

An Unprecedented Bending of a Bridging Diynyl Ligand in an Unsymmetrical Binuclear Rhodium(I) Complex

Helmut Werner,* Olaf Gevert, Paul Steinert, and Justin Wolf

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

Received November 8, 1994[®]

The reaction of $[\text{Rh}(\eta^2\text{-O}_2\text{CCH}_3)(\text{PiPr}_3)_2]$ (**2**) with 2 equiv of phenylbutadiyne leads, in the presence of Na_2CO_3 , to the formation of the five-coordinate bis(diynyl)hydridorhodium(III) complex $[\text{RhH}(\text{C}\equiv\text{CC}\equiv\text{CPh})_2(\text{PiPr}_3)_2]$ (**3**). While **3** reacts with pyridine to give the stable octahedral compound $[\text{RhH}(\text{C}\equiv\text{CC}\equiv\text{CPh})_2(\text{py})(\text{PiPr}_3)_2]$ (**4**), on treatment with carbon monoxide the square-planar complex *trans*- $[\text{Rh}(\text{C}\equiv\text{CC}\equiv\text{CPh})(\text{CO})(\text{PiPr}_3)_2]$ (**6**) is formed via the spectroscopically characterized 1:1 adduct **5** as a labile intermediate. Compound **6**, which has also been prepared from $[\text{Rh}(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)(\text{PiPr}_3)_2]$ (**7**), CO, and phenylbutadiyne, reacts with $[\text{RhCl}(\text{PiPr}_3)_2]_n$ (**1**) to yield the binuclear complex $[\text{Rh}(\text{CO})(\text{PiPr}_3)_2(\eta^1, \eta^2\text{-C}\equiv\text{CC}\equiv\text{CPh})\text{-RhCl}(\text{PiPr}_3)_2]$ (**8**). The X-ray structural analysis of **8** (triclinic space group $P\bar{1}$ (No. 2) with $a = 12.460(2)$ Å, $b = 13.954(2)$ Å, $c = 16.431(2)$ Å, $\alpha = 97.98(1)^\circ$, $\beta = 91.47(1)^\circ$, $\gamma = 109.61(1)^\circ$, $V = 2657(1)$ Å³, and $Z = 2$) reveals a square-planar coordination around each of the metal centers which are bridged by a strongly bent diynyl ligand. The reaction of **1** with phenylbutadiyne leads, via the isomeric diyne and diynyl hydrido species **9** and **10** as intermediates, to the alkynyl-substituted vinylidenerhodium(I) complex *trans*- $[\text{RhCl}(\text{=C=CHC}\equiv\text{CPh})(\text{PiPr}_3)_2]$ (**11**). In the presence of pyridine the diynyl(hydrido)rhodium derivative $[\text{RhH}(\text{C}\equiv\text{CC}\equiv\text{CPh})\text{Cl}(\text{py})(\text{PiPr}_3)_2]$ (**12**) is obtained.

Introduction

We have recently shown that the displacement of the chloro ligand in $[\text{RhCl}(\text{PiPr}_3)_2]_n$ (**1**) by acetate alters the course of the reaction of the corresponding rhodium(I) complex $[\text{Rh}(\eta^2\text{-O}_2\text{CCH}_3)(\text{PiPr}_3)_2]$ (**2**) with phenylacetylene quite significantly. While compound **1** reacts with $\text{HC}\equiv\text{CPh}$ to give the square-planar vinylidene complex *trans*- $[\text{RhCl}(\text{=C=CHPh})(\text{PiPr}_3)_2]$,¹ the octahedral alkynyl(hydrido)rhodium(III) species $[\text{RhH}(\text{C}\equiv\text{CPh})(\eta^2\text{-O}_2\text{CCH}_3)(\text{PiPr}_3)_2]$ is initially formed on treatment of **2** with the same 1-alkyne.² In the presence of base, this further reacts with a second molecule of $\text{HC}\equiv\text{CPh}$ to give *trans*- $[\text{Rh}(\text{C}\equiv\text{CPh})(\text{=C=CHPh})(\text{PiPr}_3)_2]$.² Following the observation that $\text{HC}\equiv\text{CC}\equiv\text{CH}$ as the most simple diyne behaves similarly as $\text{HC}\equiv\text{CH}$ and $\text{HC}\equiv\text{CPh}$ toward the chloro compound **1**,³ we were interested to find out whether butadiyne or derivatives thereof would react with the acetato derivative **2** to afford preferentially either an alkynyl-substituted vinylidenerhodium(I) or a diynyl(hydrido)rhodium(III) complex. During these investigations on the reactivity of compounds **1** and **2** toward $\text{HC}\equiv\text{CC}\equiv\text{CPh}$ a four-coordinate carbonyl(diynyl)rhodium(I) complex has been prepared which on subsequent treatment with **1** yields an unsymmetrical binuclear product containing a strongly bent σ, π -bonded diynyl ligand in a bridging position.

