Mononuclear (Allenylidene)metal Complexes of a d^8 System: Synthesis and Molecular Structure of *trans*-[RhCl(=C=C=CRR')($PiPr_3$)$_2$][1]

Helmut Werner,* Thomas Rappert, Ralf Wiedemann, Justin Wolf, and Norbert Mahr

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Received February 22, 1994®

The reaction of[RhCl($PiPr_3$)$_2$] (1) with 1-alkynols HC≡CCRR'OH leads to the formation of either (alkyne)- or (alkynyl)hydridorhodium complexes as the first isolable products. In toluene at room temperature (R = H, Me, R' = Ph; R, R' = $C_{12}H_8$) or on irradiation (R = R' = *i*Pr), the initially formed compounds smoothly rearrange to give the isomeric (vinylidene)rhodium derivatives *trans*-[RhCl(=C=CHCRR'OH)($PiPr_3$)$_2$] (8–11). On treatment with alumina or traces of acid, compounds 8–11 eliminate water to give the four-coordinate rhodium allenylidenes *trans*-[RhCl(=C=C=CRR')($PiPr_3$)$_2$] (12, R = H, R' = Ph; 13, R, R' = $C_{12}H_8$) or a mixture of isomeric (allenylidene)- and (vinylvinylidene)metal complexes. These mixtures are converted upon reaction with acidic Al_2O_3 to give pure samples of *trans*-[RhCl(=C=CHC(Ph)=CH_2)-($PiPr_3$)$_2$] (16) and *trans*-[RhCl(=C=CHC(*i*Pr)=CMe_2)($PiPr_3$)$_2$] (17) in nearly quantitative yields. From 1 and HC≡CCPh(*o*-Tol)OH, the complete series of (alkyne)-, (alkynyl)hydrido-, (vinylidene)-, and (allenylidene)rhodium compounds 18–21 has been prepared, and the molecular structure of *trans*-[RhCl(=C=C=CPh(*o*-Tol))($PiPr_3$)$_2$] (21) has been determined. Crystallographic data: orthorhombic, space group $Pca2_1$ (No. 29), a = 17.804(4) Å, b = 10.891(1) Å, c = 17.934(5) Å, V = 3477(1) Å^3, Z = 4. The Rh–C distance in 21 is somewhat longer than in related (vinylidene)rhodium complexes but is almost identical with that in rhodium carbenes.

Introduction

In the wake of ever-expanding research on transition-metal vinylidene complexes [L_nM=C=CRR'] over the last decade,[2] analogous metal allenylidene derivatives [L_nM=C=C=CRR'] have equally attracted considerable interest in recent years. Although several synthetic routes have been developed to obtain these cumulated π systems,[3] the most versatile seems to be the use of terminal alkynols HC≡CCR_2OH as starting materials for the generation of the M=C=C=CR_2 chain. It was Selegue who first showed in his pioneering work that the electron-rich ruthenium complex [C_5H_5Ru(PMe_3)$_2$Cl] reacts with HC≡CCPh_2OH and NH_4PF_6 in ethanol to afford the PF_6 salt of the cationic metal allenylidene [C_5H_5Ru(=C=C=CPh_2)(PMe_3)$_2$]$^+$ in 76% yield.[4] With regard to the mechanism of this reaction, the author assumed that after alkyne coordination a rearrangement occurs to give a CPh_2OH-substituted vinylidene compound as an intermediate which spontaneously dehydrates to form the final product.[4]

As part of our work on *metallaallenes* [L_nM=C=CRR'] (where M is Ru, Os, Rh, and Ir),[5] we recently reported that the γ-functionalized 1-alkynes HC≡C$CR(CH_3)X$ (R = H, CH_3; X = OH, Cl, NH_2) react with [RhCl($PiPr_3$)$_2$]$_n$ to give the square-planar (vinylidene)rhodium complexes *trans*-[RhCl(=C=CHC$R(CH_3)X$)($PiPr_3$)$_2$], which on treatment with Al_2O_3 or traces of acids undergo elimination of HX to yield the vinylvinylidene derivatives *trans*-[RhCl-(=C=CHC(R)=CH_2)($PiPr_3$)$_2$].[6,7] On reaction with HC≡CCPh_2OH, the rhodium diphenylallenylidene complex *trans*-[RhCl(=C=C=CPh_2)($PiPr_3$)$_2$] was obtained.[7] In continuation of these studies we now report in more detail about the rhodium-mediated stepwise conversion of acetylenic alcohols HC≡CCRR'OH to the isomeric vinylidenes :C=CHCRR'OH and finally to the allenylidenes :C=C=CRR'. This work includes the synthesis of the first (allenylidene)rhodium complex where one of the substituents on the γ-carbon atom is hydrogen as well as the first X-ray crystal structure analysis of a compound with a Rh=C=C=CRR' chain.

Results and Discussion

Alkyne, Alkynyl Hydrido, and Vinylidene Complexes from Alkynols. The coordinatively unsaturated

• Abstract published in *Advance ACS Abstracts,* June 1, 1994.

(1) Vinylidene Transition-Metal Complexes. 29. Part 28: Werner, H.; Baum, M.; Windmüller, B. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, in press.

(2) Reviews: (a) Bruce, M. I. *Chem. Rev.* **1991,** *91,* 197–257. (b) Antonova, A. B.; Johansson, A. A. *Usp. Khim.* **1989,** *58,* 1197–1230. (c) Werner, H. *Angew. Chem.* **1990,** *102,* 1109–1121; *Angew. Chem., Int. Ed. Engl.* **1990,** *29,* 1077–1089.

(3) Inter alia: (a) Fischer, E. O.; Kalder, H. J.; Frank, A.; Köhler, F. H.; Huttner, G. *Angew. Chem.* **1976,** *88,* 683–684; *Angew. Chem., Int. Ed. Engl.* **1976,** *15,* 623–624. (b) Berke, H. *Chem. Ber.* **1980,** *113,* 1370–1376. (c) Berke, H.; Härter, P.; Huttner, G.; Zsolnai, L. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981,** *36,* 929–937. (d) Berke, H.; Huttner, G.; von Seyerl, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981,** *36,* 1277–1288. (e) Berke, H.; Härter, P.; Huttner, G.; von Seyerl, J. *J. Organomet. Chem.* **1981,** *219,* 317–327. (f) Berke, H.; Grössmann, U.; Huttner, G.; Zsolnai, L. *Chem. Ber.* **1984,** *117,* 3432–3442. (g) Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Chechulina, I. N.; Derunov, V. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1982,** 2632–2633. (h) Binger, P.; Müller, P.; Wenz, R.; Mynott, R. *Angew. Chem.* **1990,** *102,* 1070–1071; *Angew. Chem., Int. Ed. Engl.* **1990,** *29,* 1037–1038. (i) Duetsch, M.; Stein, F.; Lackmann, R.; Pohl, E.; Herbst-Irmer, R.; de Meijere, A. *Chem. Ber.* **1992,** *125,* 2051–2065.

(4) Selegue, J. P. *Organometallics* **1982,** *1,* 217–218.

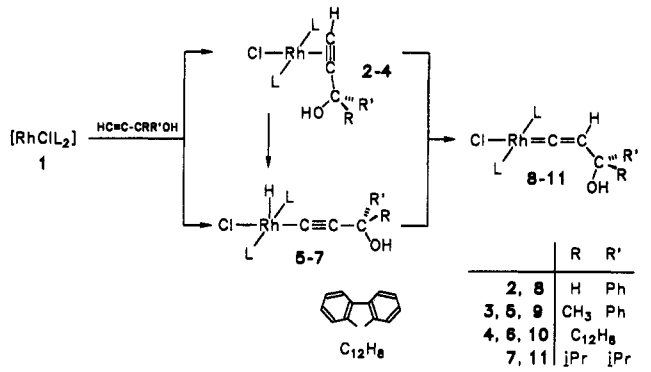
(5) Werner, H. *Nachr. Chem., Tech. Lab.* **1992,** *40,* 435–444.

