Binding Two C_2 Units to an Electron-Rich Transition-Metal Center: The Interplay of Alkyne(alkynyl), Bisalkynyl(hydrido), Alkynyl(vinylidene), Alkynyl(allene), Alkynyl(olefin), and Alkynyl(enyne) Rhodium Complexes†

Martin Schäfer, Justin Wolf, and Helmut Werner*

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

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A series of alkynyl(vinylidene)rhodium(I) complexes of the general composition *trans*-[Rh(C≡CR)(=C=CHR)(P*i*Pr$_3$)$_2$] (R = H, Me, *t*Bu, and Ph) were prepared from either [Rh(η^3-C$_3$H$_5$)(P*i*Pr$_3$)$_2$] (**1**) or [Rh(η^3-CH$_2$Ph)(P*i*Pr$_3$)$_2$] (**18**) and 2 equiv of RC≡CH as the precursors. In some cases, the four-coordinate alkynyl(alkyne)rhodium(I) compounds *trans*-[Rh(C≡CR)(RC≡CH)(P*i*Pr$_3$)$_2$] and/or the five-coordinate bis(alkynyl)hydridorhodium(III) complexes [RhH(C≡CR)$_2$(P*i*Pr$_3$)$_2$] were isolated as intermediates. In the presence of pyridine, the octahedral compounds [RhH(C≡CR)$_2$(py)(P*i*Pr$_3$)$_2$] were obtained. Upon warming, they eliminate one molecule of RC≡CH and afford *trans*-[Rh(C≡CR)(py)(P*i*Pr$_3$)$_2$]. The reaction of **18** with an equimolar amount of terminal alkyne under an atmosphere of C_2H_4 gave the alkynyl(ethene) complexes *trans*-[Rh(C≡CR)(C_2H_4)(P*i*Pr$_3$)$_2$] (**21**−**23**), which react with pyridine, CO, and PhC≡CR by displacement of the olefinic ligand. Treatment of **22** (R = *t*Bu) and **23** (R = Ph) with methylpropiolate gave the rhodium vinylidenes *trans*-[Rh(C≡CR)(=C=CHCO$_2$Me)(P*i*Pr$_3$)$_2$]. The related complex *trans*-[Rh(C≡CPh)(=C=CH$_2$)(P*i*Pr$_3$)$_2$] was prepared by two routes using *trans*-[Rh(C≡CPh)(C_2H_4)(P*i*Pr$_3$)$_2$] or *trans*-[Rh(C≡CH)(C_2H_4)(P*i*Pr$_3$)$_2$] as the precursor. The reaction of **1** or **18** and excess MeC≡CH leads, under different conditions, either to four-coordinate *trans*-[Rh(C≡CMe)(η^2-CH$_2$=C=CH$_2$)(P*i*Pr$_3$)$_2$] or to five-coordinate [Rh(C≡CMe)$_2${C(CH$_3$)=CH$_2$}(P*i*Pr$_3$)$_2$]. The latter rearranges at room temperature to yield the enyne complex *trans*-[Rh(C≡CMe){η^2-MeC≡CC(Me)=CH$_2$}(P*i*Pr$_3$)$_2$] by intramolecular C−C coupling. Treatment of **1** with excess PhC≡CH gave a mixture of *trans*-[Rh(C≡CPh)(η^2-PhC≡CCH=CHPh)(P*i*Pr$_3$)$_2$] (**43**), *trans*-[Rh(C≡CPh){η^2-PhC≡CC(Ph)=CH$_2$}(P*i*Pr$_3$)$_2$] (**45**), PhC≡CCH=CHPh (**44**), and PhC≡CC(Ph)=CH$_2$ (**46**). With catalytic amounts of **1** and excess phenylacetylene, the 1,4- and 1,3-disubstituted butenynes **44** and **46** were formed in the ratio of 70:30, probably via *trans*-[Rh(C≡CPh)(PhC≡CH)(P*i*Pr$_3$)$_2$] and [RhH(C≡CPh)$_2$(P*i*Pr$_3$)$_2$] as intermediates.

Introduction

In the search for monomeric, highly reactive bis(triisopropylphosphine)rhodium(I) complexes of the general composition [RhX(P*i*Pr$_3$)$_2$], we reported the preparation of the η^3-allyl and η^3-benzyl derivatives [Rh(η^3-C$_3$H$_4$R)(P*i*Pr$_3$)$_2$] and [Rh(η^3-CH$_2$C$_6$H$_4$R)(P*i*Pr$_3$)$_2$], which were obtained upon treatment of the dimeric chloro compound [RhCl(P*i*Pr$_3$)$_2$]$_2$[1] with Grignard reagents.[2] Due to the lability of the allyl− and benzyl−rhodium bond, the respective complexes react not only with H_2 and CO[2,3] but also with acids such as CH_3CO_2H, CF_3CO_2H, and $C_6H_5CO_2H$ to give the monomeric rhodium(I) compounds [Rh(κ^2-O$_2$CR)(P*i*Pr$_3$)$_2$] in virtually quantitative yields. The reactivity of these chelate compounds, in particular toward H_2, O_2, CO, olefins, and terminal alkynes, has been the subject of two previous publications.[4,5]

In continuation of these studies, we discuss in this paper the synthetic potential of the two complexes [Rh(η^3-C$_3$H$_5$)(P*i*Pr$_3$)$_2$] and [Rh(η^3-CH$_2$C$_6$H$_5$)(P*i*Pr$_3$)$_2$] as starting materials for the preparation of a series of rhodium compounds having two different C_2 units coordinated to the metal center. Moreover, we illustrate the possible interconversion of isomeric alkyne(alkynyl), bisalkynyl(hydrido), and alkynyl(vinylidene) rhodium derivatives

† Dedicated to Professor Helmut Fischer on the occasion of his 60th birthday, with our best wishes and congratulations for his scientific achievements.

(1) (a) Preparation in situ: Busetto, C.; D'Alfonso, A.; Maspero, F.; Perego, G.; Zazzetta, 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) Molecular structure: Binger, P.; Haas, J.; Glaser, G.; Goddard, R.; Krüger, K. *Chem. Ber.* **1994**, *127*, 1927−1929.

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

(3) Wolf, J.; Nürnberg, O.; Schäfer, M.; Werner, H. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1157−1162.

(4) Schäfer, M.; Wolf, J.; Werner, H. *J. Organomet. Chem.* **1994**, *476*, 85−91.

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

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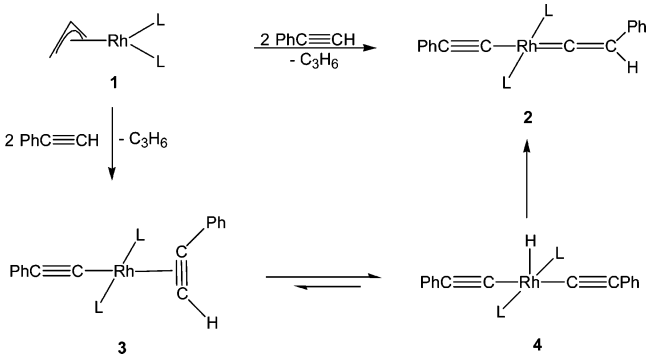
Scheme 1[a]



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

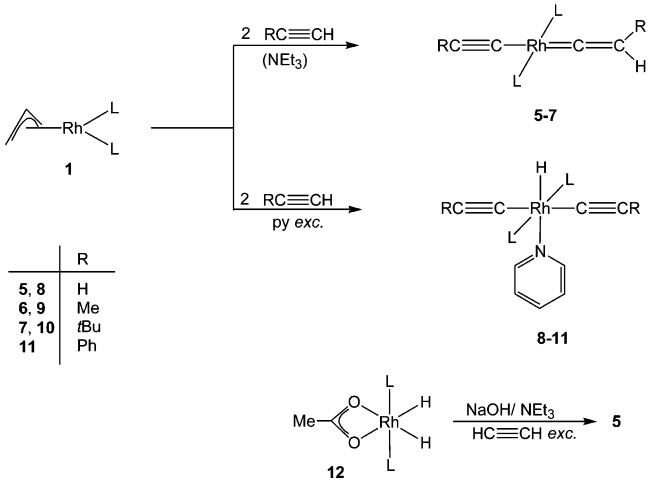
and describe the ability of the η^3-allyl complex [Rh(η^3-C_3H_5)(P*i*Pr$_3$)$_2$] to afford, by dimerization of two terminal alkyne molecules, isomeric substituted enynes. Part of this work has already been communicated.[6]

Results and Discussion

Preparation of Isomeric Alkynyl(vinylidene), Alkynyl(alkyne), and Bis(alkynyl)hydrido Rhodium Complexes. The reaction of the η^3-allyl compound **1** with 2 equiv of phenylacetylene in pentane proceeds slowly at room temperature and after 4 h affords the alkynyl(vinylidene) complex **2** in 78% yield (Scheme 1). If the reaction of **1** with phenylacetylene is carried out at −40 °C, the alkynyl(alkyne)rhodium(I) derivative **3** can be isolated. It is possibly formed via the oxidative addition product [RhH(C≡CPh)(η^3-C_3H_5)(P*i*Pr$_3$)$_2$] and the rearranged isomer *trans*-[Rh(C≡CPh)(C_3H_6)(P*i*Pr$_3$)$_2$] containing a weakly bound propene ligand as short-lived intermediates. Compound **3** is a yellow air-sensitive solid, the composition of which has been substantiated by elemental analysis and spectroscopic means. The IR spectrum of **3** displays two bands at 2080 and 1848 cm^{-1}, being assigned to the ν(C≡C) stretching modes of the alkynyl and the alkyne ligands. The ^{1}H NMR spectrum of **3** shows (in toluene-d_8 at −40 °C) for the alkyne ≡CH proton a resonance at δ 4.42 ppm, which is split into a doublet due to ^{1}H−^{103}Rh coupling. Apart from this signal, the ^{1}H NMR spectrum displays a high-field resonance at δ −29.42, indicating that in solution there is an equilibrium between compound **3** and the bis(alkynyl)hydridorhodium(III) isomer **4**. In agreement with this observation, the ^{31}P NMR spectrum shows (in toluene-d_8 at −40 °C) two doublets at δ 38.8 (for **3**) and 52.9 (for **4**) in the approximate ratio of 60:40. After increasing the temperature to 25 °C, the ratio changes to ca. 40:60. This change is reversible. Attempts to enrich the mixture in compound **4** failed, since at 25 °C or above the rhodium(III) isomer rearranges quantitatively to the vinylidene complex **2**. We note that this complex has already been prepared from [RhH(C≡CPh)-(κ^2-O_2CMe)(P*i*Pr$_3$)$_2$] and phenylacetylene in the presence of excess NaOH and a mixture of pentane and NEt$_3$ as the solvent.[5]