Results and Discussion

Reaction of the Acetato Complex 2 with $\text{HC}\equiv\text{CC}\equiv\text{CPh}$. In contrast to $1,4\text{-C}_6\text{H}_4(\text{C}\equiv\text{CH})_2$ which has already been used by us⁴ as well as by Marder et al.⁵ to prepare bi- and polynuclear diynylrhodium complexes, the more simple butadiyne $\text{HC}\equiv\text{CC}\equiv\text{CH}$ is difficult to handle due to its high tendency for polymerization and its explosive behavior in the presence of air. Although we have previously used butadiyne,³ we decided for good reasons to employ the phenyl derivative for our studies with the acetato compound **2**. Phenylbutadiyne is obtained from the alkynol $\text{PhC}\equiv\text{C}\text{-C}\equiv\text{CCMe}_2\text{OH}$ on heating with a catalytic amount of solid KOH to 70 °C and, after distillation into a cold trap (−190 °C), is used as a diluted solution in pentane.⁶ This solution reacts with a mixture of **2** and Na_2CO_3 which is suspended in diethyl ether almost instantaneously to give the bis(diynyl) hydrido complex **3** in ca. 60% yield. The orange-brown microcrystalline solid is soluble in most common organic solvents, excluding pentane and hexane, and in the solid form only slightly air-sensitive. The structural proposal shown in Scheme 1 is mainly supported by the ³¹P NMR spectrum which displays only one doublet for the two equivalent phosphine ligands and by the chemical shift of the hydride signal in the ¹H NMR spectrum (δ −28.75) which is similar to that of the crystallographically characterized bis(alkynyl)hydridorhodium(III) derivative $[\text{RhH}(\text{C}\equiv\text{CCiPr}_2\text{OH})_2(\text{PiPr}_3)_2]$.⁷ With regard to the course of the reaction of **2** with $\text{HC}\equiv\text{CC}\equiv\text{CPh}$ and Na_2CO_3 , in

[®] Abstract published in *Advance ACS Abstracts*, March 15, 1995.

(1) (a) Garcia 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.; Garcia, Alonso, F. J.; Otto, H.; Wolf, J. *Z. Naturforsch.* **1988**, *43B*, 722–726.

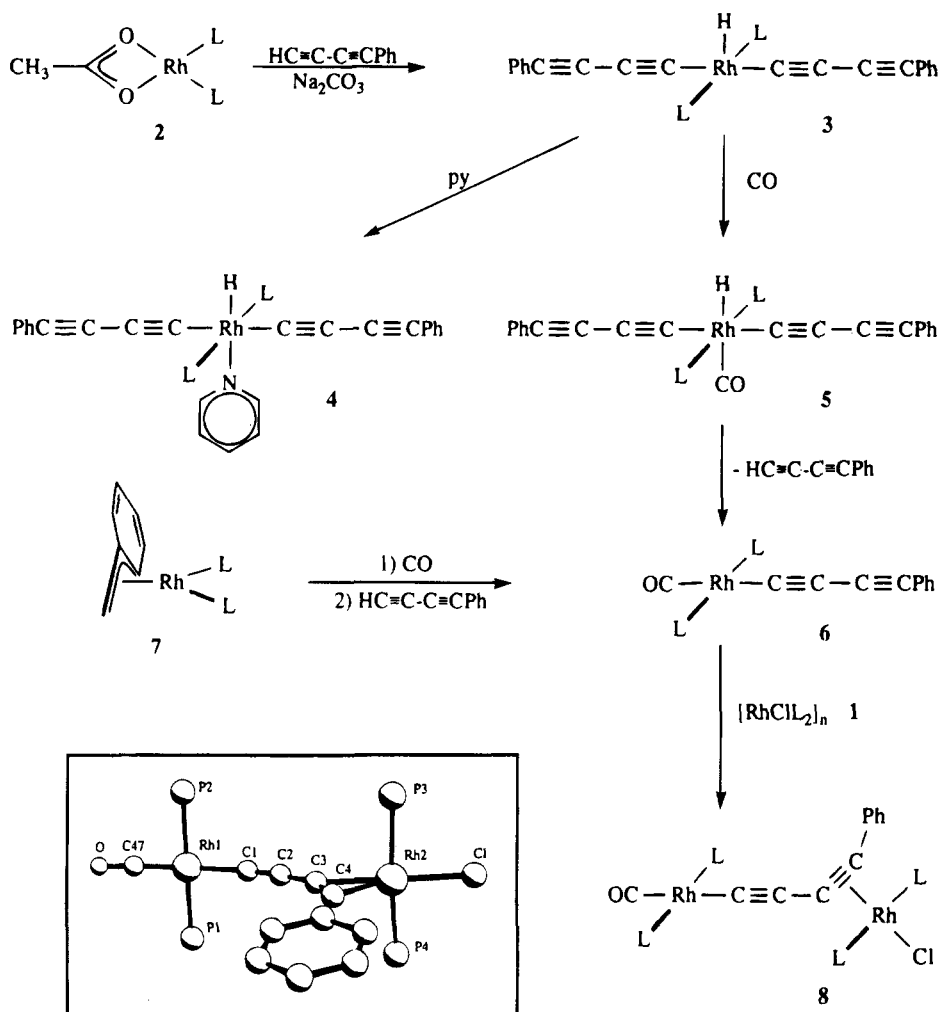
(2) Schäfer, M.; Wolf, J.; Werner, H. *J. Organomet. Chem.* **1995**, *485*, 85–100.

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

(4) (a) Werner, H.; Rappert, T.; Wolf, J. *Isr. J. Chem.* **1990**, *30*, 377–384. (b) Rappert, T. Dissertation, Universität Würzburg, 1992.

(5) Fyfe, H. B.; Mlekuz, M.; Zargarian, D.; Taylor, N. J.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1991**, 188–189.

(6) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Amsterdam, 1988; pp 212–214 and 290.

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

agreement with previous findings,^{1,2,7,8} we note that the thermodynamic stability of the $[\text{L}_n\text{RhH}(\text{C}\equiv\text{CR})]$ and $[\text{L}_n\text{Rh}(\text{C}\equiv\text{CHR})]$ isomers significantly depends both on the substituent R of the alkyne (or diyne) and the remaining ligands L with the possible trend that complexes $\text{RhH}(\text{C}\equiv\text{CR})_2$ less easily rearrange to rhodium vinylidenes than $\text{RhH}(\text{C}\equiv\text{CR})$ species.