(6) Rappert, T.; Nürnberg, O.; Mahr, N.; Wolf, J.; Werner, H. *Organometallics* **1992,** *11,* 4156–4164.

(7) Werner, H.; Rappert, T. *Chem. Ber.* **1993,** *126,* 669–678.

0276-7333/94/2313-2721$04.50/0 © 1994 American Chemical Society

Scheme 1[a]



[a] L = P*i*Pr$_3$.

(14e) compound [RhCl(P*i*Pr$_3$)$_2$] (**1**),[8] which was already used for the synthesis of the nonfunctionalized rhodium vinylidenes *trans*-[RhCl(=C=CHR)(P*i*Pr$_3$)$_2$] (R = H, alkyl, aryl),[9] reacts with HC≡CCH(Ph)OH in pentane at 0 °C to give the alkyne complex **2** in about 70% yield. If under the same conditions a pentane solution of **1** is treated with HC≡CCMe(Ph)OH or HC≡CC(C$_{12}$H$_8$)OH, the isomeric (alkynyl)hydridometal derivatives **5** and **6** are obtained instead of the corresponding (alkyne)rhodium compounds **3** and **4** (see Scheme 1). The assumption that **5** and **6** are formed via the alkyne complexes **3** and **4** has been substantiated by repeating the reactions at −78 °C. In this case, from both HC≡CCMe(Ph)OH and HC≡CC(C$_{12}$H$_8$)OH rather labile intermediates of the supposed composition *trans*-[RhCl(HC≡CCRR'OH)(P*i*Pr$_3$)$_2$] (**3**, yellow oil; **4** yellow solid) are isolated which above −20 °C rearrange to the (alkynyl)hydridorhodium(III) compounds **5** and **6**. Evidence for the coordination of an intact alkynol in **3** and **4** is provided by the IR spectra, which reveal an intense absorption at 1830–1840 cm^{-1} that is characteristic for a π-bonded C≡C system. For HC≡CC(*i*Pr)$_2$OH as the substrate, the expected alkyne complex *trans*-[RhCl(HC≡CC(*i*Pr)$_2$OH)(P*i*Pr$_3$)$_2$] cannot be detected by spectroscopic means and we thus have to assume that the isomerization to give **7** occurs readily even at low temperatures.

The five-coordinate alkynyl hydrido complex **5** can be stored at −20 °C only for a short period of time because it is slowly converted, even in the absence of a solvent, to the rhodium vinylidene **9**. In contrast, compounds **6** and **7** are stable at 0 °C both in the solid state and in solution and have been characterized by IR as well as by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The most characteristic features are the IR band at 2100 (**6**) or 2090 cm^{-1} (**7**) for the C≡C stretch, a signal (doublet of triplets) in the high-field region of the ^{1}H NMR spectrum at δ −28.23 (**6**) or −28.34 (**7**), for the hydrido ligand, and a single resonance (doublet) in the ^{31}P NMR spectrum at δ 49.83 (**6**) or 49.39 (**7**) for the two equivalent phosphine groups. Although it cannot be definitely decided from the spectroscopic data whether **6** and **7** possess a trigonal-bipyramidal (tbp) or a square-pyramidal (sqp) configuration, owing to the recently performed X-ray structural analysis of a related [RhH(C≡CR)$_2$(P*i*Pr$_3$)$_2$] derivative,[10] we assume that the sqp structure is preferred.

Both the alkyne and the alkynyl hydrido compounds **2** and **5**, **6** rearrange quite smoothly in toluene to form the vinylidene complexes **8**–**10** in almost quantitative yields. Whereas the isomerization from **2** to **8** and from **5**, **6** to **9**, **10** is completed at room temperature after 10–15 min, compound **7** is inert under these conditions. If, however, a solution of **7** in toluene is irradiated with a UV lamp for 2 h, a nearly quantitative conversion to **11** occurs. We assume that the higher activation barrier for the rearrangement in this case is due to the steric shielding of the β-C carbon of the Rh—C≡CR unit by the bulky isopropyl groups.

Similar to the parent compound *trans*-[RhCl(=C=CH$_2$)(P*i*Pr$_3$)$_2$],[9b] the rhodium vinylidenes **8**–**11** are deeply colored solids which can be handled briefly in air and which, with the exception of pentane and hexane, are easily soluble in all common organic solvents. As far as the spectroscopic data of **8**–**11** are concerned, the most typical features are the low-field signals in the ^{13}C NMR spectra at δ 285–290 and 105–115, which are assigned to the α-C and β-C vinylidene carbon atoms. The resonance of the =C*H*– proton in the ^{1}H NMR spectra of **8**–**11** appears at δ 0.0–1.0 and is thus at considerably higher field than the signal of the *H*C≡CR proton in the spectrum of **2**.

Allenylidene and Vinylvinylidene Complexes from OH-Functionalized Vinylidene Precursors. The (vinylidene)rhodium compounds *trans*-[RhCl(=C=CHCR(CH$_3$)OH)(P*i*Pr$_3$)$_2$] with R = H, CH$_3$ react with alumina by abstraction of water to give the corresponding (vinylvinylidene)rhodium derivatives *trans*-[RhCl(=C=CHC(R)=CH$_2$)(P*i*Pr$_3$)$_2$].[6,7] If the two groups R and CH$_3$ are replaced by phenyl the formation of a vinylvinylidene unit is precluded and the diphenylallenylidene complex *trans*-[RhCl(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] is formed.[7]

An analogous conversion to the allenylidene compounds **12** and **13** (Scheme 2) occurs with the rhodium vinylidenes **8** and **10** as starting materials. Whereas water elimination from **10** to give **13** is possible by passing a toluene solution of **10** over Al$_2$O$_3$ (neutral, activity grade I), the same procedure, if applied to **8**, yields a mixture of **12** and the carbonyl complex *trans*-[RhCl(CO)(P*i*Pr$_3$)$_2$].[8a] The observation that the relative amount of the carbonyl complex increases if more Al$_2$O$_3$ is used or if the rate of passing the solution through the column decreases led us to assume that the CO ligand is formed from the allenylidene by nucleophilic attack of water or OH$^-$ at the α-carbon atom of the Rh=C=C=C chain.

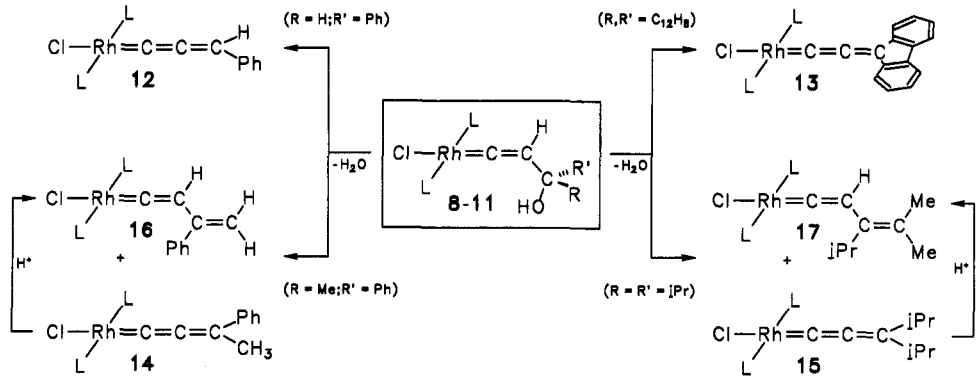
The preparation of pure samples of **12** is best achieved by treating a solution of **8** in benzene or toluene with catalytic quantities of HCl or CF$_3$CO$_2$H. The yield is 65–70%. Both compounds, **12** (yellow) and **13** (red), are moderately air-sensitive solids, the latter of which is less soluble in most organic solvents. As expected, the spectroscopic data for **12** and **13** are distinctly different from those for the corresponding rhodium vinylidenes *trans*-[RhCl(=C=CHR)(P*i*Pr$_3$)$_2$][9b,c] and in some respects

(8) (a) Preparation in situ: Busetto, C.; D'Alfonso, A.; Maspero, F.; Perego, G.; Zazetta, A. *J. Chem. Soc., Dalton Trans.* **1977**, 1828–1834. (b) Isolation: Werner, H.; Wolf, J.; Höhn, A. *J. Organomet. Chem.* **1985**, *287*, 395–407. (c) X-ray crystal structure of the dimer: Haas, J. Dissertation, Universität Kaiserslautern, 1990. We thank Professor P. Binger for this information.

