,C)$ = 2.4 Hz, Rh-C \equiv CR], 75.68 (s, $\equiv C-CPh_2OH$), 26.01 (vt, N = 21.4 Hz, $PCHCH_3$), 20.35 (s, $PCHCH_3$); ^{31}P NMR (C_6D_6 , 162.0 MHz): δ = 53.85 [d, $J(Rh,P)$ = 126.8 Hz]; $C_{34}H_{52}O_2P_2Rh$ (658.7): calcd C 62.00, H 8.11; found C 62.26, H 8.40.

trans-[$Rh(C\equiv C-CiPr_2OH)(CO)(P^iPr_3)_2$] (23): This was prepared as described for **21**, from **20** (75 mg, 0.10 mmol) as starting material. Yellow air-stable crystals; yield 54 mg (89%); m.p. 126 °C (decomp.); IR (KBr): $\tilde{\nu}$ = 3610 (O-H), 2080 ($C\equiv C$), 1945 ($C\equiv O$) cm^{-1} ; 1H NMR (C_6D_6 , 200 MHz): δ = 2.52 (m, 6H, $PCHCH_3$), 2.00 [spt, $J(H,H)$ = 6.6 Hz, 2H, $-C(CH(CH_3)_2)_2OH$], 1.45 (s, 1H, OH), 1.28 [dvt, N = 13.9, $J(H,H)$ = 7.3 Hz, 36H, $PCHCH_3$], 1.19 and 1.17 [both d, $J(H,H)$ = 6.6 Hz, 6H each, $-C(CH(CH_3)_2)_2OH$]; ^{13}C NMR (C_6D_6 , 100.6 MHz): δ = 195.82 [dt, $J(Rh,C)$ = 58.2, $J(P,C)$ = 14.0 Hz, Rh-CO], 119.34 [dt, $J(Rh,C)$ = 11.6, $J(P,C)$ = 2.8 Hz, Rh-C \equiv CR], 118.03 [dt, $J(Rh,C)$ = 42.1, $J(P,C)$ = 20.8 Hz, Rh-C \equiv CR], 78.19 (s, $\equiv C-CiPr_2OH$), 35.29 [s, $-C(CH(CH_3)_2)_2OH$], 26.13 (vt, N = 21.8 Hz, $PCHCH_3$), 20.48 (s, $PCHCH_3$), 18.59 and 17.20 [both s, $-C(CH(CH_3)_2)_2OH$]; ^{31}P NMR (C_6D_6 , 81.0 MHz): δ = 53.31 [d, $J(Rh,P)$ = 127.5 Hz]; $C_{28}H_{50}O_2P_2Rh$ (590.6): calcd C 56.94, H 9.73; found C 56.74, H 10.02.

[$RhH(C\equiv C-CMe_2OH)_2(CNMe)(P^iPr_3)_2$] (24): A solution of **5** (90 mg, 0.15 mmol) in 3 mL of benzene was treated with methylisocyanide (8 μ L, 0.17 mmol) at 10 °C; a color change from white to pale yellow resulted. After the reaction mixture had been stirred for 1 min, the solvent was removed in vacuo, the residue was washed with 3 \times 1 mL of pentane (0 °C) and dried. Pale yellow crystals; yield 84 mg (87%); m.p. 127 °C; IR (KBr): $\tilde{\nu}$ = 3600 (O-H), 2190 ($C\equiv N$), 2105 ($C\equiv C$) cm^{-1} ; 1H NMR (C_6D_6 , 200 MHz): δ = 2.90 (m, 6H, $PCHCH_3$), 1.99 (br s, 3H, $CNCH_3$), 1.63 (brs, 2H, OH), 1.56 [s, 12H, $C(CH_3)_2OH$], 1.37 [dvt, N = 13.8, $J(H,H)$ = 6.9 Hz, 36H, $PCHCH_3$], -10.81 [dt, $J(Rh,H)$ = 9.4, $J(P,H)$ = 10.8 Hz, 1H, RhH]; ^{31}P NMR (C_6D_6 , 81.0 MHz): δ = 54.69 [d, $J(Rh,P)$ = 93.0 Hz]; $C_{30}H_{40}NO_2P_2Rh$ (631.7): calcd C 57.05, H 9.58, N 2.22; found C 57.36, H 9.85, N 2.28.