Although compound **3** slowly decomposes in solution, it readily reacts with pyridine and carbon monoxide in pentane at -20°C to give the corresponding 1:1 adducts **4** and **5**, respectively. While the pyridine complex **4** is remarkably stable and only moderately soluble in benzene, the carbonyl compound **5** is rather labile and on warming in pentane to room temperature eliminates phenylbutadiyne to yield the square-planar diynylrhodium(I) complex **6**. The most characteristic features for the octahedral intermediate **5** are the doublet in the ^{31}P NMR spectrum at δ 56.87 and the resonance for the Rh–H proton in the ^1H NMR spectrum at δ –8.72 which is shifted by 20 ppm to lower field compared with **3**.

The rhodium(I) compound **6** which is a light-yellow solid resembles in most of its properties the analogous alkynyl(carbonyl)metal derivatives *trans*- $[\text{Rh}(\text{C}\equiv\text{CR})-$

$(\text{CO})(\text{P}i\text{Pr}_3)_2]$ (R = Me, Ph).⁸ It can also be prepared in more than 80% yield if a solution of the π -benzyl complex **7**⁹ in pentane at -20°C is first treated with carbon monoxide and then, upon cooling to -78°C , with 1 equiv of phenylbutadiyne. Since after CO is passed through the solution of **7** a rapid change of color from red to light-yellow occurs, we assume that initially a σ -benzyl species $[\text{Rh}(\text{CH}_2\text{C}_6\text{H}_5)(\text{CO})(\text{P}i\text{Pr}_3)_2]$ is formed⁹ which reacts with $\text{HC}\equiv\text{CC}\equiv\text{CPh}$ by protolytic cleavage of the Rh– $\text{CH}_2\text{C}_6\text{H}_5$ bond to give the final product. The diynyl complex **6** has been characterized by elemental analysis and IR as well as NMR spectroscopy. While the ^{31}P NMR spectrum shows the expected single resonance (doublet with a larger Rh–P coupling than found for **3** and **5**), the ^{13}C NMR spectrum displays four signals for the carbon atoms of the Rh– $\text{C}\equiv\text{CC}\equiv\text{C}$ chain at δ 126.33, 102.22, 79.15, and 71.95 which due to the decreasing P–C coupling constant along this sequence are supposedly assigned to C1–C4. Since in the ^1H NMR spectrum of **6** only one doublet of virtual triplets¹⁰ for the PCHCH_3 protons appears, there is no doubt that the phosphine ligands are in *trans* disposition.

In order to find out whether in contrast to *trans*- $[\text{RhCl}(\text{C}\equiv\text{C}=\text{C}=\text{C}=\text{CSiMe}_3)(\text{P}i\text{Pr}_3)_2]$ (R = H, SiMe_3)³ the

(7) Wiedemann, R.; Mahr, N.; Steinert, P.; Werner, H. Unpublished results. See: Wiedemann, R. Diploma Thesis, Universität Würzburg, 1991.

(8) Schäfer, M. Dissertation, Universität Würzburg, 1994.

(9) Werner, H.; Schäfer, M.; Nürnberg, O.; Wolf, J. *Chem. Ber.* **1994**, *127*, 27–38.

(10) Harris, R. K. *Canad. J. Chem.* **1964**, *24*, 2275–2281.

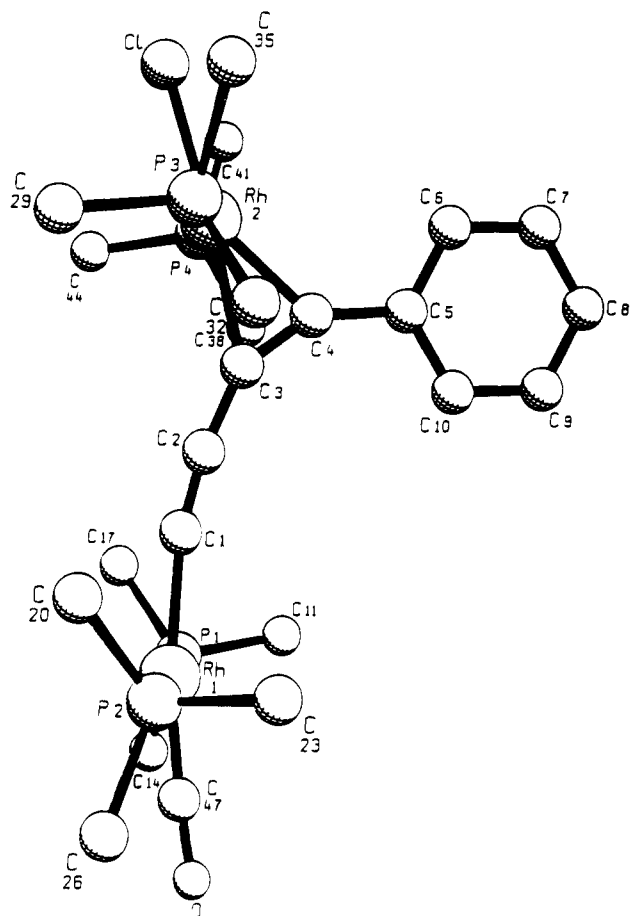


Figure 1. Molecular structure of **8** viewed perpendicular to the Rh–P axes. (The CH₃ carbon atoms of the isopropyl groups are omitted for clarity.)

outer C≡C bond in **6** can be used for π -coordination, the carbonyl diyne complex was treated with **1**. Both compounds react with each other in diethyl ether at 0 °C to give a yellow microcrystalline solid in nearly quantitative yield. The ¹H, ¹³C, and ³¹P NMR spectra of product **8** (Scheme 1) confirm that two different [Rh(PiPr₃)₂] units are present which together with the data of the elemental analysis indicate that an unsymmetrical binuclear rhodium complex is formed. This has been substantiated by an X-ray crystal structure analysis. The SCHAKAL drawing in Figure 1 reveals that the butadiynyl ligand is σ -bonded to a [Rh(CO)(PiPr₃)₂] and π -bonded to a [RhCl(PiPr₃)₂] fragment, both of which contain *trans*-disposed phosphine ligands. The most remarkable feature, however, is the crescent-shaped structure of the Rh–C≡CC≡C–C(Ph) chain which leads to an angle between the Rh–C1 and C4–C5 axes of about 95°. Whereas the deviation of the bond angles Rh–C1–C2 (167.9(3)°) and C1–C2–C3 (171.9(4)°) from the 180° value is only modest, the rehybridization of the carbon atoms C3 and C4 results in a bending of the C2–C3–C4 and C3–C4–C5 axes (149.5(4)° and 147.5(4)°, respectively) which is similar to that found in the chelate nickel complex [Ni(η^2 -HC≡CC≡CH)(iPr₂PCH₂-CH₂CH₂PiPr₂)] (146.2(6)°).¹¹ For other substituted