The starting material **1** reacts not only with PhC≡CH but also with acetylene, propyne, and *tert*-butylacetylene to give the corresponding alkynyl(vinylidene) complexes **5**−**7** (Scheme 2). These reactions are considerably slower than the reaction of **1** with phenylacetylene and take 6−10 h at room temperature (R = H, Me) or 5 h at 40 °C (R = *t*Bu). Since, in contrast to the chloro(vinylidene) compounds *trans*-[RhCl(=C=CHR)(P*i*Pr$_3$)$_2$],[7] the alkynyl analogues **5**−**7** slowly decompose in solution, the yield is rather low and for **5** amounts only to ca. 30%. However, the yield of **5** can be increased to about 80% if instead of **1** the dihydrido complex **12**, in the presence of NaOH/NEt$_3$, is used as the starting material. For compounds **6** and **7**, the yield could also be considerably improved if a mixture of pentane or hexane and NEt$_3$ is used as the solvent. The alkynyl(vinylidene) complexes **5**−**7** are blue, moderately air-sensitive solids, which in the absence of solvents are quite stable and under argon can be stored for weeks without decomposition. Typical spectroscopic features are the high-field resonance for the vinylidene proton in the ^{1}H NMR spectra at δ −0.13 (for **5**), 0.40 (for **6**), and −0.21 (for **7**) and the low-field signals for carbon atoms of the Rh=C=C unit in the ^{13}C NMR spectra at around δ 307−309 (α-C) and δ 92−121 (β-C), both of which are split into doublets of triplets. The ^1J(Rh,C) and ^2J(Rh,C) coupling constants for these signals are somewhat smaller than those of the chloro(vinylidene) counterparts *trans*-[RhCl(=C=CHR)(P*i*Pr$_3$)$_2$], pointing to a weakening of the Rh=C bond as a consequence of the strong *trans* influence of the alkynyl ligand.

Scheme 2[a]



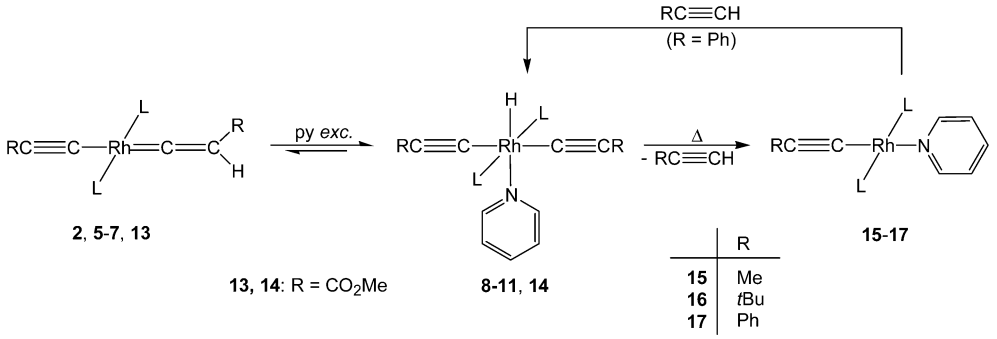
[a] L = P*i*Pr$_3$.

If the starting material **1** reacts with 2 equiv of RC≡CH in the presence of excess pyridine, instead of the four-coordinate rhodium(I) vinylidenes **5**−**7** the six-coordinate rhodium(III) complexes **8**−**11** are isolated in good to excellent yields. By taking the detection of the hydridometal derivative **4** (see Scheme 1) into consideration, we assume that not only compound **2** but also the analogous vinylidene complexes **5**−**7** are formed via five-coordinate bis(alkynyl)hydridorhodium(III) species as intermediates. The pyridine adducts **8**−**11** are white, practically air-stable solids, for which correct elemental analyses have been obtained. The ^{1}H NMR spectra of **8**−**11** display, besides the hydride resonance at δ −18 to −19 and the signals for the alkynyl and pyridine

(6) Schäfer, M.; Wolf, J.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1991**, 1341−1343.

(7) (a) Werner, H.; Garcia Alonso, F. J.; Otto, H.; Wolf, J. *Z. Naturforsch.* **1988**, *43b*, 722−726. (b) Werner, H.; Brekau, U. *Z. Naturforsch.* **1989**, *44b*, 1438−1446.

Scheme 3[a]



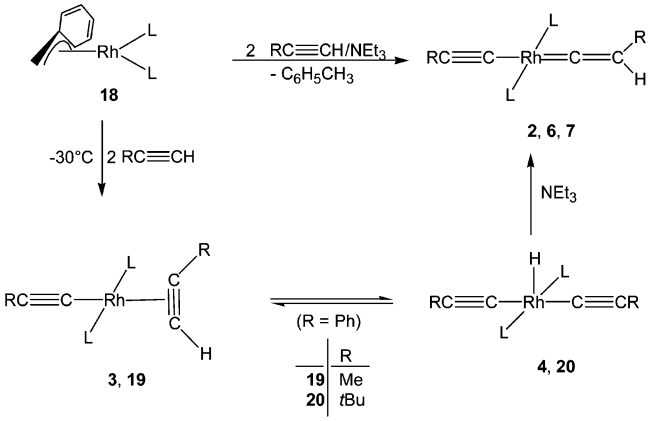
[a] L = P*i*Pr$_3$.

protons, only one set of signals for the methyl protons of the PCH(CH$_3$)$_2$ groups, indicating that both the alkynyl units and the phosphine ligands are stereochemically equivalent and thus *trans* disposed.

The bis(alkynyl)hydridorhodium(III) complexes **8**−**11** can also be prepared by treatment of a solution of the vinylidene compounds **2** and **5**−**7** in pentane with a large excess of pyridine. By using this route, the bis(propiolate)hydridorhodium(III) derivative **14** has likewise been obtained (Scheme 3). Since the ^{1}H NMR spectra of both **8** and **14** show in C$_6$D$_6$ not only the signals for the pyridine-containing rhodium(III) complexes but also those for the vinylidene compounds **5** and **13**, we conclude that in these cases an equilibrium between the six- and the four-coordinate species exists. Attempts to abstract the pyridine ligand also from **9**−**11** and to regenerate the metal vinylidenes **2**, **6**, and **7** led to the elimination of the corresponding terminal alkyne and gave the alkynyl(pyridine)rhodium(I) complexes **15**−**17** in about 50% yield. As expected, these square-planar compounds smoothly react with Broensted acids by oxidative addition, as is illustrated by the formation of **11** from **17** and phenylacetylene in pentane at room temperature.

For the preparation of the alkynyl(vinylidene) complexes **2**, **6**, and **7**, the related η^3-benzyl complex **18** can also be used instead of the η^3-allyl compound **1** as the starting material. As was shown by earlier work from our group,[2] the reaction of **18** with carboxylic acids is much faster than that of **1** with the same substrates and affords the substitution products [Rh(κ^2-O$_2$CR)(P*i*Pr$_3$)$_2$] nearly quantitatively. In agreement with this result, compound **18** reacts with phenylacetylene in pentane even at −30 °C to give as the primary product the alkynyl(alkyne) complex **3** (Scheme 4). Compared with the reaction of **1** with PhC≡CH, the yield of **3** could be improved from 27% to 54% with **18** as the starting material. Under the same conditions, also the formerly undetected propynerhodium(I) derivative **19** is generated from **18** and propyne. Since **19** is rather labile, the product isolated from the reaction mixture contained besides the propyne complex **19** (ca. 90%) small amounts of the vinylidene isomer **6** (ca. 10%), which at room temperature is formed from **18** and MeC≡CH in high yield. Diagnostic for **19** are the two ν(C≡C) stretching modes for the alkynyl and the alkyne ligand at 2100 and 1895 cm^{-1} in the IR spectrum and the doublet resonance at δ 38.5 in the ^{31}P NMR spectrum, the respective ^{31}P−^{103}Rh coupling constant being almost identical to that of **3**.

Scheme 4[a]



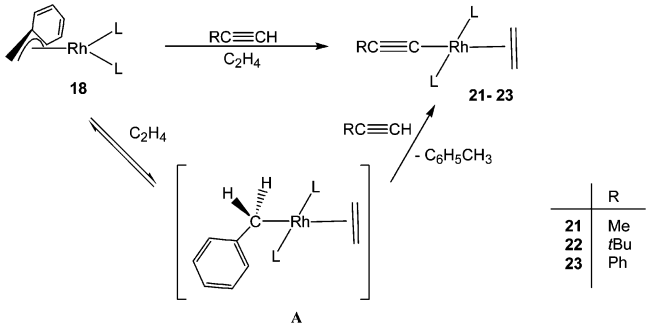
[a] L = P*i*Pr$_3$.

The reaction of **18** with *tert*-butylacetylene, which proceeds only at room temperature, affords instead of the alkynyl(alkyne)rhodium(I) complex *trans*-[Rh(C≡C*t*Bu)(HC≡C*t*Bu)(P*i*Pr$_3$)$_2$] the hydridorhodium(III) isomer [RhH(C≡C*t*Bu)$_2$(P*i*Pr$_3$)$_2$] (**20**). In contrast to **4**, the analogue **20** is quite stable (for a short period of time even in air) and has been characterized by a correct elemental analysis. Since some of the typical NMR data of **20** are similar to those of [RhH(C≡CC*i*Pr$_2$OH)$_2$(P*i*Pr$_3$)$_2$], which has been characterized by an X-ray crystal structure analysis,[8] we assume that the structure of **20** corresponds to a square pyramid with the hydrido ligand in the apical position and both the alkynyl and the phosphine units *trans*-disposed. Compound **20** rearranges in a 1:1 mixture of pentane/NEt$_3$ at 40 °C completely to give the alkynyl(vinylidene) isomer **7**.