(9) (a) García Alonso, F. J.; Höhn, A.; Wolf, J.; Otto, H.; Werner, H. *Angew. Chem.* **1985**, *97*, 401–402; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 406–407. (b) Werner, H.; García Alonso, F. J.; Otto, H.; Wolf, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1988**, *43*, 722–726. (c) Werner, H.; Brekau, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1989**, *44*, 1438–1446.

(10) Mahr, N. Dissertation, Universität Würzburg, 1994.

Scheme 2[a]



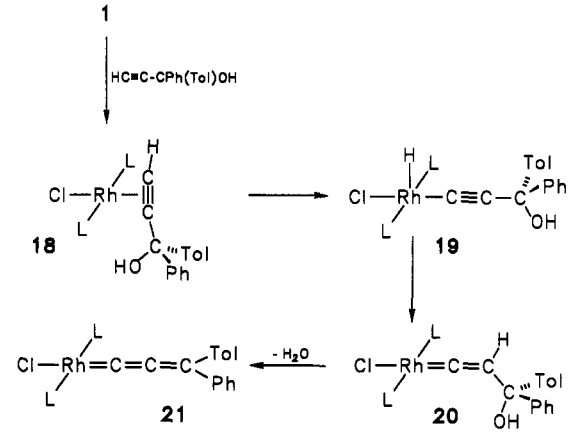
[a] L = P*i*Pr$_3$.

resemble those of organic allenes.[11] Typical features are the strong C=C=C stretch in the IR spectrum at 1875 cm^{-1}, the intense UV band at 434 (**12**) or 478 nm (**13**), and the low-field signal (with long-range Rh–H and P–H coupling) for the allenylidene C=C=C*H*Ph proton in the ^{1}H NMR spectrum of **12** at δ 12.17. (For comparison, the resonance of the C=C*H*$_2$ protons in *trans*-[RhCl(=C=CH$_2$)(P*i*Pr$_3$)$_2$] is observed at δ −0.05!). It is also worth mentioning that in the ^{13}C NMR spectra of **12** and **13** the signal for C$_\alpha$ of the Rh=C=C=C chain appears at higher field than that of C$_\beta$, which is opposite to what is found for a Rh=C=C unit.[9b,c]

The abstraction of water from the OH-functionalized vinylidene complexes **9** and **11** does not lead preferentially to rhodium allenylidenes but to the corresponding rhodium vinylvinylidenes (see Scheme 2). Whereas compound **16** is formed by applying the same procedure which has been used for the preparation of **13** (i.e., treatment of the vinylidene derivative **9** with acidic alumina), the related complex **17** cannot be generated under these conditions. It has been obtained, however, in almost quantitative yield by stirring a THF solution of **11** in the presence of NH_4Cl. In view of the observation that a mixture of **14** and **16** or **15** and **17** is formed if compound **9** is treated with neutral (instead of acidic) Al_2O_3 or compound **11** with CF_3CO_2H for only 10 min instead of hours, we suppose that the water elimination from **9** and **11** can lead to both isomers. The mixtures of products (in which the metal vinylvinylidenes dominate by at least a 9:1 ratio compared with the isomeric allenylidenes) are completely converted to the pure complexes **16** and **17**, respectively, upon treatment with acidic alumina.

In order to prove that the structural proposal for the compounds **12** and **13** as well as for the corresponding diphenylallenylidene derivative is correct, we tried, but failed, to obtain single crystals of one of the compounds. However, after we introduced a degree of dissymmetry into the molecule (e.g. by replacing one phenyl with an *o*-tolyl group at the γ-C atom of the Rh=C=C=C chain), our attempts to grow X-ray-quality single crystals were successful. The synthesis of the respective allenylidene complex **21** followed the route which was already applied for **12** and **13** and which is outlined in Scheme 3. It should be mentioned that, in contrast to the results summarized in Scheme 1, in the series of the (alkyne)-, (alkynyl)-hydrido-, and (vinylidene)rhodium compounds **18**–**20**, all

Scheme 3[a]



[a] L = P*i*Pr$_3$.

three isomers could be isolated as stable solids for which not only IR but also NMR data were obtained. The most labile species of this series is the alkyne complex **18**, which has to be prepared at −20 °C. The deep blue vinylidene derivative **20** is generated from the (alkynyl)hydridometal precursor **19** in 94% yield, and also the conversion from **20** to the allenylidene complex **21** proceeds almost quantitatively. The spectroscopic data for the cumulated π system **21** are similar to those for **12** and **13** and deserve no further comment.

Molecular Structure of 21. Since there were no structural parameters for an (allenylidene)rhodium complex available, a single-crystal X-ray analysis of **21** was carried out. The SCHAKAL drawing (Figure 1) reveals that the coordination geometry about the rhodium(I) center is square planar with the two phosphine ligands in a *trans* disposition. The Rh–C1 distance (1.855(5) Å) is significantly shorter than that expected for an sp-carbon–rhodium single bond (ca. 2.02 Å)[6,12] but somewhat longer than in the corresponding four-coodinate (vinylidene)-rhodium complexes with [RhCl(P*i*Pr$_3$)$_2$] as a molecular unit (cf. 1.775(6) Å in *trans*-[RhCl(=C=CHMe)(P*i*Pr$_3$)$_2$][9b] or 1.78(1) Å in *trans*-[RhCl(=C=CHC(Me)=CH$_2$)-(P*i*Pr$_3$)$_2$][6]). The Rh–C1 bond length, however, is comparable to that in the related carbene derivative *trans*-[RhCl(=CPh$_2$)(P*i*Pr$_3$)$_2$] (1.876(3) Å).[13] The two carbon–carbon distances in the Rh=C=C=C chain (see Table 1)

(11) Silverstein, R. M.; Bassler, G. C.; Morill, T. C. *Spectrometric Identification of Organic Compounds*, 3rd ed.; Wiley: New York, 1974; p 88.

(12) Werner, H.; Baum, M.; Schneider, D.; Windmüller, B. *Organometallics* **1994**, *13*, 1089–1097.

(13) Steinert, P. Unpublished results. See: Schwab, P. Dissertation, Universität Würzburg, 1994.

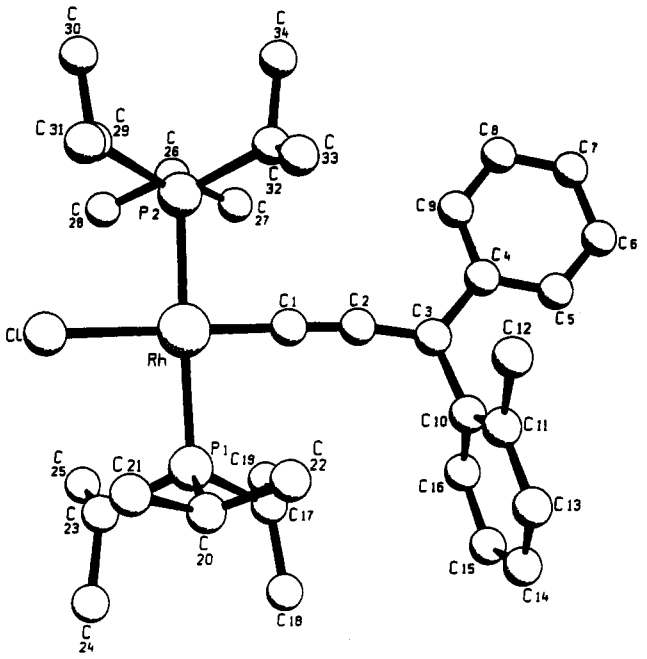


Figure 1. SCHAKAL diagram for the molecular structure of **21**.