Table 1. Selected Bond Distances and Angles with Esd's for Compound **8**

Bond Distances (Å)			
Rh1–P1	2.316(1)	Rh2–C1	2.369(1)
Rh1–P2	2.314(1)	Rh2–C3	2.154(4)
Rh1–C1	2.061(4)	Rh2–C4	2.041(4)
Rh1–C47	1.884(5)	C1–C2	1.213(5)
C47–O	1.133(5)	C2–C3	1.393(6)
Rh2–P3	2.350(1)	C3–C4	1.271(5)
Rh2–P4	2.354(1)	C4–C5	1.440(5)
Bond Angles (deg)			
P1–Rh1–P2	178.22(4)	P3–Rh2–C1	88.35(4)
P1–Rh1–C1	90.1(1)	P3–Rh2–C3	91.3(1)
P1–Rh1–C47	90.4(1)	P3–Rh2–C4	95.2(1)
P2–Rh1–C1	90.3(1)	P4–Rh2–C1	87.49(4)
P2–Rh1–C47	89.5(1)	P4–Rh2–C3	92.0(1)
Rh1–C47–O	176.0(5)	P4–Rh2–C4	93.3(1)
Rh1–C1–C2	167.9(3)	C1–Rh2–C3	175.2(1)
C1–Rh1–C47	171.4(2)	C1–Rh2–C4	149.6(1)
C1–C2–C3	171.9(4)	Rh2–C3–C2	142.9(3)
C2–C3–C4	149.5(4)	Rh2–C3–C4	67.6(2)
C3–C4–C5	147.5(4)	Rh2–C4–C3	77.3(2)
C4–C5–C6	121.7(4)	Rh2–C4–C5	134.9(3)
C4–C5–C10	119.4(4)	C3–Rh2–C4	35.2(1)
P3–Rh2–P4	169.51(4)		

butadiyne metal compounds a smaller bending of the C–C–C angle (156(2) and 158.5(5)°) has been observed.^{3,12}

The rhodium, the four carbon atoms of the diyne chain, and the *ipso*-carbon atom of the phenyl group lie exactly in the same plane which is almost perpendicular to the planes containing the metal centers, the phosphorus atoms, and the Cl or CO ligands. The dihedral angle between [Rh1, P1, P2, C1, C47] and [C1, C2, C3, C4, C5] is 82.0(2)° and that between [Rh2, P3, P4, C1] and [C1, C2, C3, C4, C5] is 85.4(2)°. The two rhodium-containing planes [Rh1, P1, P2, C1, C47] and [Rh2, P3, P4, C1] are slightly tilted with respect to each other which could be due to some steric hindrance between the phenyl group and the triisopropylphosphine ligands. Although the coordination around Rh2 can be described as square-planar, the Rh2–C3 and Rh2–C4 distances differ significantly (2.154(4) and 2.041(4) Å) which is in marked contrast to the above-mentioned nickel complex¹¹ but very similar to the situation found in the mononuclear diynerhodium(I) compound *trans*-[RhCl(η^2 -Me₃SiC≡CC≡CSiMe₃)(PiPr₃)₂].³ The C3–C4 bond (see Table 1) is elongated by ca. 0.06 Å compared to C1–C2 and by ca. 0.08 Å compared with that in free butadiyne.¹³

The bond length Rh–C1 of 2.061(4) Å is slightly longer than that found for the Rh–C(sp) single bond in the five-coordinated alkynyl complex [Rh(C≡CCH₂-OMe)(HgPh)Cl(PiPr₃)₂] (1.986(5) Å)¹⁴ and in the six-coordinate bis(alkynyl)hydridorhodium(III) derivative [RhH(C≡CSiMe₃)₂(py)(PiPr₃)₂] (2.032(6) and 2.020(6) Å, respectively).¹⁵ The distance Rh–C1 is, however, almost identical to the Ru–C distances of the ruthenium compounds [Ru(C≡CC≡CR)₂(CO)₂(PEt₃)₂] (R = H, SiMe₃) where two diyne units are linked to the metal center.¹⁶

(12) Cash, G. G.; Pettersen, R. C. *J. Chem. Soc., Dalton Trans.* **1979**, 1630–1633.

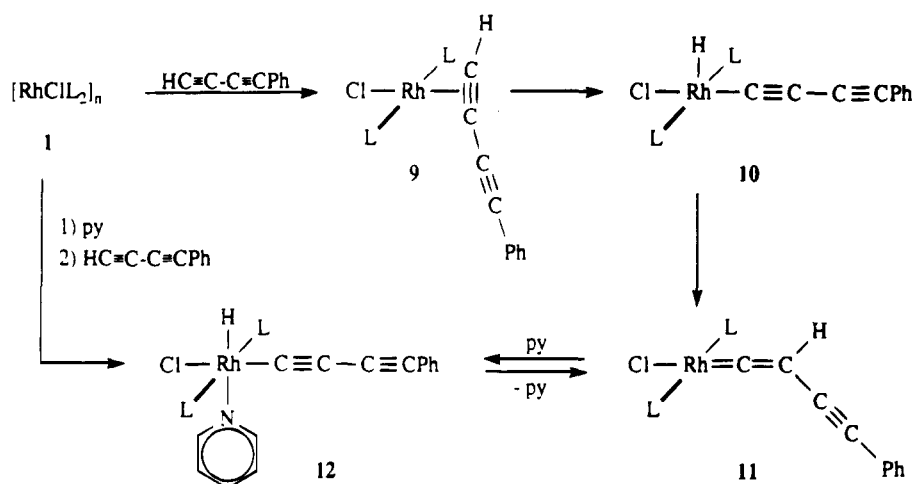
(13) Pauling, L.; Springall, H. D.; Palmer, K. J. *J. Am. Chem. Soc.* **1939**, *61*, 927–937.