Synthesis and Reactivity of Four-Coordinate Alkynyl(ethene) Rhodium(I) Complexes. To find out whether complexes of the general composition *trans*-[Rh(C≡CR)(CH$_2$=CHR′)(P*i*Pr$_3$)$_2$], which for R′ = CH$_3$ were supposed to be formed in the reaction of **1** with RC≡CH as intermediates, can be prepared using **18** as the starting material, the reactivity of the η^3-benzyl compound toward terminal alkynes in the presence of excess ethene has been investigated. Stirring a solution of **18** in neat NEt$_3$ under an ethene atmosphere leads, after addition of a solution of propyne in pentane, to a gradual change of color from orange to orange-brown and gives the alkynyl(ethene) complex **21** in 52%

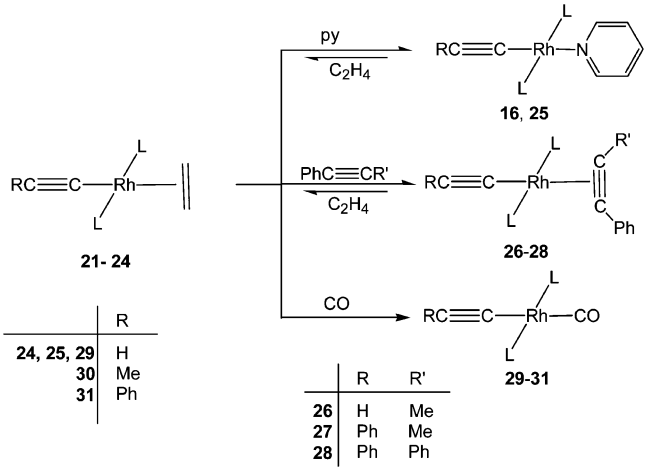
(8) Werner, H.; Wiedemann, R.; Mahr, N.; Steinert, P.; Wolf, J. *Chem. Eur. J.* **1996**, *5*, 561−569.

Scheme 5[a]



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

Scheme 6[a]



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

isolated yield (Scheme 5). In a similar way the Rh(C≡C*t*Bu) and Rh(C≡CPh) counterparts **22** and **23** are also accessible. For both **21** and **23** an alternative route has already been described using [RhH(C≡CMe)(κ^2-O_2CMe)(P*i*Pr$_3$)$_2$] or [RhH$_2$(κ^2-O_2CMe)(P*i*Pr$_3$)$_2$] as the precursors.[5] The formerly unknown *tert*-butyl-substituted alkynyl complex **22** is thermally remarkably stable and readily soluble in common organic solvents without decomposition. Diagnostic for the coordinated ethene in **22** is the signal at δ 3.03 in the ^{1}H NMR spectrum (observed as a doublet of triplets due to ^{1}H−^{103}Rh and ^{1}H−^{31}P couplings) and the resonance at δ 51.9 in the ^{13}C NMR spectrum, which is also split into a doublet of triplets.

Regarding the mechanism of formation of **21**−**23** from **18** as the starting material, we assume that in the initial step an intermediate **A** containing a σ-bonded benzyl ligand is generated, which reacts with the alkyne by protolytic cleavage of the Rh−CH_2Ph bond and elimination of toluene to give the required product. In this respect, it is worth mentioning that we have illustrated by variable-temperature NMR measurements the highly fluxional behavior of compound **18** in solution.[2] At room temperature, besides a very fast metallotropic shift a somewhat slower η^3−η^1−η^3 rearrangement occurs which involves the 14-electron species [Rh(η^1-CH_2Ph)(P*i*Pr$_3$)$_2$] as an intermediate. This intermediate probably reacts with ethene instantaneously to give the 16-electron compound **A**, which upon treatment with RC≡CH affords the product. We note that we failed to prepare the ethynyl complex *trans*-[Rh(C≡CH)(C_2H_4)(P*i*Pr$_3$)$_2$] (**24**) from **18** and acetylene. However, similarly to **23** this compound is accessible from [RhH$_2$(κ^2-O_2CMe)(P*i*Pr$_3$)$_2$] and HC≡CH at low temperature.[5]

Due to the strong *trans* influence of the alkynyl ligand, the metal−ethene bond in **21**−**24** is rather labile, and thus the olefinic ligand can be easily displaced by various Lewis bases (see Scheme 6). If the reactions of **22** and **24** with an equimolar amount of pyridine are monitored by NMR spectroscopy, an equilibrium between the starting material and the substitution product **16** or **25** is observed, which in the presence of an excess of pyridine or by removing the ethene under reduced pressure can be shifted to the product side. Under these conditions, the yield of isolated **16** and **25** is, respectively, 63% and 84%.

The reactions of **23** and **24** with the internal alkynes PhC≡CMe and PhC≡CPh also lead to an equilibrium, which after removal of the olefin is completely shifted to the side of the alkyne complexes **26**−**28**. These are isolated as orange solids in 88−92% yield. If a solution of **26**, **27**, or **28** in benzene is stirred under an ethene atmosphere, the precursors **23** and **24** are regenerated. Similarly to **3**, the ^{1}H NMR spectra of **26** and **27** display two signals for the protons of the diastereotopic methyl groups of the P-bonded isopropyl fragments, indicating that the rotation of the alkyne ligand, lying perpendicular to the coordination plane, around the Rh−(η^2-PhC≡CMe) axis is considerably hindered.

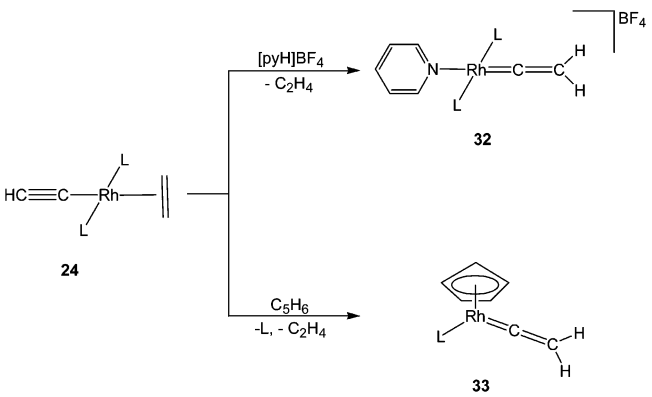
In contrast to the reactions of **21**−**24** with pyridine and internal alkynes, the corresponding reactions of **21**, **23**, and **24** with CO are irreversible and afford in pentane at room temperature the square-planar rhodium(I) complexes **29**−**31** in nearly quantitative yield. The Rh(C≡CPh) derivative **31** is known and has recently been prepared from *trans*-[Rh(CH_2Ph)(CO)(P*i*Pr$_3$)$_2$] and phenylacetylene.[5] The alkynyl(carbonyl) compounds are pale yellow, practically air-stable solids, the composition of which has been confirmed by elemental analysis and spectroscopic techniques. We note that by comparing the chemical shift of the alkynyl ^{13}C carbon resonances for the two pairs of complexes **25/29** and **17/31** there is only a small difference, which is surprising insofar as the σ-donor/π-acceptor capabilities of pyridine on one hand and CO on the other differ significantly.

If the ethynyl(ethene)rhodium(I) compound **24** is treated with acidic substrates, the ethynyl ligand is readily converted to a vinylidene unit. Thus, the reaction of **24** with [pyH]BF_4 in acetone/diethyl ether affords the cationic complex **32** (Scheme 7), which is also accessible upon treatment of **1** with [pyH]BF_4 in the presence of acetylene.[9] Moreover, compound **24** reacts with the weak acid cyclopentadiene in benzene at room temperature to give the cyclopentadienyl complex **33** in 85% yield. This half-sandwich-type compound was previously prepared from *trans*-[RhCl(HC≡CH)(P*i*Pr$_3$)$_2$] and NaC_5H_5 in THF.[10] The formation of **33** from **24** as the precursor possibly proceeds via the η^2-cyclopentadienerhodium(I) intermediate *trans*-[Rh(C≡CH)(η^2-C_5H_6)(P*i*Pr$_3$)$_2$], which after elimination of one phosphine ligand and proton transfer from the coordinated diolefin to the metal and subsequently to the β-carbon atom of the

(9) Nürnberg, O.; Werner, H. *J. Organomet. Chem.* **1993**, *460*, 163−175.

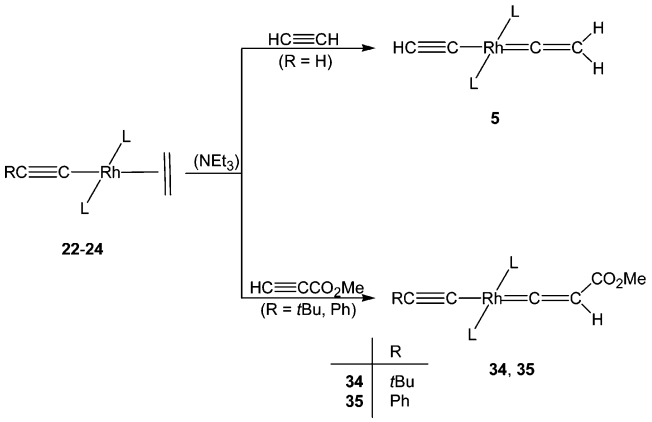
(10) Werner, H.; Wolf, J.; Garcia Alonso, F. J.; Ziegler, M. L.; Serhadli, O. *J. Organomet. Chem.* **1987**, *336*, 397−411.

Scheme 7[a]



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

Scheme 8[a]



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

ethynyl ligand yields the product. With regard to this proposal it should be mentioned that the reaction of alkynyl complexes with electrophiles is one of the standard methods to generate a vinylidene unit at a transition-metal center.[11]

The alkynyl(ethene) complexes also react with terminal alkynes by substitution of the olefinic ligand. By using this route, it is possible to prepare not only the parent Rh(C≡CH)(=C=CH$_2$) derivative **5** (see Scheme 8) but also alkynyl(vinylidene)rhodium compounds *trans*-[Rh(C≡CR)(=C=CHR′)(P*i*Pr$_3$)$_2$] with two different substituents R and R′, which are not accessible directly from **1** or **18** as the starting material. As exemplified with methyl propiolate as the substrate, the corresponding complexes **34** and **35** with R = *t*Bu or Ph and R′ = CO$_2$Me have been obtained from **23** and **24**, in a 1:1 mixture of pentane and NEt$_3$ as the solvent, in 67−76% yield. Regarding this methodology, an interesting facet is that the related Rh(C≡CPh)(=C=CH$_2$) compound **36** can be prepared from either **23** or **24** as the precursor. A proposed mechanism for these reactions is shown in Scheme 9. By taking the formation of **26**−**28** from **23** and **24** into account (see Scheme 6), we assume that the initial step in the synthesis of **36** is the displacement of ethene by acetylene or phenylacetylene to give the intermediates **B** and **D**. Similarly to **3** (see Scheme 1), these intermediates are converted via an intramolecular oxidative addition to the hydridorhodium(III) isomer **C**, which then rearranges to the product. To explain the stereoselective formation of **36** instead of the isomer *trans*-[Rh(C≡CH)(=C=CHPh)(P*i*Pr$_3$)$_2$], we point to the fact that for the related six-coordinate alkynyl(hydrido) complexes [RhH(C≡CR)(η^2-O$_2$CMe)(P*i*Pr$_3$)$_2$] the rate of conversion to the isomeric rhodium(I) vinylidenes *trans*-[Rh(κ^1-O$_2$CMe)(=C=CHR)(P*i*Pr$_3$)$_2$] increases in the order R = alkyl < aryl < H ≈ CO$_2$Me.[5] The question whether the formation of **36** compared with that of the isomer *trans*-[Rh(C≡CH)(=C=CHPh)(P*i*Pr$_3$)$_2$] is not only kinetically but also thermodynamically favored cannot be answered as yet.