[$RhH(C\equiv C-CPh_2OH)_2(CNMe)(P^iPr_3)_2$] (25): This was prepared as described for **24**, from **6** (70 mg, 0.08 mmol) and methylisocyanide (4 μ L, 0.09 mmol) as starting materials. White air-stable crystals; yield 63 mg (86%); m.p. 128 °C (decomp.); IR (KBr): $\tilde{\nu}$ = 3600 (O-H), 2190 ($C\equiv N$), 2100 ($C\equiv C$) cm^{-1} ; 1H NMR (C_6D_6 , 200 MHz): δ = 7.83 and 7.10 (both m, 20H, C_6H_5), 2.69 (m, 6H, $PCHCH_3$), 2.48 (s, 2H, OH), 2.10 (brs, 3H, $CNCH_3$), 1.22 [dvt, N = 13.8, $J(H,H)$ = 6.9 Hz, 36H, $PCHCH_3$], -10.69 [dt, $J(Rh,H)$ = 10.4, $J(P,H)$ = 10.3 Hz, 1H, RhH]; ^{13}C NMR (C_6D_6 , 50.3 MHz): δ = 148.94, 127.66, 127.08, 126.47 (all s, C_6H_5), 107.53 [d, $J(Rh,C)$ = 7.3 Hz, $-C\equiv CR$], 106.07 [dt, $J(Rh,C)$ = 34.2, $J(P,C)$ = 14.6 Hz, $-C\equiv CR$], 75.73 (s, $\equiv C-CPh_2OH$), 27.72 (s, $CNCH_3$), 25.27 (vt, N = 24.4 Hz, $PCHCH_3$), 19.25 (s, $PCHCH_3$); signal of CNMe carbon atom not observed; ^{31}P NMR (C_6D_6 , 81.0 MHz): δ = 55.23 [d, $J(Rh,P)$ = 93.0 Hz]; $C_{50}H_{68}NO_2P_2Rh$ (880.0): calcd C 68.25, H 7.79, N 1.59; found C 68.55, H 7.82, N 1.53.

[$RhH(C\equiv C-CPh_2OH)_2(CN^iBu)(P^iPr_3)_2$] (26): This was prepared as described for **24**, from **6** (130 mg, 0.15 mmol) and CN^iBu (18 μ L, 0.16 mmol) as starting materials. White air-stable crystals; yield 129 mg (90%); m.p. 127 °C (decomp.); IR (KBr): $\tilde{\nu}$ = 3600, 3580 (O-H), 2170 ($C\equiv N$), 2100 ($C\equiv C$) cm^{-1} ; 1H NMR (C_6D_6 , 200 MHz): δ = 7.85 (m, 8H, $o-C_6H_5$), 7.07 (m, 12H, C_6H_5), 2.66 (m, 6H, $PCHCH_3$), 2.46 (s, 2H, OH), 1.21 [dvt, N = 13.8, $J(H,H)$ = 6.9 Hz, 36H, $PCHCH_3$], 1.09 [s, 9H, $CNC(CH_3)_3$], -10.76 [dt, $J(Rh,H)$ = 9.3, $J(P,H)$ = 10.8 Hz, 1H, RhH]; ^{13}C NMR (C_6D_6 , 50.3 MHz): δ = 149.03 (s, *ipso*- C_6H_5), 127.66, 127.13, 126.45 (all s, C_6H_5), 107.58 [d, $J(Rh,C)$ = 7.3 Hz, $-C\equiv CR$], 106.58 [dt, $J(Rh,C)$ = 34.2, $J(P,C)$ = 14.7 Hz, $-C\equiv CR$], 75.68 (s, $\equiv C-CPh_2OH$), 55.74 [s, $CN-C(CH_3)_3$], 29.69 [s, $CN-C(CH_3)_3$], 25.44 (vt, N = 24.4 Hz, $PCHCH_3$), 19.35 (s, $PCHCH_3$); signal of CN^iBu carbon atom not observed; ^{31}P NMR (C_6D_6 , 81.0 MHz): δ = 55.53 [d, $J(Rh,P)$ = 91.5 Hz]; $C_{53}H_{74}NO_2P_2Rh$ (922.0): calcd C 69.04, H 8.09, N 1.52; found C 69.47, H 8.51, N 1.41.