(14) Baum, M.; Mahr, N.; Werner, H. *Chem. Ber.* **1994**, *127*, 1877–1886.

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

(16) Sun, Y.; Taylor, N. J.; Carty, A. J. *Organometallics* **1992**, *11*, 4293–4300.

(11) Bonrath, W.; Pörschke, K. R.; Wilke, G.; Angermund, K.; Krüger, C. *Angew. Chem.* **1988**, *100*, 853–855; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 833–835.

Scheme 2^a^a L = $PiPr_3$.

The Rh–Cl, Rh–CO, and Rh–P bond lengths in **8** correspond to what could be expected for square-planar complexes of rhodium(I).^{1,3,17} and deserve no further comments.

Reaction of the Chloro Complex 1 with $HC\equiv CC\equiv CPh$. Since compound **1** is monomeric in solution¹⁸ and therefore contains a coordinatively unsaturated metal center, it is not surprising that it readily reacts both with alkynes¹⁹ as well as diynes. If a solution of **1** in pentane is treated at $-20^\circ C$ with $HC\equiv CC\equiv CPh$, after a few minutes a light-yellow precipitate is formed which has to be quickly separated from the remaining solution. The ^{31}P NMR spectrum of the new compound (if measured in $CDCl_3$ at $-20^\circ C$) displays two doublets of unequal intensity and with different rhodium–phosphorus coupling constants. The more intense signal at δ 34.36 with $J(RhP) = 112$ Hz resembles both in the chemical shift and in the size of Rh–P coupling the resonance observed in the ^{31}P NMR spectrum of *trans*- $[RhCl(\eta^2-Me_3SiC\equiv CC\equiv CSiMe_3)(PiPr_3)_2]$,³ and thus we assume that it belongs to the initially formed π -alkyne complex **9** (Scheme 2). The less intense signal appears (in $CDCl_3$) at δ 49.85, and since it shows a Rh–P coupling (96 Hz) which is almost identical to that of $[(PiPr_3)_2Cl(H)Rh(C\equiv CC\equiv C)Rh(H)Cl(PiPr_3)_2]$,³ we attribute this doublet to the five-coordinate diynyl(hydrido)rhodium(III) derivative **10**. The 1H NMR spectrum of the yellow precipitate supports this proposal because it displays in the high-field region at δ -27.50 a doublet of triplets [$J(RhH) = 42.1$, $J(PH) = 12.3$ Hz] which again is very similar to that of the above mentioned $HRh(C\equiv CC\equiv C)RhH$ species.³

Stirring a solution of the mixture of **9** and **10** in diethyl ether for 2 h at room temperature leads to a change of color from yellow to green, and after the solvent has been removed dark-green crystals are isolated in about 80% yield. Compound **11** which is

soluble in most common organic solvents has been characterized by elemental analysis and IR as well as NMR spectroscopy. The most typical feature besides the doublet in the ^{31}P NMR spectrum at δ 42.92 ($J(RhP) = 133.7$ Hz) and the $C=CH$ proton signal in the 1H NMR spectrum at δ 1.03 are the low-field resonances at δ 293.76 and 91.46 (both doublets of triplets due to Rh–C and P–C coupling) in the ^{13}C NMR spectrum which are characteristic of compounds of the general type *trans*- $[RhCl(=C=CRR')(PiPr_3)_2]$.^{1,3,4,14,15}

The octahedral pyridine adduct **12** (Scheme 2) is most conveniently prepared on stepwise reaction of **1** with pyridine and phenylbutadiyne at $-20^\circ C$. However, if in analogy to previous work^{3,20} the mixture of **9** and **10** is treated with pyridine in diethyl ether at $0^\circ C$, besides **12** the vinylidene complex **11** is equally formed. Although **11** slowly reacts with pyridine to give **12**, only in the presence of a larger excess of NC_5H_5 the equilibrium can be completely shifted to the side of the rhodium(III) species. Therefore, the synthetic route to **12** using **1** as the starting material is preferred. Compound **12** is a white crystalline solid which can be briefly handled in air but even if stored under argon slowly decompose to give dark oily, possibly polymeric products.

Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk tube techniques. The starting materials $[RhCl(PiPr_3)_2]_n$ (**1**),²¹ $[Rh(\eta^2-O_2CCH_3)(PiPr_3)_2]$ (**2**),⁹ $[Rh(\eta^3-CH_2C_6H_5)(PiPr_3)_2]$ (**7**),⁹ and $HC\equiv CC\equiv CPh$ ^{6,22} were prepared as described in the literature. NMR spectra were recorded at room temperature on Bruker AC 200 and Bruker AMX 400 instruments, and IR spectra, on a Perkin-Elmer 1420 infrared spectrophotometer. Melting points were measured by DTA.