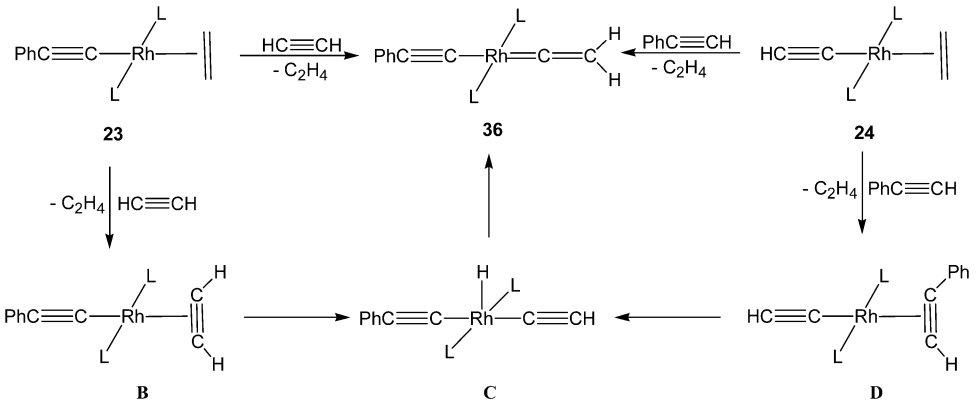
The properties of the "mixed substituted" alkynyl(vinylidene)rhodium(I) compounds **34**−**36** are quite similar to those of the "nonmixed" counterparts **2** and **5**−**7** (see Schemes 1 and 2). The deeply colored microcrystalline solids, for which correct elemental analyses were obtained, are only slightly air-sensitive and soluble in most common organic solvents. The ^{13}C NMR spectra display in the low-field region two signals at around δ 300−310 (Rh=*C*=C) and δ 92−109 (Rh=C=*C*) for the vinylidene carbon atoms and also two resonances at around δ 135−145 (Rh−C≡*C*) and δ 108−125 (Rh−*C*≡C) for the alkynyl carbon atoms. The ^{13}C−^{103}Rh coupling constants for the signals of the respective α-C atoms lie between 36 and 53 Hz and those for the β-C atoms between 9 and 14 Hz.

Analogously to **2**, **5**−**7,** and **13**, the "mixed substituted" complexes **35** and **36** also react with pyridine by proton transfer from the vinylidene ligand to the metal and formation of the bis(alkynyl)hydridorhodium(III) compounds **37** and **38** (Scheme 10). In benzene solution, the six-coordinate complexes partially rearrange to the four-coordinate starting materials and free pyridine; at equilibrium the ratios **37**:**35** and **38**:**36** are approximately 2:1.

Allene, Vinyl, and Enynyl Rhodium Complexes from Terminal Alkynes as Substrates. A surprising result was obtained when we treated the starting materials **1** and **18** with an excess of propyne in pentane at −50 °C. After the reaction mixture was warmed to room temperature, instead of the alkynyl(alkyne) compound **6** (which is dark green) a yellow microcrystalline solid was isolated, which turned out to be the isomeric alkynyl(allene) complex **39** (Scheme 11). Although there are some similarities in the spectroscopic data of the two isomers **6** and **39** (e.g., the ^{31}P NMR spectra are nearly identical), the IR spectrum of **39** shows an intense absorption at 1740 cm^{-1}, being assigned to the ν(C=C=C) stretching mode of coordinated allene. The ^{13}C NMR spectrum of **39** displays three resonances for the C$_3$H$_4$ carbon atoms at δ 182.4 (=C=), 94.2 (=CH$_2$ uncoordinated), and 17.2 (=CH$_2$ coordinated), which are all split into doublets of triplets due to ^{13}C−^{103}Rh and ^{13}C−^{31}P couplings. The inequivalence of the terminal CH$_2$ units is also confirmed by the ^{1}H NMR spectrum of **39**, in which one signal at relatively high field (δ 2.48) for the two protons of the metal-bonded CH$_2$ group and two signals at lower field (δ 5.45 and 5.25) for the *exo*- and *endo*-protons of the uncoordinated CH$_2$ group

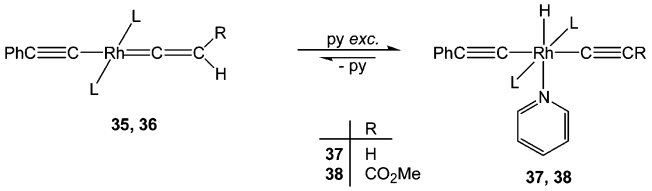
(11) Reviews: (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59−128. (b) Antonova, A. B.; Ioganson, A. A. *Russ. Chem. Rev.* **1989**, *58*, 693−710. (c) Werner, H. *Angew. Chem.* **1990**, *102*, 1109−1121; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1077−1089. (d) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197−257. (e) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *193*−*195*, 977−1025.

Scheme 9[a]



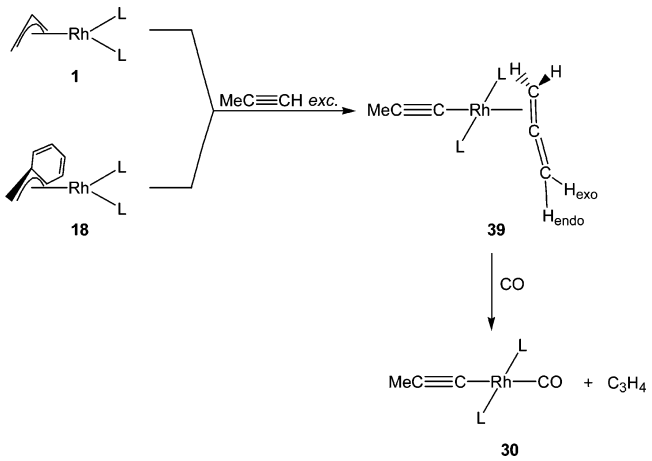
[a] L = P*i*Pr$_3$.

Scheme 10[a]



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

Scheme 11[a]



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

appear. These data are in good agreement with those for other allene-transition-metal compounds.[12,13]

There is some precedent for the metal-initiated rearrangement of an alkyne into the isomeric allene. For example, Richards et al. described the formation of [ReCl(η^2-CH$_2$=C=CHPh)(diphos)$_2$] from [ReCl(N$_2$)(diphos)$_2$] (diphos = Ph$_2$PCH$_2$CH$_2$PPh$_2$) and PhC≡CMe,[14] and we reported the conversion of *trans*-[IrCl(MeC≡CMe)(P*i*Pr$_3$)$_2$] to the methylallene isomer *trans*-[IrCl(η^2-CH$_2$=C=CHMe)(P*i*Pr$_3$)$_2$].[15] With respect to rhodium as the metal center, it was shown that the ethene complex *trans*-[RhCl(C$_2$H$_4$)(As*i*Pr$_3$)$_2$] reacts with propyne and internal alkynes MeC≡CR to give the isomeric allene derivatives *trans*-[RhCl(η^2-CH$_2$=C=CHR)(As*i*Pr$_3$)$_2$] (R = H, Me, *t*Bu).[16] With MeC≡CD as the substrate, the bisdeuterated compound *trans*-[RhCl(η^2-CH$_2$=C=CD$_2$)(As*i*Pr$_3$)$_2$] was obtained.[16] We note that in contrast to *trans*-[RhCl(η^2-CH$_2$=C=CH$_2$)(As*i*Pr$_3$)$_2$], which reacts quite slowly with CO, the reaction of **39** with carbon monoxide in benzene at room temperature proceeds in a few seconds and affords allene and the alkynyl(carbonyl) complex **30** in quantitative yield.

With regard to the mechanism of formation of **39**, we have considered two different routes (see Scheme 12). After it was shown that the starting material **18** reacts with a slight excess of propyne to generate **19** (see Scheme 4), we assume that this alkynyl(alkyne) complex is formed in the initial stage of the reaction as an intermediate. Following path a it could rearrange via the zwitterionic species **E** and the hydrido compound **F** to give **39**. Alternatively, on path b **19** can be converted by intramolecular oxidative addition to **G**, which reacts with another molecule of propyne by insertion into the Rh−H bond to afford the alkynyl(vinyl) intermediate **H**. This intermediate could undergo a β-hydride shift to yield isomer **I**, which subsequently forms via reductive elimination the isolated product **39**. Although a tungsten[17] as well as some iron-group compounds,[18−20] containing a C$_3$ fragment similar to that postulated in transient **F**, are known, we nevertheless consider path b as more likely since only in the presence of an excess of propyne is the alkynyl(allene) complex **39** formed.