Table 1. Selected Bond Distances and Angles with Esd's for 21

	Bond Distanes (Å)		
Rh–Cl	2.354 (3)	C1–C2	1.239 (8)
Rh–P1	2.354 (2)	C2–C3	1.370 (9)
Rh–P2	2.348 (2)	C3–C4	1.480 (9)
Rh–C1	1.855 (5)	C3–C10	1.527 (8)
	Bond Angles (deg)		
Cl–Rh–C1	178.4 (2)	Rh–C1–C2	176.0 (5)
P1–Rh–P2	178.34 (6)	C1–C2–C3	170.9 (1)
Cl–Rh–P1	90.84 (7)	C2–C3–C4	123.1 (6)
Cl–Rh–P2	90.50 (6)	C2–C3–C10	116.9 (6)
P1–Rh–C1	89.2 (2)	C4–C3–C10	119.7 (6)
P2–Rh–C1	89.5 (2)		

are quite similar to those found in $[C_5H_5Ru(=C=C=CPh_2)(PMe_3)_2]^+$ [4] as well as in other metal allenylidenes[3a,d,e,f,14] and indicate that, besides the usual bonding formulation **A**, a second resonance structure **B**

A B

has to be taken into consideration. Remarkably, the distance C2–C3 is almost identical with that of the central C—C bond of the disubstituted buta-1,3-diyne in *trans*-$[RhCl(\eta^2\text{-}Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3)(PiPr_3)_2]$.[15]

In agreement with the two resonance forms **A** and **B**, the Rh–C–C–C chain is almost linear, with only a slight bending at the carbon atom C2. Whereas the phenyl group at C3 lies in the same plane as the carbon atoms C2, C3, C4, and C10, the plane of the *o*-tolyl unit is perpendicular to this (dihedral angle 95.5(3)°). With this arrangement the steric repulsion between the hydrogens on the two six-membered rings is most probably minimized. We note that in contrast to what is expected for a "metallabutatriene", the atoms bound to the rhodium and to the γ-carbon of the chain are not in the same plane, the dihedral angle between [Rh,Cl,P1,P2,C1] and [C2,C3,C4,C10] being 18.5(7)°.

Conclusions

The present investigations have shown that the 1-alkynol route to transition-metal allenylidene complexes can not only be applied to d^6 systems such as Ru(II)[4,14,16] but also to d^8 systems such as Rh(I). The substituents R and R' at the γ-carbon of the substrate HC≡CCRR'OH can be aryl but eventually can also be hydrogen, as has been proved by the preparation of **12**. If one of the groups R or R' is methyl or, in general, an alkyl that contains a β-H atom, the formation of a (vinylvinylidene)metal compound is thermodynamically and in most cases also kinetically preferred.

Two points should be finally emphasized. (1) For practical purposes, it is important to note that the synthesis of the (allenylidene)rhodium as well as of the (vinylvinylidene)rhodium complexes can be accomplished as a one-pot reaction by starting with $[RhCl(C_8H_{14})_2]_2$, $PiPr_3$, and the 1-alkynol HC≡CCRR'OH. As is described in the Experimental Section for both **13** and **16**, after the crude intermediate has been treated with alumina, the yield of the final product is 70–75%. (2) The common intermediate in the conversion of the π-coordinated 1-alkynol to the allenylidene or vinylvinylidene unit is an OH-functionalized vinylidene ligand. Although there is still some discussion[17] whether the isomerization from $M(\eta^2\text{-}HC{\equiv}CR)$ to M=C=CHR occurs stepwise via MH(C≡CR) or directly by a 1,2-hydrogen shift as has been proposed on theoretical grounds,[18] owing to recent observations[7,12] and to this work there is no doubt that the vinylidene complexes can be retransformed, e.g., on treatment with N-donors, to give (alkynyl)hydridometal derivatives. Accordingly, the reaction of **9** with pyridine affords the octahedral rhodium(III) complex $[RhH(C{\equiv}CCH_3(Ph)OH)Cl(py)(PiPr_3)_2]$ (**22**) in 84% yield. There seem to be two possible energetically comparable mechanisms for the isomerization of terminal alkynes to vinylidenes (and vice versa),[19] and evidence for this based on kinetic and theoretical studies from our laboratory will be presented in a forthcoming paper.

Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk tube techniques. The starting material $[RhCl(PiPr_3)_2]_n$ (**1**) (**7**)[8b] and the alkynol HC≡CCPh(*o*-Tol)OH[20] were prepared as described in the literature. The other alkynols were commercial products from Aldrich and ABCR. NMR spectra

(14) (a) Pirio, N.; Touchard, D.; Toupet, L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1991**, 980–982. (b) Wolinska, A.; Touchard, D.; Dixneuf, P. H.; Romero, A. *J. Organomet. Chem.* **1991**, *420*, 217–226. (c) Pirio, N.; Touchard, D.; Dixneuf, P. H.; Fettouhi, M.; Ouahab, L. *Angew. Chem.* **1992**, *104*, 664–666; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 651–653.

(15) Rappert, T.; Nürnberg, O.; Werner, H. *Organometallics* **1993**, *12*, 1359–1364.

(16) (a) Le Bozec, H.; Ouzzine, K.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1989**, 219–221. (b) Romero, A.; Peron, D.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1410–1412. (c) Pilette, D.; Ouzzine, K.; Le Bozec, H.; Dixneuf, P. H.; Rickard, C. E. F.; Roper, W. R. *Organometallics* **1992**, *11*, 809–817. (d) Pirio, N.; Touchard, D.; Dixneuf, P. H. *J. Organomet. Chem.* **1993**, *462*, C18–C20.

(17) (a) Bullock, R. M. *J. Am. Chem. Soc.* **1987**, *109*, 8087–8089. (b) Bullock, R. M. *J. Chem. Soc., Chem. Commun.* **1989**, 165–167. (c) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Ramirez, J. A.; Vacca, A.; Zanobini, F. *Organometallics* **1989**, *9*, 2179–2189.

(18) Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461–1506.

(19) Wakatsuki, Y. Unpublished results. We thank Professor Y. Wakatsuki for this information.

(20) Saunders, J. H. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. 3, pp 416–418.

were recorded at room temperature on JEOL FX 90Q, Bruker AC 200, and Bruker AMX 400 instruments, IR spectra on a Perkin-Elmer 1420 infrared spectrophotometer, and mass spectra on a Varian MAT CH7 instrument. Melting points were measured by DTA.

Preparation of *trans*-[RhCl(HC≡CCH(Ph)OH)(P*i*Pr$_3$)$_2$] (2). To a solution of 1 (200 mg, 0.43 mmol for n = 1) in 20 mL of pentane was added a pentane solution of HC≡CCH(Ph)OH dropwise at 0 °C until the yellow color of the solution remained unchanged. The solvent was removed, and the residue was extracted with 10 mL of pentane. The extract was concentrated in vacuo to ca. 3 mL and stored at −78 °C. Yellow crystals were formed, which were filtered off, repeatedly washed with pentane (0 °C), and dried in vacuo, yield 175 mg (69%); mp 69 °C dec. Anal. Calcd for $C_{27}H_{50}ClOP_2Rh$: C, 54.87; H, 8.53. Found: C, 55.08; H, 8.54. IR (KBr): ν(OH) 3390, ν(≡CH) 3100, ν(C≡C) 1855 cm^{-1}. ^{1}H NMR (C_6D_6, 90 MHz): δ 7.70–7.16 (m, 5H, C_6H_5), 4.09 (br s, 1H, C*H*(Ph)OH), 3.36 (m, 1H, ≡CH), 2.26 (m, 6H, PC*H*CH$_3$), 1.27, 1.22, 1.20, 1.16 (all dvt, N = 13.6, J(HH) = 7.3 Hz, 36H, PCHC*H*$_3$), signal of OH not observed. ^{31}P NMR (C_6D_6, 36.2 MHz): truncated ABX pattern, four lines centered at δ 32.5 (J(AX) = 115.1, J(BX) = 115.1 Hz).