Preparation of $[RhH(C\equiv CC\equiv CPh)_2(PiPr_3)_2]$ (3**).** Diethyl ether (15 mL) was poured on a mixture of **2** (237 mg, 0.49 mmol) and excess Na_2CO_3 (ca. 500 mg), and upon cooling of the mixture to $0^\circ C$, a solution of phenylbutadiyne (124 mg, 0.98 mmol) in 10 mL of pentane was added. After the mixture was stirred for 5 min, the solution was separated and stored

(17) (a) Nürnberg, O.; Werner, H. *J. Organomet. Chem.* **1993**, 460, 163–175. (b) Wiedemann, R.; Steinert, P.; Schäfer, M.; Werner, H. *J. Am. Chem. Soc.* **1993**, 115, 9864–9865. (c) Werner, H.; Rappert, T.; Wiedemann, R.; Wolf, J.; Mahr, N. *Organometallics* **1994**, 13, 2721–2727.

(18) Schneider, D.; Werner, H. *Angew. Chem.* **1991**, 103, 710–712; *Angew. Chem., Int. Ed. Engl.* **1991**, 30, 700–702.

(19) Short reviews: (a) Werner, H. *Nachr. Chem. Tech. Lab.* **1992**, 40, 435–444. (b) Werner, H. *J. Organomet. Chem.* **1994**, 475, 45–55.

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

(21) Werner, H.; Wolf, J.; Höhn, A. *J. Organomet. Chem.* **1985**, 287, 395–407.

(22) Gevert, O. Diploma Thesis, Universität Würzburg, 1994.

in a cooled Schlenk tube at 0 °C. The orange-brown precipitate was extracted twice with 5 mL of diethyl ether each, and the extracts were combined with the reaction solution. After the solvent was removed in vacuo, the yellow residue was repeatedly washed with small portions of acetone (−20 °C) and dried in vacuo: yield 203 mg (61%); mp 64 °C dec; IR (KBr) $\nu(\text{C}\equiv\text{C})$ 2140, 2010 cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz) δ 7.35 (m, C_6H_5), 2.92 (m, PCHCH_3), 1.37 [dvt, $N = 13.8$, $J(\text{HH}) = 6.5$ Hz, PCHCH_3], −28.75 [dt, $J(\text{RhH}) = 52.2$, $J(\text{PH}) = 11.7$ Hz, RhH]; ^{31}P NMR (C_6D_6 , 81.0 MHz) δ 53.77 [d, $J(\text{RhP}) = 97.4$]. Anal. Calcd for $\text{C}_{38}\text{H}_{53}\text{P}_2\text{Rh}$: C, 67.73; H, 7.93. Found: C, 67.54; H, 7.98.

Preparation of $[\text{RhH}(\text{C}\equiv\text{CC}=\text{CPh})_2(\text{py})(\text{PiPr}_3)_2]$ (4). A suspension of **3** (120 mg, 0.18 mmol) in 5 mL of pentane was treated at −20 °C with excess pyridine (0.1 mL) and under continuous stirring slowly warmed to room temperature (ca. 5–8 min). A white precipitate was formed, which was filtered off, washed three times with 2 mL of pentane each (0 °C), and dried in vacuo: yield 130 mg (96%); mp 117 °C dec; IR (KBr) $\nu(\text{C}\equiv\text{C})$ 2140, 2010 cm^{-1} ; ^1H NMR (C_6D_6 , 200 MHz) δ 8.50–6.80 (m, C_6H_5 and NC_5H_5), 2.84 (m, PCHCH_3), 1.17 [dvt, $N = 14.5$, $J(\text{HH}) = 7.3$ Hz, PCHCH_3], −17.51 [dt, $J(\text{RhH}) = 17.4$, $J(\text{PH}) = 13.1$ Hz, RhH]; ^{31}P NMR (C_6D_6 , 81.0 MHz) δ 42.16 [d, $J(\text{RhP}) = 94.5$ Hz]. Anal. Calcd for $\text{C}_{43}\text{H}_{58}\text{N}_2\text{P}_2\text{Rh}$: C, 68.52; H, 7.75; N, 1.86. Found: C, 68.56; H, 7.59; N, 1.99.

Intermediate Formation of $[\text{RhH}(\text{C}\equiv\text{CC}=\text{CPh})_2(\text{CO})(\text{PiPr}_3)_2]$ (5). A slow stream of CO was passed for 2 min through a suspension of **3** (50 mg, 0.07 mmol) in 5 mL of pentane at −20 °C. After the reaction mixture was stirred for 5 min at the same temperature, the solvent was removed in vacuo. The ^1H and ^{31}P NMR spectra of the yellow-brown residue, measured at −20 °C, reveal the presence of at least two compounds of which **5** is the main component: ^1H NMR (C_6D_6 , 200 MHz) δ 7.25 (m, C_6H_5), 2.75 (m, PCHCH_3), 1.23 [dvt, $N = 14.5$, $J(\text{HH}) = 7.3$ Hz, PCHCH_3], −8.72 [dt, $J(\text{RhH}) = 8.7$, $J(\text{PH}) = 9.4$ Hz, RhH]; ^{31}P NMR (C_6D_6 , 81.0 MHz) δ 56.87 [d, $J(\text{RhP}) = 87.5$ Hz].

Preparation of $\text{trans}[\text{Rh}(\text{C}\equiv\text{CC}=\text{CPh})(\text{CO})(\text{PiPr}_3)_2]$ (6). Method a. The yellow-brown solid, obtained from **3** and CO at −20 °C as described above, was dissolved in 3 mL of toluene at room temperature. The solution was stirred for 3 min, the solvent was removed, and the residue was recrystallized from 2 mL of acetone (25 to −78 °C). A bright-yellow solid was obtained, yield ca. 90%.