By changing the conditions, the reaction of the labile intermediate **19** with MeC≡CH can follow a route that does not lead to **39**. If a slow stream of propyne is passed through either a solution of **1** in pentane/NEt$_3$ (1:1) at −20 °C or a solution of **19**, generated from **18** and propyne in pentane at −40 °C, the color changes from orange-yellow to red and, after recrystallization of the crude product from pentane or acetone, the bisalkynyl-

(12) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245−283, and references therein.
(13) Pu, J.; Peng, T.-S.; Gladysz, J. A. *Organometallics* **1992**, *11*, 3232−3241.
(14) Hughes, D. L.; Pombeiro, A. J. L.; Pickett, C. J.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1984**, 992−993.
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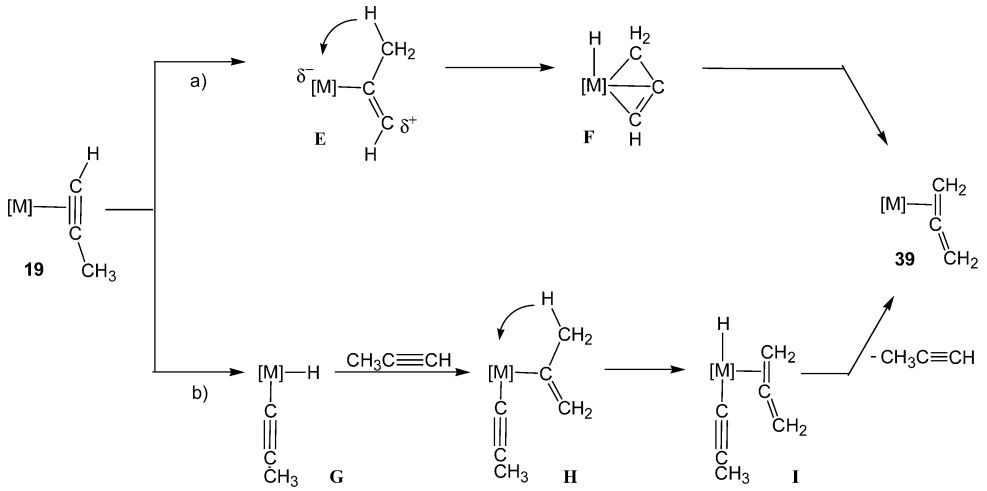
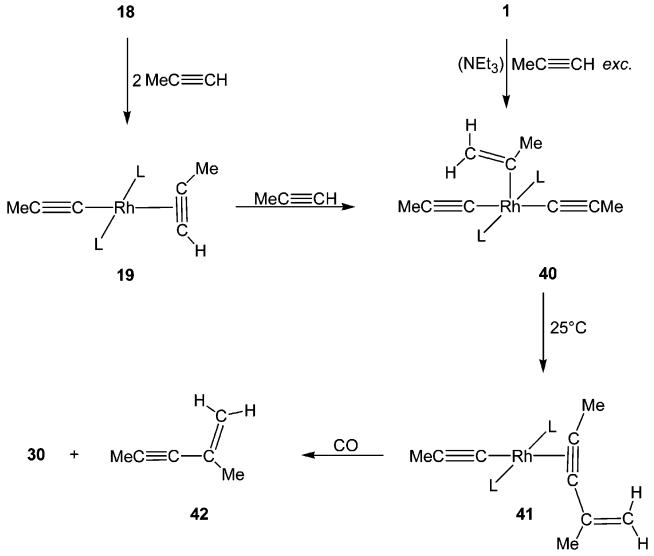
(17) McMullen, A. K.; Selegue, J. P.; Wang, J.-G. *Organometallics* **1991**, *10*, 3421−3423.
(18) Gotzig, H.; Otto, H.; Werner, H. *J. Organomet. Chem.* **1985**, *287*, 247−254.
(19) (a) Jia, G.; Rheingold, A. L.; Meek, D. W. *Organometallics* **1989**, *8*, 1378−1380. (b) Jia, G.; Meek, D. W. *Organometallics* **1991**, *10*, 1444−1450.
(20) (a) Field, L. D.; George, A. V.; Hambley, T. W. *Inorg. Chem.* **1990**, *29*, 4565−4569. (b) Hills, A.; Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J.; McGeary, C. A.; Rowley, A. T.; Bravo, M.; McKenna, C. E.; McKenna, M.-C. *J. Chem. Soc., Chem. Commun.* **1991**, 522−524.

Scheme 12[a]



[a] [M] = Rh(C$_2$Me)(P*i*Pr$_3$)$_2$.

Scheme 13[a]



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

(vinyl)rhodium(III) complex **40** could be isolated (Scheme 13). As far as the structure of **40** is concerned, the most characteristic feature consists of the position of the methyl group at the α-carbon atom of the vinyl ligand. If one assumes that the insertion of a terminal alkyne RC≡CH into a metal−hydride bond occurs via a four-center transition state, it is to be expected that mainly for steric reasons the group R should be linked to the *β*-carbon atom of the vinyl ligand.[12] There is, however, precedence for the regioselectivity observed in the formation of **40**, as the insertion of $CF_3C{\equiv}CH$ into the M−H bond of the niobium and tantalum hydrides [(η^5-$C_5H_5)_2$MH(CO)][21] and of HC≡CCO$_2$Me into the Os−H bond of [OsHCl(CO)(PMe*t*Bu$_2$)$_2$][22] affords vinylmetal derivatives having the substituent R in the α-position. Moreover, the iridium counterpart of **40** is known and has been prepared from [IrH$_5$(P*i*Pr$_3$)$_2$] and propyne.[23]

Mechanistically, it is conceivable that the formation of **40** proceeds via the bis(alkynyl)hydrido intermediate **I** (see Scheme 12), which instead of eliminating propyne could lose, under different conditions, allene and generate the five-coordinate [RhH(C≡CMe)$_2$(P*i*Pr$_3$)$_2$], which reacts with MeC≡CH by insertion into the Rh−H bond to produce the bis(alkynyl)vinyl complex **40**.

Compound **40** is significantly more labile than the analogous iridium complex [Ir(C≡CMe)$_2${C(CH$_3$)=CH$_2$}-(P*i*Pr$_3$)$_2$]. If a solution of **40** is stirred in benzene at room temperature for 24 h, an intramolecular C−C coupling takes place and the isomer **41** is formed in virtually quantitative yield. In agreement with the stereochemistry of the vinyl unit in the precursor, the enyne ligand contains a carbon−carbon double bond with a nonsubstituted =CH$_2$ moiety. This is confirmed by the ^{1}H NMR spectrum of **41**, which displays two multiplets at *δ* 5.91 and 5.27 for the nonequivalent methylene protons. The ^{13}C NMR spectrum of **41** shows two singlets for the carbon atoms of the olefinic C=C bond at *δ* 133.6 (=*C*Me−) and 117.4 (=CH$_2$, assignment substantiated by DEPT measurements) and two doublet of triplets for the carbon atoms of the alkyne C≡C bond at *δ* 89.3 and 77.9. The resonances for the alkynyl ^{13}C atoms are also split into a doublet of triplets and appear at *δ* 117.1 and 105.8, respectively. Compound **41** reacts with CO in C_6D_6 at room temperature nearly instantaneously and affords the alkynyl(carbonyl) complex **30** and the substituted enyne **42**.

In contrast to [η^3-C_3H_5)Ir(P*i*Pr$_3$)$_2$], which upon treatment with phenylacetylene gives [Ir(C≡CPh)$_3$(P*i*Pr$_3$)$_2$],[24] the reaction of **1** with excess phenylacetylene yields a mixture of products (Scheme 14). The major organometallic components are the enyne complex **45** (the phenyl-substituted analogue of **41**) and the isomer **43**, the ratio of these two compounds being approximately 2:3. Besides **43** and **45**, somewhat larger amounts of the free enynes **44** and **46** were formed. If the reaction mixture obtained from **1** and PhC≡CH was worked up by column chromatography, an orange fraction eluted from which **43** and **44** could be isolated by fractional crystallization from pentane. The identity of **43** was furthermore

(21) Amaudrut, J.; Leblanc, J.-C.; Moise, C.; Sala-Pala, J. *J. Organomet. Chem.* **1985**, *295*, 167−174.
(22) Werner, H.; Meyer, U.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1989**, *122*, 2097−2107.
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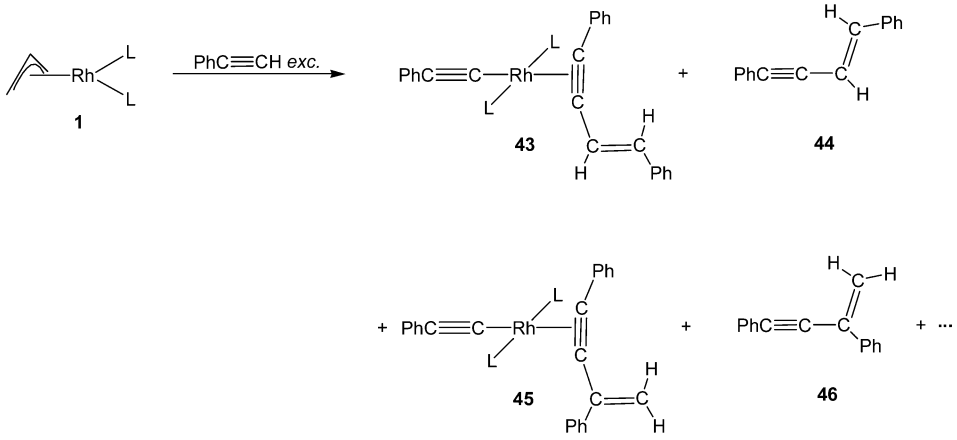
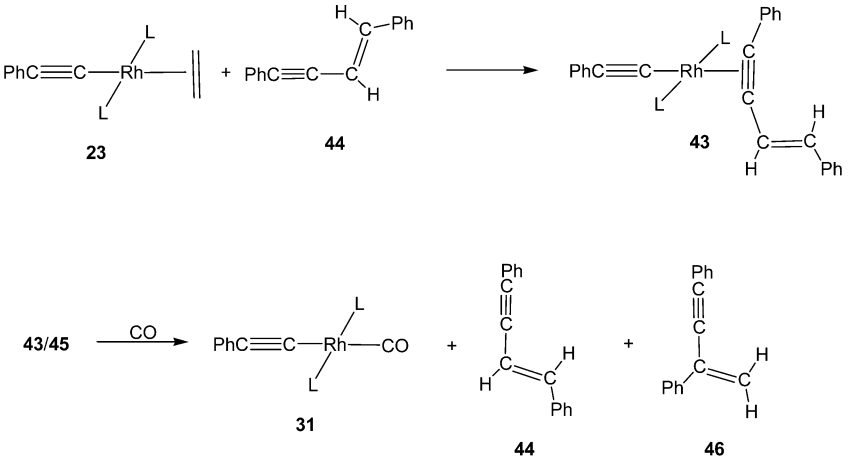
(24) Schulz, M.; Werner, H. *J. Organomet. Chem.* **1994**, *470*, 243−247.