Preparation of *trans*-[RhCl(HC≡CCCH$_3$(Ph)OH)(P*i*Pr$_3$)$_2$] (3). To a solution of 1 (100 mg, 0.22 mmol for n = 1) in 10 mL of pentane was added a pentane solution of HC≡CCCH$_3$(Ph)-OH dropwise at −78 °C until the yellow color of the solution remained unchanged. The solvent was then immediately removed and a yellow oil was obtained, yield 92 mg (69%). IR (KBr): ν(C≡C) 1845 cm^{-1}.

Preparation of *trans*-[RhCl(HC≡CC($C_{12}H_8$)OH)(P*i*Pr$_3$)$_2$] (4). This compound was prepared as described for 3. The pentane solution was concentrated in vacuo until a precipitate occurred and was then stored at −78 °C. A yellow microcrystalline solid was isolated, yield 105 mg (72%). IR (KBr): ν(C≡C) 1832 cm^{-1}.

Preparation of [RhH(C≡CCCH$_3$(Ph)OH)Cl(P*i*Pr$_3$)$_2$] (5). This compound was prepared as described for 2, using 1 (200 mg, 0.43 mmol for n = 1) and an equimolar amount of HC≡CCCH$_3$-(Ph)OH in pentane at 0 °C. After the pentane extract was evaporated, an orange-yellow oil was obtained which even at −78 °C smoothly rearranged to give 9. For 5: IR (KBr) ν(C≡C) 2105 cm^{-1}.

Preparation of [RhH(C≡CC($C_{12}H_8$)OH)Cl(P*i*Pr$_3$)$_2$] (6). This compound was prepared as described for 2, using 1 (181 mg, 0.40 mmol for n = 1) and an equimolar amount of HC≡CC-($C_{12}H_8$)OH. Orange-yellow crystals were obtained: yield 199 mg (76%); mp 106 °C dec. Anal. Calcd for $C_{33}H_{52}ClOP_2Rh$: C, 59.60; H, 7.88. Found: C, 59.45; H, 7.61. IR (KBr): ν(OH) 3460, ν(C≡C) 2100 cm^{-1}. ^{1}H NMR (C_6D_6, 90 MHz): δ 7.71–7.04 (m, 8H, $C_{12}H_8$), 2.69 (m, 6H, PC*H*CH$_3$), 1.14 (dvt, N = 13.7, J(HH) = 7.3 Hz, 36H, PCHC*H*$_3$), −28.23 (dt, J(RhH) = 43.0, J(PH) = 12.7 Hz, 1H, RhH), signal of OH not observed. ^{31}P NMR (C_6D_6, 36.2 MHz): δ 49.83 (d, J(RhP) = 96.2 Hz).

Preparation of [RhH(C≡CC(*i*Pr)$_2$OH)Cl(P*i*Pr$_3$)$_2$] (7). This compound was prepared as described for 2, using 1 (205 mg, 0.44 mmol for n = 1) and an equimolar amount of HC≡CC-(*i*Pr)$_2$OH. Orange-yellow crystals were obtained: yield 209 mg (81%); mp 88 °C dec. Anal. Calcd for $C_{27}H_{58}ClOP_2Rh$: C, 54.13; H, 9.76. Found: C, 54.02; H, 10.07. IR (KBr): ν(OH) 3450, ν-(C≡C) 2090 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.88 (m, 6H, PC*H*CH$_3$), 1.96 (m, 2H, CC*H*CH$_3$), 1.26 and 1.25 (both dvt, N = 14.1, J(HH) = 7.3 Hz, 36H, PCHC*H*$_3$), 1.13 and 1.11 (both d, J(HH) = 6.8 Hz, 12H, CCHC*H*$_3$), −28.34 (dt, J(RhH) = 43.0, J(PH) = 12.1 Hz, 1H, RhH), signal of OH not observed. ^{13}C NMR ($CDCl_3$, 22.5 MHz): δ 112.12 (d, J(RhC) = 10.7 Hz, RhC≡*C*), 93.57 (dt, J(RhC) = 47.9, J(PC) = 14.7 Hz, RhC≡C), 78.90 (s, C(*i*Pr)$_2$OH), 35.35 (s, C*C*HCH$_3$), 23.69 (vt, N = 22.5 Hz, PCHCH$_3$), 20.27 and 20.09 (both s, PCH*C*H$_3$), 18.53 and 17.20 (both s, CCH*C*H$_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 49.39 (d, J(RhP) = 98.2 Hz).

Preparation of *trans*-[RhCl(=C=CHCH(Ph)OH)(P*i*Pr$_3$)$_2$] (8). After a solid sample of 2 (118 mg, 0.20 mmol) was dissolved in 10 mL of toluene at room temperature, a rapid change of color from yellow to green occurred. The solvent was removed in vacuo, and the residue was recrystallized from pentane (25 to −78 °C) to give green air-stable crystals; yield 98 mg (83%); mp 62 °C dec. Anal. Calcd for $C_{27}H_{50}ClOP_2Rh$: C, 54.87; H, 8.53. Found: C, 54.77; H, 8.68. IR (KBr): ν(OH) 3400, ν(C=C) 1666 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.24–7.11 (m, 5H, C_6H_5), 5.46 (d, J(HH) = 10.0 Hz, 1H, C*H*(Ph)OH), 2.67 (m, 6H, PC*H*CH$_3$), 1.64 (s, 1H, OH), 1.23 and 1.21 (both dvt, N = 13.5, J(HH) = 6.5 Hz, 36H, PCHC*H*$_3$), 0.85 (ddt, J(RhH) = 0.7, J(PH) = 3.1, J(HH) = 10.0 Hz, 1H, =C*H*). ^{13}C NMR ($CDCl_3$, 50.2 MHz): δ 286.68 (dt, J(RhC) = 61.0, J(PC) = 15.0 Hz, Rh=C=C), 144.21, 128.49, 127.83, 125.72 (all s, C_6H_5), 109.68 (dt, J(RhC) = 16.8, J(PC) = 6.2 Hz, Rh=C=*C*), 61.39 (s, *C*H(Ph)OH), 23.18 (vt, N = 20.6 Hz, PCHCH$_3$), 20.01 and 19.96 (both s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 42.50 (d, J(RhP) = 134.8 Hz).

Preparation of *trans*-[RhCl(=C=CHCCH$_3$(Ph)OH)-(P*i*Pr$_3$)$_2$] (9). This compound was prepared as described for 8, using 5 (118 mg, 0.20 mmol) in toluene. After the solution was stirred for 15 min, the solvent was removed, and the residue was recrystallized from pentane (25 to −78 °C) to give violet air-stable crystals: yield 112 mg (95%); mp 68 °C dec. Anal. Calcd for $C_{28}H_{52}ClOP_2Rh$: C, 55.59; H, 8.66. Found: C, 55.34; H, 8.91. IR (KBr): ν(OH) 3430, ν(C=C) 1646 cm^{-1}. ^{1}H NMR (C_6D_6, 90 MHz): δ 7.40–7.00 (m, 5H, C_6H_5), 2.73 (m, 6H, PC*H*CH$_3$), 1.49 (s, 3H, CC*H*$_3$), 1.27 (dvt, N = 13.5, J(HH) = 7.2 Hz, 36H, PCHC*H*$_3$), 0.53 (dt, J(RhH) = 0.5, J(PH) = 3.2 Hz, 1H, =C*H*), signal of OH not observed. ^{13}C NMR ($CDCl_3$, 50.2 MHz): δ 287.02 (dt, J(RhC) = 60.8, J(PC) = 15.0 Hz, Rh=*C*=C), 149.47, 127.88, 126.51, 123.78 (all s, C_6H_5), 117.21 (dt, J(RhC) = 15.3, J(PC) = 6.2 Hz, Rh=C=*C*), 64.57 (s, *C*CH$_3$(Ph)(OH), 33.08 (s, C*C*H$_3$), 23.21 (vt, N = 20.4 Hz, PCHCH$_3$), 19.95 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 41.45 (d, J(RhP) = 134.8 Hz).