[$RhH(C\equiv C-CiPr_2OH)_2(CNMe)(P^iPr_3)_2$] (27): This was prepared as described for **24**, from **7** (85 mg, 0.12 mmol) and methylisocyanide (8 μ L, 0.12 mmol) as starting materials. White microcrystalline solid; yield 81 mg (90%); m.p. 131 °C; IR (KBr): $\tilde{\nu}$ = 3610 (O-H), 2180 ($C\equiv N$), 2100 ($C\equiv C$) cm^{-1} ; 1H NMR (C_6D_6 , 200 MHz): δ = 2.86 (m, 6H, $PCHCH_3$), 2.28 (brs, 3H, $CNCH_3$), 1.98 [m, 4H, $-C(CH(CH_3)_2)_2OH$], 1.38 (brs, 2H, OH), 1.34 [dvt, N = 13.3, $J(H,H)$ = 6.9 Hz, 36H, $PCHCH_3$], 1.20 and 1.16 [both d, $J(H,H)$ = 8.4 Hz, 12H each, $-C(CH(CH_3)_2)_2OH$], -10.95 [dt, $J(Rh,H)$ = 10.4, $J(P,H)$ = 10.3 Hz, 1H, RhH]; ^{13}C NMR (C_6D_6 , 50.3 MHz): δ = 152.92 [brd, $J(Rh,C)$ = 38.2 Hz, Rh-CN], 105.10 [d, $J(Rh,C)$ = 7.6 Hz, Rh-C \equiv CR], 99.81 [dt, $J(Rh,C)$ = 34.3 Hz, $J(P,C)$ = 15.3 Hz, Rh-C \equiv CR], 78.09 (s, $\equiv C-CiPr_2OH$), 35.08 [s, $-C(CH(CH_3)_2)_2OH$], 27.24 (brs, $CN-CH_3$), 25.02 (vt, N = 25.4 Hz, $PCHCH_3$), 19.21 (s, $PCHCH_3$), 18.37 and 17.01 [both s, $-C(CH(CH_3)_2)_2OH$]; ^{31}P NMR (C_6D_6 , 81.0 MHz): δ = 55.08 [d, $J(Rh,P)$ = 94.5 Hz]; $C_{35}H_{76}NO_2P_2Rh$ (743.9): calcd C 61.36, H 10.30, N 1.88; found C 61.06, H 10.47, N 1.95.

trans-[$RhCl(\eta^2-Ph_2C=C=C=C=CPh_2)(P^iPr_3)_2$] (29):

Method a: A solution of **9** (140 mg, 0.17 mmol) in 1 mL of benzene was passed through a column of Al_2O_3 (acidic, activity grade I, height of column 8 cm). [Note: Al_2O_3 acidic, commercially available from Aldrich or Woelms Pharma, contains ca. 2 mg of Cl⁻ for 1 g of Al_2O_3 .] Almost instantaneously, the color changed from dark blue to red. With benzene, two red fractions were eluted, of which the second (slow-running) contained *trans*-[$RhCl(=C=C=CPh_2)(P^iPr_3)_2$] (**28**); yield 21 mg (19%). The first fraction was brought to dryness in vacuo; the residue was washed with 2 \times 3 mL of pentane (0 °C) and then dissolved in 3 mL of benzene. After the solution had been stirred for 2 h at room temperature, the solvent was removed, the residue was washed twice with 2 mL of pentane (0 °C) each and dried. Red air-stable crystals; yield 98 mg (70%).

Method b: Analogous to the procedure described for method a but with **6** (120 mg, 0.14 mmol) as starting material; yield 78 mg (65%).

Method c: A solution of **32** (100 mg, 0.11 mmol) in 2 mL of benzene was treated at 10 °C with a solution of **31** (83 mg, 0.22 mmol) in 3 mL of benzene and, after it had been warmed to room temperature, stirred for 2 h. The solvent was removed, the residue was washed with 3 \times 5 mL of pentane (0 °C) and dried; yield 176 mg (96%).

Method d: A solution of **33** (50 mg, 0.06 mmol) in 1 mL of benzene was stirred for 2 h at room temperature and worked up as described for method c. Red crystals were isolated; yield 49 mg (98%); m.p. 185 °C; IR (KBr): $\tilde{\nu}$ = 2000 ($C=C=C$) cm^{-1} ; 1H NMR (C_6D_6 , 200 MHz): δ = 8.69, 7.65, 7.48 (all m, 2H each, *o*- C_6H_5), 7.20 (m, 14H, C_6H_5), 2.03 (m, 6H, $PCHCH_3$), 1.12 [dvt, N = 14.2, $J(H,H)$ = 7.1 Hz, 18H, $PCHCH_3$], 0.87 [dvt, N = 12.8, $J(H,H)$ = 6.7 Hz, 18H, $PCHCH_3$]; ^{13}C NMR (C_6D_6 , 100.6 MHz): δ = 163.70 (s, $=C=$), 141.54, 140.77, 139.56, 138.99 (all s, *ipso*- C_6H_5), 135.33 (s, $=C=$), 131.85 [dt, $J(Rh,C)$ = 20.2, $J(P,C)$ = 4.9 Hz, Rh-C], 130.08, 129.24, 128.87, 128.80, 128.61, 128.60, 128.54, 128.44, 127.88, 127.45, 127.42, 126.90 (all s, C_6H_5), 123.29 (s, CPH_2), 117.54 [dt, $J(Rh,C)$ = 16.6, $J(P,C)$ = 4.9 Hz, Rh-C], 117.12 (s, CPH_2), 23.88 (vt, N = 19.5 Hz, $PCHCH_3$), 20.89 and 19.63 (both s, $PCHCH_3$); ^{31}P NMR (C_6D_6 , 81.0 MHz): δ = 32.49 [d, $J(Rh,P)$ = 111.9 Hz]; $C_{48}H_{62}ClP_2Rh$ (839.3): calcd C 68.69, H 7.45; found C 68.61, H 7.79.