Method b. A slow stream of CO was passed for 2 min through a solution of **7** (80 mg, 0.16 mmol) in 5 mL of pentane at −20 °C which was accompanied by a change of color from red to light-yellow. After the solution was stirred for 10 min at −20 °C under a CO atmosphere, it was cooled to −78 °C and then a solution of phenylbutadiyne (20 mg, 0.16 mmol) in 2 mL of pentane was added dropwise. The reaction mixture was stirred for 10 min at −78 °C, the volatile components were removed in vacuo, and the residue was worked up as described in method a: yield 75 mg (89%); mp 158 °C dec; IR (KBr) $\nu(\text{C}\equiv\text{C})$ 2150, $\nu(\text{C}=\text{O})$ 1935 cm^{-1} ; ^1H NMR (C_6D_6 , 200 MHz) δ 7.10 (m, C_6H_5), 2.45 (m, PCHCH_3), 1.27 [dvt, $N = 13.9$, $J(\text{HH}) = 6.9$ Hz, PCHCH_3]; ^{13}C NMR (C_6D_6 , 100.6 MHz) δ 196.03 [dt, $J(\text{RhC}) = 58.9$, $J(\text{PC}) = 13.8$ Hz, CO], 132.45, 128.27, 127.24 (all s, C_6H_5), 106.33 (s, *ipso*-C of C_6H_5), 126.33 [dt, $J(\text{RhC}) = 43.4$, $J(\text{PC}) = 21.6$ Hz], 102.22 [dt, $J(\text{RhC}) = 12.7$, $J(\text{PC}) = 3.2$ Hz], 79.15 (m), 71.95 [t, br, $J(\text{PC}) = 2.1$ Hz] (these four signals are assigned to the carbon atoms of the C_4 chain), 26.32 [vt, $N = 23.3$ Hz, PCHCH_3], 20.42 (s, PCHCH_3); ^{31}P NMR (C_6D_6 , 81.0 MHz) δ 54.21 [d, $J(\text{RhP}) = 125$ Hz]. Anal. Calcd for $\text{C}_{29}\text{H}_{47}\text{OP}_2\text{Rh}$: C, 60.42; H, 8.22. Found: C, 59.98; H, 8.03.

Preparation of $\text{trans}[\text{Rh}(\text{CO})(\text{PiPr}_3)_2(\eta^1, \eta^2\text{-C}\equiv\text{CC}=\text{CPh})\text{RhCl}(\text{PiPr}_3)_2]$ (8). A solution of **6** (102 mg, 0.18 mmol) in 5 mL of diethyl ether was treated at 0 °C with a solution of **1** (83 mg, 0.18 mmol for $n = 1$) in 5 mL of diethyl ether. With continuous stirring, the solution was slowly warmed to room temperature (ca. 20 min), the solvent was then removed, and the residue was dissolved in 3 mL of acetone. After the

solution was stored at −78 °C, a yellow microcrystalline precipitate was formed which was filtered off, repeatedly washed with small portions of acetone (0 °C), and dried: yield 157 mg (85%); mp 117 °C dec; IR (KBr) $\nu(\eta^1\text{-C}\equiv\text{C})$ 1995, $\nu(\text{C}=\text{O})$ 1930, $\nu(\eta^2\text{-C}\equiv\text{C})$ 1800 cm^{-1} ; ^1H NMR (C_6D_6 , 400 MHz) δ 8.20 (m, *ortho*-H of C_6H_5), 7.36 (m, *meta*-H of C_6H_5), 7.14 (m, *para*-H of C_6H_5), 2.72, 2.61 (both m, PCHCH_3), 1.57 [dvt, $N = 13.5$, $J(\text{HH}) = 6.9$ Hz, PCHCH_3], 1.47 [dvt, $N = 13.9$, $J(\text{HH}) = 7.1$ Hz, PCHCH_3], 1.38 [dvt, $N = 12.9$, $J(\text{HH}) = 6.3$ Hz, PCHCH_3]; ^{13}C NMR (C_6D_6 , 100.6 MHz) δ 196.55 [dt, $J(\text{RhC}) = 58.4$, $J(\text{PC}) = 14.6$ Hz, CO], 131.62 (s, *ipso*-C of C_6H_5), 130.58, 127.82, 126.02 (all s, C_6H_5), 139.32 [dt, $J(\text{RhC}) = 44.3$, $J(\text{PC}) = 21.1$ Hz], 106.29, 82.28, 65.51 (all m), (these four signals are assigned to the carbon atoms of the C_4 chain), 26.52 [vt, $N = 21.3$ Hz, PCHCH_3], 23.38 [vt, $N = 17.0$ Hz, PCHCH_3], 21.32, 20.73, 20.09 (all s, PCHCH_3); ^{31}P NMR (C_6D_6 , 162.0 MHz) δ 55.10 [d, $J(\text{RhP}) = 126.4$ Hz], 33.76 [d, $J(\text{RhP}) = 119.2$ Hz]. Anal. Calcd for $\text{C}_{47}\text{H}_{89}\text{ClO}_2\text{P}_4\text{Rh}_2$: C, 54.52; H, 8.66. Found: C, 54.66; H, 8.43.