Preparation of *trans*-[RhCl(=C=CHC($C_{12}H_8$)OH)-(P*i*Pr$_3$)$_2$] (10). This compound was prepared as described for 8, using 6 (133 mg, 0.20 mmol) in toluene. After recrystallization from pentane (25 to −78 °C) violet air-stable crystals were obtained: yield 124 mg (93%); mp 125 °C dec. Anal. Calcd for $C_{33}H_{52}ClOP_2Rh$: C, 59.60; H, 7.88. Found: C, 59.84; H, 7.82. IR (KBr): ν(OH) 3400, ν(C=C) 1646 cm^{-1}. ^{1}H NMR (C_6D_6, 90 MHz): δ 7.47–7.02 (m, 8H, $C_{12}H_8$), 2.60 (m, 6H, PC*H*CH$_3$), 1.18 (dvt, N = 13.3, J(HH) = 7.1 Hz, 36H, PCHC*H*$_3$), 0.60 (dt, J(RhH) = 0.9, J(PH) = 3.0 Hz, 1H, =C*H*), signal of OH not observed. ^{13}C NMR ($CDCl_3$, 50.2 MHz): δ 285.34 (dt, J(RhC) = 62.4, J(PC) = 15.4 Hz, Rh=*C*=C), 148.91, 138.34, 128.76, 127.74, 123.74, 119.49 (all s, $C_{12}H_8$), 109.42 (dt, J(RhC) = 16.0, J(PC) = 6.3 Hz, Rh=C=*C*), 71.75 (s, *C*($C_{12}H_8$)OH), 23.46 (vt, N = 20.4 Hz, PCHCH$_3$), 19.87 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 41.49 (d, J(RhP) = 134.8 Hz).

Preparation of [RhCl(=C=CHC(*i*Pr)$_2$OH)(P*i*Pr$_3$)$_2$] (11). A solution of 7 (120 mg, 0.20 mmol) in 10 mL of pentane was irradiated for 2 h with a 500-W UV lamp (Osram HBO). A change of color from yellow to red-violet occurred. The solvent was removed, and the residue was repeatedly washed with pentane (0 °C) and dried in vacuo. A red-violet microcrystalline solid was obtained: yield 106 mg (88%); mp 139 °C dec. Anal. Calcd for $C_{27}H_{58}ClOP_2Rh$: C, 54.13; H, 9.76. Found: C, 54.07; H, 10.05. IR (KBr): ν(OH) 3440, ν(C=C) 1650 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.72 (m, 6H, PC*H*CH$_3$), 1.61 (m, 2H, CC*H*CH$_3$), 1.25 (dvt, N = 13.5, J(HH) = 6.8 Hz, 36H, PCHC*H*$_3$), 0.88 and 0.75 (both d, J(HH) = 6.7 Hz, 12H, CCHC*H*$_3$), −0.09 (dt, J(RhH) = 1.2, J(PH) = 3.2 Hz, 1H, =C*H*), signal of OH not observed. ^{13}C NMR ($CDCl_3$, 50.2 MHz): δ 288.95 (dt, J(RhC) = 61.0, J(PC) = 15.3 Hz, Rh=C=C), 106.17 (dt, J(RhC) = 15.3, J(PC) = 6.5 Hz, Rh=C=*C*), 75.79 (s, *C*(*i*Pr)$_2$OH), 36.29 (s, C*C*HCH$_3$), 23.46 (vt, N = 19.4 Hz, PCHCH$_3$), 20.08 (s, PCH*C*H$_3$), 18.74 and 17.23 (both s, CCH*C*H$_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 40.62 (d, J(RhP) = 136.3 Hz).

Preparation of *trans*-[RhCl(=C=C=CHPh)(P*i*Pr$_3$)$_2$] (12). A solution of 8 (115 mg, 0.20 mmol) in 10 mL of toluene was treated with 1 drop of CF_3CO_2H and stirred for 5 min at room temperature. The solution was then concentrated to ca. 2 mL and stored at −78 °C. Yellow crystals were formed, which were

filtered off, washed with pentane (0 °C), and dried in vacuo: yield 77 mg (67%); mp 90 °C dec. Anal. Calcd for $C_{27}H_{48}ClP_2Rh$: C, 56.60; H, 8.44. Found: C, 56.37; H, 8.84. MS (70 eV): m/z 573 (M^+). IR (KBr): ν(C=C=C) 1875 cm^{-1}. UV (CH_2Cl_2): λ(max) 434 nm. ^{1}H NMR (C_6D_6, 90 MHz): δ 12.17 (dt, J(RhH) = 1.1, J(PH) = 5.6 Hz, 1H, =C*H*), 8.09–6.63 (m, 5H, C_6H_5), 3.05 (m, 6H, PC*H*CH$_3$), 1.38 (dvt, N = 13.5, J(HH) = 7.3 Hz, 36H, PCHC*H*$_3$). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 250.02 (dt, J(RhC) = 15.1, J(PC) = 7.0 Hz, Rh=C=*C*=C), 223.95 (dt, J(RhC) = 65.4, J(PC) = 17.1 Hz, Rh=*C*=C=C), 151.66 (s, Rh=C=C=*C*), 143.16, 131.14, 127.68, 124.40 (all s, C_6H_5), 22.85 (vt, N = 19.6 Hz, P*C*HCH$_3$), 19.05 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 37.35 (d, J(RhP) = 130.4 Hz).

Preparation of *trans*-[RhCl(=C=C=C($C_{12}H_8$))($PiPr_3$)$_2$] (13). A solution of **10** (146 mg, 0.22 mmol) in 2 mL of toluene was chromatographed on Al_2O_3 (neutral, activity grade I, length of column 8 cm). With toluene, a red fraction was eluted from which the solvent was removed in vacuo. The residue was repeatedly washed with pentane (0 °C) to give a deep red microcrystalline solid: yield 130 mg (91%); mp 178 °C dec. Anal. Calcd for $C_{33}H_{50}ClP_2Rh$: C, 61.25; H, 7.79. Found: C, 60.80; H, 7.48. MS (70 eV): m/z 647 (M^+). IR (KBr): ν(C=C=C) 1875 cm^{-1}. UV (CH_2Cl_2): λ(max) 478 nm. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 8.24–6.80 (m, 8H, $C_{12}H_8$), 3.18 (m, 6H, PC*H*CH$_3$), 1.42 (dvt, N = 13.3, J(HH) = 7.3 Hz, 36H, PCHC*H*$_3$). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 151.84 (s, Rh=C=C=*C*), 142.70, 138.09, 131.69, 127.59, 123.14, 119.16 (all s, $C_{12}H_8$), 24.08 (vt, N = 19.7 Hz, P*C*HCH$_3$), 20.36 (s, PCH*C*H$_3$), signals, of Rh=*C* and Rh=C=*C* not definitely assigned. ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 33.14 (d, J(RhP) = 129.0 Hz).