trans-[$RhCl(\eta^2-Ph_2C=C=C=C=C=CPh_2)(P^iPr_3)_2$] (**33**): A solution of **32** (66 mg, 0.07 mmol) in 0.5 mL of toluene was treated at -30 °C with a solution of **31** (53 mg, 0.14 mmol) in 1 mL of toluene. The color changed from violet to yellow. After the

solution had been stirred for 1 min at -30°C , the solvent was removed, the residue was washed with $3 \times 2\text{ mL}$ of pentane (-20°C) and dried. Yellow air-stable crystals; yield 88 mg (73%); m.p. 216°C ; IR (KBr): $\tilde{\nu} = 1590\text{ (C}=\text{C)}\text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3 , 200 MHz): $\delta = 7.33\text{ (m, 20 H, C}_6\text{H}_5\text{)}, 2.56\text{ (m, 6 H, PCHCH}_3\text{)}, 1.19\text{ [d vt, } N = 13.0, J(\text{H,H}) = 6.4\text{ Hz, 36 H, PCHCH}_3\text{]}; ^{31}\text{P NMR}$ (CDCl_3 , 81.0 MHz): $\delta = 36.89\text{ [d, } J(\text{Rh,P}) = 112.7\text{ Hz]; C}_{48}\text{H}_{62}\text{ClP}_2\text{Rh}$ (839.3): calcd C 68.69, H 7.45; found C 68.10, H 6.97.

Reaction of 29 with CO: A slow stream of CO was passed through a solution of 29 (75 mg, 0.09 mmol) in 1 mL of benzene for 1 min at room temperature. After the solution had been stirred for 30 min at 20°C , a red solid precipitated, which was separated from the solution, washed with $2 \times 2\text{ mL}$ of hexane, and dried; yield 19 mg (57%). The solid was identified by elemental analysis and mass spectra as 31. The remaining solution was brought to dryness in vacuo, and the orange residue characterized by IR, $^1\text{H NMR}$, and $^{31}\text{P NMR}$ spectroscopy as 30 [18]; yield 40 mg (91%).

X-ray structure determination of compounds 7 and 29 [28]: Single crystals of 7 were grown from diethyl ether at -20°C and from a solution of 29 in toluene at room temperature. Crystal data collection parameters are summarized in Table 1. Intensity data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (SHELXS-86). Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by the full-matrix least-squares method (Enraf–Nonius SDP) [29]. The positions of the hydrogen atoms were calculated according to ideal geometry (distance C–H = 0.95 \AA) and used only in structure factor calculation. The 1:1 disordered hydrides of 7 were found by a final Fourier synthesis and the corresponding positions were taken with a weighting scheme of 0.5 to 0.5 and refined isotropically. For other details see Table 1.

Table 1. Crystal structure data of compounds 7 and 29.

	7	29
formula	$\text{C}_{36}\text{H}_{72}\text{O}_2\text{P}_2\text{Rh}$	$\text{C}_{48}\text{H}_{62}\text{ClP}_2\text{Rh}$
mol. mass	702.83	839.33
cryst. size [mm]	$0.35 \times 0.2 \times 0.15$	$0.33 \times 0.40 \times 0.50$
cryst. system	triclinic	monoclinic
space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a [\AA]	8.1896(4)	13.217(7)
b [\AA]	12.907(1)	17.068(6)
c [\AA]	19.589(2)	20.25(1)
α [$^{\circ}$]	83.085(9)	90
β [$^{\circ}$]	88.888(8)	105.23(3)
γ [$^{\circ}$]	76.393(8)	90
V [\AA^3]	1997.8(3)	4408(1)
Z	2	4
d_{calc} [g cm^{-3}]	1.17	1.26
diffractometer	Enraf–Nonius CAD4	Enraf–Nonius CAD4
radiation (graphite-monochromated)	$\text{MoK}\alpha$	$\text{MoK}\alpha$
T [K]	295	295
μ [cm^{-1}]	5.2	5.4
transmission min. [%]	98.4	96.5
h, k, l	$+8, \pm 13, \pm 20$	$+13, +17, \pm 21$
scan method	$\omega/2\theta$	ω/θ
2θ (max) [$^{\circ}$]	44	44
absorption correction	not applied	ψ -scan
total reflections	5327	5901
unique reflections	4903	5323
observed reflections	4060	3340
$[F_o > 3\sigma(F_o)]$		
parameters refined	378	469
R	0.024	0.043
R_w	0.028	0.053
reflections/parameter ratio	10.74	7.12
residual electron density	$+0.18/-0.28$	$+0.53/-0.44$
$[\text{e \AA}^{-3}]$		
$F(000)$	760	1768

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