Scheme 14[a]



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

Scheme 15[a]

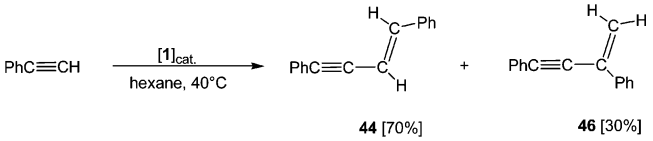


[a] L = P*i*Pr$_3$.

confirmed by the independent preparation of the complex (yield 78%) from the corresponding ethene derivative **23** and the 1,4-disubstituted butenyne PhCH=CHC≡CPh (see Scheme 15). Typical spectroscopic features of **43** are the two ν(C≡C) stretching modes in the IR spectrum for the alkynyl and enyne ligand at 2080 and 1885 cm^{-1} and the two doublet resonances in the ^{1}H NMR spectrum for the vinylic protons at δ 7.41 and 7.11. Owing to the relatively large ^3J(H,H) coupling constant of 15.7 Hz, there is no doubt that these protons are *trans*-disposed to each other. The mixture of **43** and **45** (of which we could not isolate the latter in analytically pure form) reacts with CO to give the carbonyl complex **31** and both **44** and **46**. The two isomeric enynes have been identified by comparison of their ^{1}H NMR spectra with reference data.[25]

The dimerization of phenylacetylene to the butenynes **44** and **46** could also be achieved with catalytic amounts of the starting material **1**. With 0.11 mmol of the catalyst and a 100-fold excess of PhC≡CH in 9 mL of hexane, after 4 h at 40 °C ca. 50% of the alkyne was consumed and a mixture of **44** and **46** in the molar ratio of 70:30 was obtained (Scheme 16). Quite remarkably, an increase of the time of the reaction did not lead to a significant increase of the yield of the dimers. With

Scheme 16



regard to the observed ratio of the 1,4- and the 1,3-disubstituted isomers, we note that by using the Wilkinson catalyst [RhCl(PPh$_3$)$_3$] and PhC≡CH as the substrate also both butenynes **44** and **46** are generated, the ratio being 65:35.[25] In contrast, the dimerization of phenylacetylene with [RhCl(PMe$_3$)$_2$]$_2$ as the catalyst leads exclusively to isomer **46**.[26]

The proposed mechanistic scheme for the catalytic reaction of **1** with PhC≡CH is shown in Scheme 17. Taking into account that upon treatment of **1** with 2 equiv of phenylacetylene at room temperature the alkynyl(alkyne) complex **3** is formed (see Scheme 1), we assume that this compound is also generated under catalytic conditions. In solution, complex **3** is in equilibrium with the bis(alkynyl)hydrido isomer **4**, which can react with another molecule of PhC≡CH by insertion to give either intermediate **M** or **N**. Subsequent intramolecular C−C coupling would lead to the enyne

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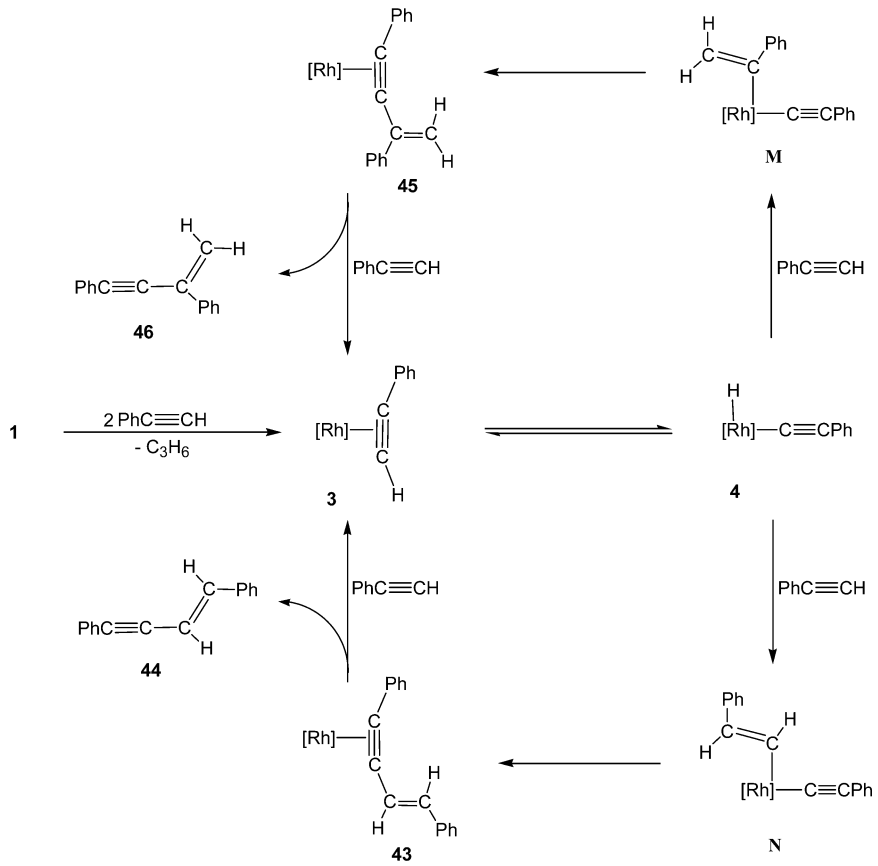
(26) Boese, W. T.; Goldman, A. S. *Organometallics* **1991**, *10*, 782−786.

Scheme 17[a]



[a] [Rh] = $Rh(C_2Ph)(P\textit{i}Pr_3)_2$.

complexes **43** and **45**, from which in the presence of a large excess of the alkyne the coupling product is displaced and compound **3** regenerated. Since not only the substituent R of the terminal alkyne but also the steric bulk around the metal center determine whether the insertion of the alkyne into the metal−hydride bond affords a vinylmetal species such as **M** or **N**,[27,28] it is not unexpected that with the bis(trimethylphosphine) complex $[RhCl(PMe_3)_2]_2$ as the catalyst the dimerization of PhC≡CH yields only **46** while with the bis(triisopropylphosphine) derivative **1** both isomers **44** and **46** are formed. The substitution of the enyne in **43** and **45** by phenylacetylene is probably reversible, and thus with decreasing concentration of PhC≡CH the rate of dimerization also decreases.

Conclusions

The present investigation has shown that from rhodium(I) precursors containing a labile or an easy-to-labilize ligand such as η^3-benzyl or η^3-allyl, treatment with 2 equiv of terminal alkynes affords four-coordinate complexes of the general composition *trans*-[Rh(C≡CR)(=C=CHR)($P\textit{i}Pr_3$)$_2$] in high yields. The conversion of a coordinated alkyne RC≡CH to the isomeric vinylidene :C=CHR occurs, in the coordination sphere of rhodium(I),[29] stepwise via intramolecular oxidative addition followed by a β-H shift from metal to carbon by either a monomolecular or a bimolecular mechanism.[30] Depending on the substituent R of the alkyne and the reaction conditions, it is possible to isolate intermediate alkynyl(alkyne)rhodium(I) and bis(alkynyl)hydridorhodium(III) complexes which finally rearrange to the most stable alkynyl(vinylidene) isomers. The reaction of the η^3-benzyl complex **18** with an equimolar amount of RC≡CH under an ethene atmosphere affords the alkynyl(ethene) compounds *trans*-[Rh(C≡CR)(C_2H_4)($P\textit{i}Pr_3$)$_2$], which are rather labile. The olefinic ligand is easily displaced not only by pyridine, CO, and internal alkynes PhC≡CR but also by acetylene and methylpropiolate. This process thus opens a preparative route to complexes *trans*-[Rh(C≡CR)(=C=CHR′)($P\textit{i}Pr_3$)$_2$] having different substituents at the β-carbon atoms of the alkynyl and the vinylidene units. A noteworthy result is that the "mixed-substituted" compound *trans*-[Rh(C≡CPh)(=C=CH_2)($P\textit{i}Pr_3$)$_2$] can be prepared either from *trans*-[Rh(C≡CPh)(C_2H_4)($P\textit{i}Pr_3$)$_2$] and acetylene or from *trans*-

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(28) (a) Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002−3011. (b) Clark, H. C.; Ferguson, G.; Goel, A. B.; Janzen, E. G.; Ruegger, H.; Siew, P. Y.; Wong, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 6961−6972.

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[Rh(C≡CH)(C_2H_4)(P*i*Pr$_3$)$_2$] and phenylacetylene as the precursors.

The reactions of the starting materials **1** and **18** with terminal alkynes do not lead necessarily to the alkynyl(vinylidene) complexes *trans*-[Rh(C≡CR)(=C=CHR)(P*i*Pr$_3$)$_2$]. Depending on the reaction conditions, from **1** or **18** and excess MeC≡CH either the four-coordinate allenerhodium(I) compound *trans*-[Rh(C≡CMe)(η^2-CH_2=C=CH_2)(P*i*Pr$_3$)$_2$] or the five-coordinate vinylrhodium(III) complex [Rh(C≡CMe)$_2${C(CH_3)=CH_2}(P*i*Pr$_3$)$_2$] can be isolated. We assume that in both cases the alkynyl(alkyne) derivative *trans*-[Rh(C≡CMe)(MeC≡CH)(P*i*Pr$_3$)$_2$] is generated as an intermediate. The bis(alkynyl)vinylrhodium(III) complex [Rh(C≡CMe)$_2${C(CH_3)=CH_2}(P*i*Pr$_3$)$_2$] rearranges already at room temperature to the enynerhodium(I) isomer *trans*-[Rh(C≡CMe){η^2-MeC≡CC(Me)=CH_2}(P*i*Pr$_3$)$_2$] by intramolecular C−C coupling. With excess phenylacetylene, the reaction of **1** affords not only the analogous butenyne complex *trans*-[Rh(C≡CPh){η^2-PhC≡CC(Ph)=CH_2}(P*i*Pr$_3$)$_2$] (**45**) but also the stereoisomer *trans*-[Rh(C≡CPh){η^2-PhC≡CCH=CHPh}(P*i*Pr$_3$)$_2$] (**43**). Under similar conditions, with catalytic amounts of compound **1**, a dimerization of PhC≡CH can be performed leading to a mixture of the two disubstituted butenynes PhC≡CCH=CHPh and PhC≡CC(Ph)=CH_2 in a 70:30 ratio. Also in this case, the key intermediate seems to be the alkynyl(alkyne) complex *trans*-[Rh(C≡CPh)(PhC≡CH)(P*i*Pr$_3$)$_2$] (**3**), which in the absence of exess PhC≡CH could be isolated and fully characterized. Some preliminary results indicate that with the vinylidene compounds *trans*-[Rh(C≡CPh)(=C=CHPh)(P*i*Pr$_3$)$_2$] and *trans*-[Rh(κ^1-O_2CCF_3)(=C=CHPh)(P*i*Pr$_3$)$_2$] as catalysts, also a dimerization of phenylacetylene takes place, but the mechanistic scheme for these processes remains to be elucidated by further experiments.

Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **1**,[2] **12**,[5] **13**,[5] **18**,[2] and **24**[5] were prepared as described in the literature. The alkynes were commercial products from Aldrich and Messer Griesheim. NMR spectra were recorded on JEOL FX 90 Q, Bruker AC 200, and Bruker AMX 400 instruments at room temperature, if not otherwise stated. IR spectra were recorded on a Perkin-Elmer 1420 infrared spectrometer and mass spectra on a Varian MAT CH 7 instrument. Melting points were measured by DTA. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broadened signal. The term vt indicates a virtual triplet, and $N = {}^3J(P,H) + {}^5J(P,H)$ or ${}^1J(P,C) + {}^3J(P,C)$.

Preparation of *trans*-[Rh(C≡CPh)(=C=CHPh)(P*i*Pr$_3$)$_2$] (2). Method a: A solution of **1** (244 mg, 0.53 mmol) in pentane (8 mL) was treated with phenylacetylene (115 μL, 1.06 mmol) and stirred for 4 h at room temperature. A smooth change of color from yellow to dark blue-green occurred. The solvent was evaporated, the residue was extracted with pentane (30 mL), and the extract was concentrated in vacuo until the first crystals precipitated. After the solution was stored at −78 °C for 12 h, a blue microcrystalline solid was formed. It was separated from the mother liquor, washed twice with small amounts of pentane (0 °C), and dried: yield 236 mg (72%). The yield could be improved to ca. 85%, if instead of pentane a 1:1 mixture of pentane and NEt_3 was used as the solvent. Method b: A solution of **18** (348 mg, 0.68 mmol) in a 1:1 mixture of pentane and NEt_3 (10 mL) was treated at −30 °C with phenylacetylene (149 μL, 1.36 mmol). The solution was slowly warmed to room temperature, stirred for 1 h, and then worked up as described for method a: yield 334 mg (79%). The product was characterized by comparison of the ^{1}H and ^{31}P NMR data with those of an authentic sample.[5]

Preparation of *trans*-[Rh(C≡CPh)(HC≡CPh)(P*i*Pr$_3$)$_2$] (3). Method a: A solution of **1** (302 mg, 0.65 mmol) in pentane (30 mL) was treated dropwise under stirring during 30 min with a 0.1 M solution of phenylacetylene in pentane (13 mL, 1.30 mmol) at room temperature. The solution was concentrated in vacuo to ca. 2 mL and then stored at −78 °C for 12 h. A yellow microcrystalline solid precipitated, which was separated from the mother liquor, washed three times with small amounts of pentane (0 °C), and dried: yield 109 mg (27%). Method b: A solution of **18** (204 mg, 0.40 mmol) in pentane (10 mL) was treated at −30 °C with phenylacetylene (87 μL, 0.80 mmol) and stirred for 3 min. The solvent was evaporated in vacuo, the residue was dissolved in pentane (5 mL), and the solution was stored at −78 °C for 12 h to give yellow crystals: yield 131 mg (54%); mp 96 °C dec. Anal. Calcd for $C_{34}H_{53}P_2Rh$: C, 65.18; H, 8.53. Found: C, 65.39; H, 8.53. IR (KBr): ν(C≡C) 2080, ν(η^2-C≡C) 1850 cm^{-1}. ^{1}H NMR (400 MHz, $C_6D_5CD_3$, −40 °C): δ 8.13 (br m, 2 H, *ortho*-H of HC≡CC_6H_5), 7.50 (br m, 2 H, *ortho*-H of RhC≡CC_6H_5), 7.01−6.83 (br m, 6 H, *meta*- and *para*-H of C_6H_5), 4.42 [d, J(Rh,H) = 2.2 Hz, 1 H, *H*C≡CPh], 2.32 (m, 6 H, PC*H*CH_3), 1.27, 1.06 (both m, 18 H each, PCHC*H*$_3$). ^{31}P NMR (36.2 MHz, $C_6D_5CD_3$, −40 °C): δ 38.8 [d, J(Rh,P) = 124.5 Hz].

Generation of [RhH(C≡CPh)$_2$(P*i*Pr$_3$)$_2$] (4). A solution of **3** (31 mg, 0.05 mmol) in toluene-d_8 (0.5 mL) was stirred for 15 min at −40 °C. The ^{1}H and ^{31}P NMR spectra revealed that a mixture of **3** and **4** in the approximate ratio of 3:2 was formed. After the temperature had been increased to 25 °C, the ratio of **3** to **4** changed to 2:3. By further increasing the temperature to ca. 40 °C, a fast rearrangement of **4** to the vinylidene complex **2** occurred. Data for **4**: ^{1}H NMR (400 MHz, $C_6D_5CD_3$, −40 °C): δ 7.50 (br m, *ortho*-H of RhC≡CC_6H_5), 7.01−6.83 (br m, *meta*- and *para*-H of C_6H_5), 2.74 (m, 6 H, PC*H*CH_3), 1.25 [dvt, N = 14.0, J(H,H) = 7.0 Hz, 36 H, PCHC*H*$_3$], −29.42 [dt, J(Rh,H) = 50.4, J(P,H) = 12.9 Hz, 1 H, RhH]. ^{31}P NMR (36.2 MHz, $C_6D_5CD_3$, −40 °C): δ 52.9 [d, dd in off-resonance, J(Rh,P) = 99.6 Hz].

Preparation of Compound 2 from 3 as the Precursor. A solution of **3** (81 mg, 0.13 mmol) in benzene (2 mL) was stirred for 3 h at room temperature. The solvent was evaporated in vacuo and the residue recrystallized from pentane at −78 °C to give blue crystals of **2**: yield 72 mg (89%).

Preparation of *trans*-[Rh(C≡CH)(=C=CH_2)(P*i*Pr$_3$)$_2$] (5). Method a: A slow stream of acetylene was passed for 30 s through a solution of **1** (132 mg, 0.28 mmol) in pentane (5 mL) at room temperature. While the solution was stirred for 10 h at ca. 20 °C, a smooth change of color from yellow to brownish green occurred and a dark violet solid precipitated. The solvent was evaporated, the oily residue was dissolved in pentane (2 mL), and the solution was chromatographed at −30 °C on Al_2O_3 (basic, activity grade V, height of column 5 cm). With pentane a blue fraction was eluted from which after removal of the solvent and recrystallization from pentane at −78 °C a blue microcrystalline solid was isolated: yield 43 mg (32%). Method b: A solution of **12** (171 mg, 0.35 mmol) in a 1:1 mixture of pentane and NEt_3 (8 mL) was treated with NaOH (140 mg, 3.50 mmol) at room temperature. After the mixture was cooled to −30 °C, a slow stream of acetylene was passed through the solution until a change of color from pale yellow to deep orange occurred. The reaction mixture was concentrated to ca. 4 mL in vacuo and then slowly warmed to room temperature. This led to a change of color from deep orange to blue. The solvent was evaporated in vacuo, the residue was extracted with pentane (30 mL), and the extract was filtered. After the filtrate was concentrated to ca. 3 mL in vacuo, it was stored for 6 h at −78 °C. A blue microcrystalline solid

precipitated, which was separated from the mother liquor, washed twice with small amounts of pentane (0 °C), and dried: yield 130 mg (78%); mp 85 °C dec. Anal. Calcd for $C_{22}H_{45}P_2Rh$: C, 55.70; H, 9.56. Found: C, 55.63; H, 9.80. MS (70 eV): *m/z* 474 (M^+). IR (hexane): ν(≡CH) 3290, ν(C≡C) 1940, ν(C═C) 1620 cm^{-1}. ^1H NMR (90 MHz, C_6D_6): δ 3.22 [dt, J(Rh,H) = 1.3, J(P,H) = 0.5 Hz, 1 H, ≡CH], 2.89 (m, 6 H, PC*H*CH_3), 1.37 [dvt, N = 13.4, J(H,H) = 7.0 Hz, 36 H, PCHC*H*$_3$], −0.13 [t, J(P,H) = 3.4 Hz, 2 H, ═CH_2]. ^{13}C NMR (50.3 MHz, C_6D_6): δ 309.0 [dt, J(Rh,C) = 50.0, J(P,C) = 15.3 Hz, Rh═C], 121.7 [dt, J(Rh,C) = 36.6, J(P,C) = 18.3 Hz, Rh*C*≡C], 118.8 [d, J(Rh,C) = 9.2 Hz, RhC≡*C*], 92.4 [dt, J(Rh,C) = 14.1, J(P,C) = 7.0 Hz, ═CH_2], 25.1 (vt, N = 20.9 Hz, P*C*HCH_3), 20.6 (s, PCHC*H*$_3$). ^{31}P NMR (36.2 MHz, C_6D_6): δ 45.6 [d, J(Rh,P) = 137.0 Hz].