A second procedure for **13** is as follows. A suspension of [RhCl(C_8H_{14})$_2$]$_2$ (150 mg, 0.21 mmol) in 10 mL of pentane was first treated with $PiPr_3$ (0.2 mL, 1.0 mmol) and then dropwise with a solution of HC≡CC($C_{12}H_8$)OH in pentane until the yellow color of the solution remained unchanged. The solvent was removed in vacuo, the residue was dissolved in 2 mL of toluene, and the solution was chromatographed as described above. The yield of **13** was 187 mg (69%).

Preparation of *trans*-[RhCl(=C=CHC(Ph)=CH_2)($PiPr_3$)$_2$] (16). A solution of **9** (118 mg, 0.20 mmol) in 1 mL of CH_2Cl_2 was chromatographed on Al_2O_3 (acidic, activity grade I, length of column 5 cm). With CH_2Cl_2/hexane (2:1), a green fraction was eluted which was brought to dryness in vacuo. After recrystallization from pentane (25 to −78 °C), green crystals were obtained, which were filtered off, repeatedly washed with pentane (0 °C), and dried in vacuo: yield 89 mg (76%); mp 82 °C dec. Anal. Calcd for $C_{28}H_{50}ClP_2Rh$: C, 57.29; H, 8.58. Found: C, 57.42; H, 8.85. MS (70 eV): m/z 587 (M^+). IR (KBr): ν(C=C) 1623 and 1580 cm^{-1}. UV (CH_2Cl_2): λ(max) 582 and 440 nm. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.46–7.06 (m, 5H, C_6H_5), 5.49 and 5.27 (both d, J(HH) = 1.6 Hz, 2H, one H each of =CH_2), 2.71 (m, 6H, PC*H*CH$_3$), 1.31 (dvt, N = 13.7, J(HH) = 7.2 Hz, 36H, PCHC*H*$_3$), signal of =C*H* probably covered by signal of PCHC*H*$_3$. ^{13}C NMR ($CDCl_3$, 22.5 MHz): δ 296.20 (dt, J(RhC) = 60.6, J(PC) = 16.6 Hz, Rh=*C*=C), 141.83, 128.09, 127.36, 125.80 (all s, C_6H_5), 130.78 (t, J(PC) = 2.9 Hz, *C*(Ph)=CH_2), 110.80 (s, C(Ph)=CH_2), 109.54 (dt, J(RhC) = 15.6, J(PC) = 5.7 Hz, Rh=C=*C*), 23.26 (vt, N = 17.6 Hz, P*C*HCH$_3$), 20.19 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 42.58 (d, J(RhP) = 134.8 Hz).

If the solution of **9** in CH_2Cl_2 was chromatographed on Al_2O_3 (neutral, activity grade I) with CH_2Cl_2/hexane (2:1), a red fraction was eluted. After it was worked up as described above, a red solid was isolated which according to the IR and ^{31}P NMR spectra proved to be a mixture of **16** (ca. 90%) and *trans*-[RhCl(=C=C=C(Ph)CH$_3$)($PiPr_3$)$_2$] (**14**) (ca. 10%). Data for **14**: IR (KBr) ν(C=C=C) 1885 cm^{-1}; ^{31}P NMR (C_6D_6, 36.2 MHz) δ 38.26 (d, J(RhP) = 131.9 Hz). The mixture of **14** and **16** was converted quantitatively into **16** after a solution in benzene was treated with ca. 5 g of Al_2O_3 (acidic, activity grade I) and stirred for 15 min at room temperature. The solution was filtered, and the filtrate was worked up as described for **16**.

A second procedure for **16** is as follows. A suspension of [RhCl(C_8H_{14})$_2$]$_2$ (150 mg, 0.21 mmol) in 10 mL of pentane was first treated with $PiPr_3$ (0.2 mL, 1.0 mmol) and then dropwise with a solution of HC≡CCCH$_3$(Ph)OH in pentane until the orange-yellow color of the solution remained unchanged. The solvent was removed in vacuo, the residue was dissolved in 2 mL of toluene, and the solution was chromatographed on Al_2O_3 (acidic, activity grade I) as described above. The yield of **16** was 184 mg (75%).

Preparation of *trans*-[RhCl(=C=CHC(*i*Pr)=CMe_2)($PiPr_3$)$_2$] (17). A solution of **11** (120 mg, 0.20 mmol) in 10 mL of THF was treated with NH_4Cl (91 mg, 1.70 mmol) and stirred for 12 h at room temperature. The solvent was removed in vacuo, and the residue was extracted with 10 mL of pentane. The extract was concentrated in vacuo to ca. 2 mL and stored at −78 °C. Green crystals precipitated, which were filtered off, repeatedly washed with pentane (0 °C), and dried in vacuo: yield 103 mg (89%); mp 87 °C dec. Anal. Calcd for $C_{27}H_{58}ClP_2Rh$: C, 55.81; H, 9.71. Found: C, 55.98; H, 10.23. IR (CH_2Cl_2): ν(C=C) 1626 and 1600 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 2.74 (m, 6H, PC*H*CH$_3$), 2.21 and 1.78 (both s, 6H, 3H each of =CMe_2), 1.52 (m, 1H, CC*H*CH$_3$), 1.35 (dvt, N = 13.5, J(HH) = 6.6 Hz, 36H, PCHC*H*$_3$), 0.93 (d, J(HH) = 6.8 Hz, 6H, CCHC*H*$_3$), signal of =C*H* probably covered by signal of PCHC*H*$_3$. ^{13}C NMR ($CDCl_3$, 50.2 MHz): δ 297.13 (dt, J(RhC) = 58.9, J(PC) = 15.3 Hz, Rh=*C*=C), 126.30 (s, *C*(*i*Pr)=CMe_2), 123.10 (s, C(*i*Pr)=*C*Me$_2$), 105.28 (dt, J(RhC) = 15.7, J(PC) = 6.2 Hz, Rh=C=*C*), 31.10 and 26.86 (both s, one *C*H$_3$ each of =CMe_2), 24.35 (vt, N = 19.6 Hz, P*C*HCH$_3$), 23.93 (s, CCHCH$_3$), 21.53 (s, CCHCH$_3$), 20.41 (s, PCHCH$_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 41.39 (d, J(RhP) = 136.3 Hz).

If a solution of **11** in toluene was treated with a drop of CF_3CO_2H and stirred for 10 min at room temperature, the green color of the solution remained unchanged. After the solvent was removed, the residue was investigated by IR and ^{31}P NMR spectroscopy. Besides **11** and **17**, small amounts of *trans*-[RhCl(=C=C=C*i*Pr$_2$)($PiPr_3$)$_2$] (**15**) could be detected: IR (KBr) ν(C=C=C) 1889 cm^{-1}; ^{31}P NMR (C_6D_6, 36.2 MHz) δ 38.52 (d, J(RhP) = 133.4 Hz).

Preparation of *trans*-[RhCl(HC≡CCPh(*o*-Tol)OH)($PiPr_3$)$_2$] (18). A solution of **1** (100 mg, 0.22 mmol for n = 1) in 10 mL of pentane was treated at −20 °C with HC≡CCPh(*o*-Tol)OH (50 mg, 0.22 mmol), which led to a rapid change of color from red to pale yellow. After the solution was stirred for 5 min, the solvent was removed and the yellow residue was washed three times with 5 mL of pentane and dried in vacuo: yield 140 mg (95%); mp 111 °C dec. IR (KBr): ν(OH) 3400, ν(≡CH) 3100, ν(C≡C) 1830 cm^{-1}. ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ 32.91 (d, J(RhP) = 113.6 Hz).