Preparation of $\text{trans}[\text{RhCl}(\text{C}=\text{CHC}=\text{CPh})(\text{PiPr}_3)_2]$ (11). A solution of **1** (293 mg, 0.64 mmol for $n = 1$) in 10 mL of pentane was treated dropwise at −20 °C with a solution of phenylbutadiyne (80 mg, 0.64 mmol) in 8 mL of pentane. After the solution was stirred for 3–5 min, a light-yellow solid precipitated which was separated from the mother liquor and dried in vacuo. The solid was dissolved in 5 mL of diethyl ether, and the solution was stirred for 2 h at room temperature. The volatile components were removed in vacuo, and the residue was dissolved in 2 mL of acetone. After the solution was stored for 16 h at −78 °C, a dark-green precipitate was formed which was filtered off, repeatedly washed with acetone (0 °C), and dried: yield 301 mg (80%); mp 73 °C dec; IR (KBr) $\nu(\text{C}\equiv\text{C})$ 2170, $\nu(\text{C}=\text{C})$ 1605 cm^{-1} ; ^1H NMR (CDCl_3 , 200 MHz) δ 7.26 (m, C_6H_5), 2.87 (m, PCHCH_3), 1.40 [dvt, $N = 13.7$, $J(\text{HH}) = 7.1$ Hz, PCHCH_3], 1.03 [dt, $J(\text{RhH}) = 0.7$, $J(\text{PH}) = 3.1$ Hz, $\text{Rh}=\text{C}=\text{CH}$]; ^{13}C NMR (CDCl_3 , 50.3 MHz) δ 293.76 [dt, $J(\text{RhC}) = 62.3$, $J(\text{PC}) = 16.5$ Hz, $\text{Rh}=\text{C}$], 130.90, 128.85, 127.61 (all s, C_6H_5), 125.37 (s, *ipso*-C of C_6H_5), 100.24 (s, $\text{C}=\text{CPh}$), 91.46 [dt, $J(\text{RhC}) = 17.8$, $J(\text{PC}) = 6.0$ Hz, $\text{Rh}=\text{C}=\text{C}$], 67.10 [t, br, $J(\text{PC}) = 3.5$ Hz, $\text{C}=\text{CPh}$], 24.00 [vt, $N = 20.3$ Hz, PCHCH_3], 20.74 (s, PCHCH_3); ^{31}P NMR (CDCl_3 , 81.0 MHz) δ 42.92 [d, $J(\text{RhP}) = 133.7$ Hz]. Anal. Calcd for $\text{C}_{28}\text{H}_{48}\text{ClP}_2\text{Rh}$: C, 57.49; H, 8.27. Found: C, 57.20; H, 8.21.

Preparation of $[\text{RhH}(\text{C}\equiv\text{CC}=\text{CPh})\text{Cl}(\text{py})(\text{PiPr}_3)_2]$ (12). A solution of **1** (163 mg, 0.40 mmol for $n = 1$) in 15 mL of diethyl ether was treated first with pyridine (0.1 mL, 1.2 mmol) and then at −20 °C with a solution of phenylbutadiyne (50 mg, 0.40 mmol) in 5 mL of pentane. An almost immediate change of color from red to light-yellow occurred. After the reaction mixture was stirred for 15 min at 0 °C, the volatile components were removed and the yellow-green residue was repeatedly washed with small portions of acetone (0 °C) and dried in vacuo: yield 155 mg (58%); mp 78 °C dec; IR (KBr) $\nu(\text{C}\equiv\text{C})$ 2165, 2050 cm^{-1} ; ^1H NMR (C_6D_6 , 200 MHz) δ 9.77 (m, *ortho*-H of NC_5H_5), 7.44–6.64 (m, C_6H_5 and NC_5H_5), 2.93 (m, PCHCH_3), 1.54 [dvt, $N = 13.9$, $J(\text{HH}) = 7.3$ Hz, PCHCH_3], 1.33 [dvt, $N = 13.1$, $J(\text{HH}) = 6.2$ Hz, PCHCH_3], −17.03 [dt, $J(\text{RhH}) = 13.1$, $J(\text{PH}) = 13.1$ Hz, RhH]; ^{31}P NMR (C_6D_6 , 81.0 MHz) δ 38.38 [d, $J(\text{RhP}) = 97.4$ Hz]. Anal. Calcd for $\text{C}_{33}\text{H}_{53}\text{ClNP}_2\text{Rh}$: C, 59.68; H, 8.04; N, 2.11. Found: C, 59.56; H, 8.35; N, 2.07.

X-ray Structural Analysis of 8. Single crystals were grown from diethyl ether at −20 °C. Crystal data (from 23 reflections, $10^\circ < \theta < 12^\circ$): triclinic, space group $P\bar{1}$ (No. 2), $a = 12.460(2)$ Å, $b = 13.954(2)$ Å, $c = 16.431(2)$ Å, $\alpha = 97.98(1)^\circ$, $\beta = 91.47(1)^\circ$, $\gamma = 109.61(1)^\circ$, $V = 2657(1)$ Å³, $Z = 2$, $D_{\text{calcd}} = 1.284$ g cm^{-3} , $\mu(\text{Mo K}\alpha) = 8.0$ cm^{-1} . Crystal size: $0.13 \times 0.23 \times 0.40$ mm. Solution details: Enraf-Nonius CAD4 diffractometer, Mo K α radiation (0.709 30 Å), graphite monochromator, zirconium filter (factor 16.4), $T = 293$ K, ω/θ -scan, maximum $2\theta = 42^\circ$, 6064 reflections measured, 5388 independent, 4867

regarded as being observed [$F_o > 3\sigma(F_o)$]; intensity data corrected for Lorentz and polarization effects, empirical absorption correction (ψ -scan method) applied, minimum transmission 95.82%; structure solved by direct methods (SHELXS-86); atomic coordinates and anisotropic thermal parameters refined by full-matrix least squares (Enraf-Nonius SDP);²³ positions of the hydrogen atoms calculated according to ideal geometry and used only in structure factor calculation; $R = 0.035$, $R_w = 0.035$; reflection/parameter ratio 9.81; residual electron density $\pm 1.53/-0.52$ e \AA^{-3} .

(23) Frenz, B. A. The Enraf-Nonius CAD 4 SDP—a real time system for concurrent X-ray data collection and structure determination. In *Computing in Crystallography*; Delft University Press: Delft, Holland, 1978; pp 64–71.

Acknowledgment. We thank the Volkswagen Stiftung and the Fonds der Chemischen Industrie for financial support. We also gratefully acknowledge support by Mrs. U. Neumann, Mrs. R. Schedl, and Mr. C. P. Kneis (elemental analysis and DTA), Mrs. M. L. Schäfer, Dr. W. Buchner, and Mr. B. Stempfle (NMR measurements) and Degussa AG (chemicals).

Supplementary Material Available: Tables of data collection parameters, bond lengths and angles, positional and thermal parameters, and least-squares planes for **8** (15 pages). Ordering information is given on any current masthead page.

OM9408472