Preparation of *trans*-[RhH(C≡CCPh(*o*-Tol)OH)Cl($PiPr_3$)$_2$] (19). A solution of **1** (248 mg, 0.54 mmol for n = 1) in 5 mL of benzene was treated at 10 °C with HC≡CCPh(*o*-Tol)OH (122 mg, 0.55 mmol), which led to a rapid change of color from red to yellow. After the solution was stirred for 1 min, it was worked up as described for **18**: yield 353 mg (96%); mp 122 °C dec. IR (KBr): ν(OH) 3590, ν(C≡C) 2090, 2070 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.58 and 7.05 (both m, 9H, C_6H_5 and C_6H_4), 2.74 (m, 6H, PC*H*CH$_3$), 2.55 (s, 1H, OH), 2.22 (s, 3H, $C_6H_4CH_3$), 1.18 and 1.13 (both dvt, N = 13.3, J(HH) = 6.8 Hz, 36H, PCHC*H*$_3$), −28.25 (dt, J(RhH) = 43.4, J(PH) = 6.8 Hz, 1H, RhH). ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ 50.55 (d, J(RhP) = 98.3 Hz).

Preparation of *trans*-[RhCl(=C=CHCPh(*o*-Tol)OH)($PiPr_3$)$_2$] (20). A solution of **19** (330 mg, 0.48 mmol) in 3 mL of a 1:1 mixture of C_6H_6/NEt_3 was stirred for 2 h at room temperature. A change of color from yellow to blue occurred. After the solvent was removed, the residue was dissolved in 15 mL of toluene/pentane (1:4) and the solution was stored at −30 °C. Blue crystals precipitated, which were separated from the mother liquor, repeatedly washed with pentane, and dried in vacuo: yield 310 mg (94%); mp 142 °C dec. Anal. Calcd for $C_{34}H_{56}ClOP_2Rh$: C, 59.96; H, 8.29. Found: C, 60.24; H, 8.34. IR

(KBr): ν(OH) 3600, ν(C=C) 1660 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.73 and 7.14 (both m, 9H, C_6H_5 and C_6H_4), 2.73 (m, 6H, PC*H*CH_3), 2.60 (s, 1H, OH), 1.95 (s, 3H, $C_6H_4CH_3$), 1.29 and 1.22 (both dvt, N = 14.0, J(HH) = 7.0 Hz, 36H, PCHCH_3), 0.91 (t, J(PH) = 3.2 Hz, 1H, =C*H*). ^{13}C NMR ($CDCl_3$, 50.2 MHz): δ 285.99 (dt, J(RhC) = 61.2, J(PC) = 15.4 Hz, Rh=C=C), 147.67, 144.93, 136.18, 132.28, 127.58, 127.25, 124.86, 124.46 (all s, C_6H_5 and C_6H_4), 117.51 (dt, J(RhC) = 15.1, J(PC) = 5.5 Hz, Rh=C=*C*), 68.69 (s, *C*Ph(*o*-Tol)OH), 23.09 (vt, N = 20.0 Hz, P*C*HCH$_3$), 20.91 (s, $C_6H_4CH_3$), 19.81 (s, PCH*C*H$_3$). ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ 42.04 (d, J(RhP) = 132.4 Hz).

Preparation of *trans*-[RhCl(=C=C=CPh(*o*-Tol))(P*i*Pr$_3$)$_2$] (21). A solution of **20** (300 mg, 0.44 mmol) in 3 mL of benzene was chromatographed on Al_2O_3 (acidic, activity grade I, length of column 5 cm). On the column a change of color from blue to red occurred. With benzene, a red fraction was eluted, which was worked up as described for **13**. Red crystals were isolated: yield 260 mg (89%); mp 165 °C dec. Anal. Calcd for $C_{34}H_{54}ClP_2Rh$: C, 61.58; H, 8.21. Found: C, 61.04; H, 8.40. IR (KBr): ν(C=C=C) 1865 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.04 and 7.22 (both m, 9H, C_6H_5 and C_6H_4), 2.78 (m, 6H, PC*H*CH_3), 2.02 (s, 3H, $C_6H_4CH_3$), 1.25 (dvt, N = 13.5, J(HH) = 7.0 Hz, 36H, PCHC*H*$_3$). ^{13}C NMR ($CDCl_3$, 50.2 MHz): δ 245.54 (dt, J(RhC) = 9.2, J(PC) = 6.5 Hz, Rh=C=*C*=C), 226.24 (dt, J(RhC) = 66.9, J(PC) = 17.2 Hz, Rh=*C*=C=C), 152.95 (s, Rh=C=C=*C*), 152.76, 144.46, 131.46, 130.13, 128.20, 127.35, 126.95, 124.22, 123.86, 118.95 (all s, C_6H_5 and C_6H_4), 23.58 (vt, N = 19.8 Hz, P*C*HCH$_3$), 19.99 (s, PCH*C*H$_3$), 19.61 (s, $C_6H_4CH_3$). ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ 37.65 (d, J(RhP) = 130.7 Hz).

Preparation of *trans*-[RhH(C≡CCH$_3$(Ph)OH)Cl(py)(P*i*Pr$_3$)$_2$] (22). A solution of **9** (121 mg, 0.20 mmol) in 10 mL of pentane was treated at 10 °C with excess pyridine (1 mL, 1.22 mmol) and stirred for 15 h at room temperature. The solution became colorless, and a few crystals already precipitated. To complete the precipitation, the solution was concentrated to ca. 3 mL and stored at −60 °C. A white solid was formed, which was filtered off, repeatedly washed with pentane (0 °C), and dried in vacuo: yield 115 mg (84%); mp 79 °C dec. IR (KBr): ν(OH) 3200, ν(RhH) 2180, ν(C≡C) 2100 cm^{-1}. ^{1}H NMR (C_6D_6, 90 MHz): δ 8.88–6.60 (m, 10H, NC_5H_5 and C_6H_5), 2.86 (m, 6H, PC*H*CH_3), 1.51 (s, 3H, CH_3), 1.28 and 1.14 (both dvt, N = 13.3, J(HH) = 7.3 Hz, 36H, PCHC*H*$_3$), −17.53 (dt, J(RhH) = 13.6, J(PH) = 13.6 Hz, 1H, RhH). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 37.59 (d, J(RhP) = 98.2 Hz).

Crystal Structure Analysis of 21. Single crystals were grown from acetone. Crystal data (from 23 reflections, 9° < θ < 15°): orthorhombic, space group $Pca2_1$ (No. 29); a = 17.804(4) Å, b = 10.891(1) Å, c = 17.934(5) Å, V = 3477(1) Å^3, Z = 4, d_{calcd} = 1.267 g cm^{-3}, μ(Mo Kα) = 6.7 cm^{-1}; crystal size 0.2 × 0.2 × 0.2 mm; Enraf-Nonius CAD4 diffractometer, Mo Kα radiation (0.709 30 Å), graphite monochromator, zirconium filter (factor 15.41); T = 293 K; ω/θ scan, max 2θ = 52°; 3834 reflections measured, 3833 independent reflections, 2416 regarded as being observed ($I_o > 3\sigma(I_o)$). Intensity data were corrected for Lorentz and polarization effects, and an empirical absorption correction (ψ-scan method) was applied (minimum transmission 95.08%). The structure was solved by direct methods (SHELXS-86). Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares (342 parameters, unit weights, Enraf-Nonius SDP). The positions of all hydrogen atoms were calculated according to an ideal geometry (C–H distance 0.95 Å) and were included in the structure factor calculation in the last refinement cycle: R = 0.037, R_w = 0.038; reflex/parameter ratio 7.05; residual electron density +0.420/−0.331 e Å^{-3}.

Acknowledgment. We thank the Volkswagen Stiftung and the Fonds der Chemischen Industrie for financial support, and in particular Degussa AG for various gifts of chemicals. We also gratefully acknowledge support by Mrs. M.-L. Schäfer and Dr. W. Buchner (NMR spectra), Mrs. A. Burger, Mrs. R. Schedl, and C. P. Kneis (elemental analyses and DTA), and Dr. G. Lange and F. Dadrich (mass spectra).

Supplementary Material Available: Tables giving crystal data and data collection and refinement parameters, all bond distances and angles, least-squares planes and deviations therefrom, anisotropic thermal parameters, and positional parameters for **21** (13 pages). Ordering information is given on any current masthead page.

OM940134J