Preparation of *trans*-[Rh(C≡CMe)(═C═CHMe)(P*i*Pr$_3$)$_2$] (6). Method a: A solution of **1** (235 mg, 0.51 mmol) in a 1:1 mixture of pentane and NEt_3 (6 mL) was cooled to −20 °C, and a slow stream of propyne was passed through the solution for 20 s. After the reaction mixture was warmed to room temperature, it was stirred for 6 h, which led to a change of color from yellow to green. The solution was then worked up as described for **5**, method b, to give dark green crystals: yield 100 mg (39%). Method b: A solution of **18** (112 mg, 0.22 mmol) in NEt_3 (3 mL) was treated at −20 °C with a 0.15 M solution of propyne in hexane (3 mL, 0.45 mmol). After the reaction mixture was warmed to room temperature, it was stirred for 4 h and then worked up as described for method a: yield 68 mg (62%); mp 65 °C dec. Anal. Calcd for $C_{24}H_{49}P_2Rh$: C, 57.36; H, 9.83. Found: C, 57.30; H, 10.03. IR (KBr): ν(C≡C) 2125, ν(C═C) 1670 cm^{-1}. ^1H NMR (90 MHz, C_6D_6): δ 2.74 (m, 6 H, PC*H*CH_3), 2.18 [t, J(P,H) = 2.0 Hz, 3 H, ≡CCH_3], 1.79 [ddt, J(Rh,H) = 0.5, J(P,H) = 2.6, J(H,H) = 7.5 Hz, 3 H, ═CHC*H*$_3$], 1.39 [dvt, N = 13.3, J(H,H) = 7.1 Hz, 36 H, PCHC*H*$_3$], 0.40 [tq, J(P,H) = 3.3, J(H,H) = 7.5 Hz, 1 H, ═C*H*CH_3]. ^{13}C NMR (50.3 MHz, C_6D_6): δ 307.6 [dt, J(Rh,C) = 46.1, J(P,C) = 15.8 Hz, Rh═C], 129.8 [d, J(Rh,C) = 10.0 Hz, RhC≡*C*], 111.1 [dt, J(Rh,C) = 38.0, J(P,C) = 18.8 Hz, Rh*C*≡C], 102.0 [dt, J(Rh,C) = 12.7, J(P,C) = 6.0 Hz, ═*C*HCH$_3$], 25.2 (vt, N = 20.0 Hz, P*C*HCH_3), 20.6 (s, PCHC*H*$_3$), 7.2 (s, ≡C*C*H_3), −2.0 [d, J(Rh,C) = 2.0 Hz, ═CH*C*H$_3$]. ^{31}P NMR (36.2 MHz, C_6D_6): δ 46.5 [d, J(Rh,P) = 138.5 Hz].

Preparation of *trans*-[Rh(C≡C*t*Bu)(═C═CH*t*Bu)(P-*i*Pr$_3$)$_2$] (7). Method a: A solution of **1** (146 mg, 0.31 mmol) in a 1:1 mixture of pentane and NEt_3 (4 mL) was treated with *tert*-butylacetylene (77 μL, 0.62 mmol) and stirred for 5 h at 40 °C. A smooth change of color from yellow to green occurred. After the solution was cooled to room temperature, the solvent was evaporated, the oily residue was extracted with pentane (20 mL), and the extract was brought to dryness in vacuo. After recrystallization of the residue from acetone (2 mL) at −78 °C, a dark green microcrystalline solid was obtained: yield 119 mg (65%). Method b: A solution of **18** (182 mg, 0.54 mmol) in a 1:1 mixture of pentane and NEt_3 (6 mL) was treated with *tert*-butylacetylene (133 μL, 1.08 mmol) and stirred for 4 h at 40 °C. It was then worked up as described for method a: yield 262 mg (82%); mp 119 °C dec. Anal. Calcd for $C_{30}H_{61}P_2Rh$: C, 61.42; H, 10.48. Found: C, 60.94; H, 10.78. IR (hexane): ν(C≡C) 2125, ν(C═C) 1660, 1630 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 2.91 (m, 6 H, PC*H*CH_3), 1.39 [dvt, N = 13.2, J(H,H) = 7.0 Hz, 36 H, PCHC*H*$_3$], 1.26 [s, 9 H, ≡CC(CH_3)$_3$], 1.04 [s, 9 H, ═CHC(C*H*$_3$)$_3$], −0.21 [dt, J(Rh,H) = 0.8, J(P,H) = 3.7 Hz, 1 H, ═C*H*(CH_3)$_3$]. ^{13}C NMR (100.6 MHz, C_6D_6): δ 307.0 [dt, J(Rh,C) = 48.6, J(P,C) = 15.8 Hz, Rh═C], 144.5 [dt, J(Rh,C) = 9.2, J(P,C) = 1.7 Hz, RhC≡*C*], 121.2 [dt, J(Rh,C) = 12.3, J(P,C) = 5.4 Hz, ═*C*H*t*Bu], 109.3 [dt, J(Rh,C) = 37.0, J(P,C) = 19.2 Hz, Rh*C*≡C], 32.4, 32.3 [both t, J(P,C) = 1.2 Hz, C*C*H_3], 29.7 (s, *C*CH_3), 25.0 [t, J(P,C) = 1.6 Hz, *C*CH_3], 25.2 [dvt, N = 19.9, J(Rh,C) = 1.2 Hz, P*C*HCH_3], 20.7 (s, PCHC*H*$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ 45.8 [d, J(Rh,P) = 137.9 Hz].

Preparation of [RhH(C≡CH)$_2$(py)(P*i*Pr$_3$)$_2$] (8). Method a: A solution of **1** (67 mg, 0.14 mmol) in pentane (5 mL) was treated with pyridine (0.1 mL, 1.20 mmol) at room temperature. After a slow stream of acetylene was passed through the solution for 30 s, the reaction mixture was stirred for 1 h. The solvent was evaporated, the residue was extracted with pentane (30 mL), and the extract was brought to dryness in vacuo. A white microcrystalline solid precipitated, which was separated from the mother liquor, washed three times with small amounts of pentane (2 mL each), and dried: yield 40 mg (52%). Method b: A solution of **5** (74 mg, 0.16 mmol) in pentane (5 mL) was treated with pyridine (0.1 mL, 1.20 mmol) and stirred for 3 h at room temperature. The reaction mixture was then worked up as described for method a: yield 78 mg (90%); mp 90 °C dec. Anal. Calcd for $C_{27}H_{50}NP_2Rh$: C, 58.58; H, 9.10; N, 2.53. Found: C, 58.13; H, 9.61; N, 2.29. IR (KBr): ν(≡CH) 3290, ν(RhH) 2190, ν(C≡C) 1940 cm^{-1}. ^1H NMR (90 MHz, C_6D_6): δ 10.03 (br m, 2 H, *ortho*-H of C_5H_5N), 6.90−6.60 (br m, 3 H, *meta*- and *para*-H of C_5H_5N), 3.06 (m, 6 H, PC*H*CH_3), 2.25 [dt, J(Rh,H) = 1.7, J(P,H) = 1.7 Hz, 2 H, ≡CH], 1.25 [dvt, N = 13.0, J(H,H) = 6.2 Hz, 36 H, PCHC*H*$_3$], −18.10 [dt, J(Rh,H) = 16.0, J(P,H) = 14.0 Hz, 1 H, RhH]. ^{31}P NMR (36.2 MHz, C_6D_6): δ 40.1 [d, dd in off-resonance, J(Rh,P) = 98.2 Hz].

Preparation of [RhH(C≡CMe)$_2$(py)(P*i*Pr$_3$)$_2$] (9). This compound was prepared analogously as described for **8**, using either (method a) **1** (98 mg, 0.21 mmol), pyridine (0.5 mL, 6.0 mmol), and propyne or (method b) **6** (67 mg, 0.13 mmol) and pyridine (0.5 mL, 6.0 mmol) as starting materials. For method b, the reaction mixture was stirred for 20 min at 40 °C. A white microcrystalline solid was obtained: yield for method a 107 mg (87%) and for method b 68 mg (88%); mp 104 °C dec. Anal. Calcd for $C_{29}H_{54}NP_2Rh$: C, 59.89; H, 9.36; N, 2.41. Found: C, 59.73; H, 9.51; N, 2.23. IR (KBr): ν(RhH) 2195, ν(C≡C) 2100 cm^{-1}. ^1H NMR (90 MHz, C_6D_6): δ 9.84 (br m, 2 H, *ortho*-H of C_5H_5N), 6.92−6.60 (br m, 3 H, *meta*- and *para*-H of C_5H_5N), 2.84 (m, 6 H, PC*H*CH_3), 2.14 [t, J(P,H) = 1.5 Hz, 6 H, ≡CCH_3], 1.30 [dvt, N = 13.0, J(H,H) = 7.0 Hz, 36 H, PCHC*H*$_3$], −18.74 [dt, J(Rh,H) = 15.1, J(P,H) = 15.1 Hz, 1 H, RhH]. ^{31}P NMR (36.2 MHz, C_6D_6): δ 41.8 [d, dd in off-resonance, J(Rh,P) = 101.1 Hz].

Preparation of [RhH(C≡C*t*Bu)$_2$(py)(P*i*Pr$_3$)$_2$] (10). Method a: A solution of **1** (95 mg, 0.20 mmol) in pentane (5 mL) was treated first with pyridine (0.5 mL, 6.0 mmol) and second with *tert*-butylacetylene (53 μL, 0.41 mmol) at room temperature. After the reaction mixture was stirred for 6 h at 40 °C, it was cooled to room temperature and the solvent was evaporated in vacuo. The residue was dissolved with acetone (3 mL), and the solution was stored for 12 h at −20 °C. A white microcrystalline solid precipitated, which was separated from the mother liquor, washed twice with acetone (1 mL each, −20 °C), and dried: yield 83 mg (61%). Method b: A solution of **7** (142 mg, 0.24 mmol) in pentane (8 mL) was treated with pyridine (0.5 mL, 6.0 mmol) and stirred for 30 min at 40 °C. The reaction mixture was then worked up as described for method a: yield 155 mg (96%); mp 109 °C dec. Anal. Calcd for $C_{35}H_{66}NP_2Rh$: C, 63.14; H, 9.99; N, 2.10. Found: C, 63.33; H, 10.10; N, 2.07. IR (KBr): ν(RhH) 2150, ν(C≡C) 2100 cm^{-1}. ^1H NMR (90 MHz, C_6D_6): δ 10.21 (br m, 2 H, *ortho*-H of C_5H_5N), 6.93 (br m, 1 H, *para*-H of C_5H_5N), 6.71 (br m, 2 H, *meta*-H of C_5H_5N), 3.02 (m, 6 H, PC*H*CH_3), 1.42 (s, 18 H, C(CH_3)$_3$), 1.26 [dvt, N = 12.9, J(H,H) = 7.1 Hz, 36 H, PCHC*H*$_3$], −18.84 [dt, J(Rh,H) = 17.1, J(P,H) = 15.1 Hz, 1 H, RhH]. ^{31}P NMR (36.2 MHz, C_6D_6): δ 42.2 [d, dd in off-resonance, J(Rh,P) = 101.1 Hz].

Preparation of [RhH(C≡CPh)$_2$(py)(P*i*Pr$_3$)$_2$] (11). Method a: A solution of **1** (131 mg, 0.28 mmol) in pentane (10 mL) was treated first with pyridine (0.5 mL, 6.0 mmol) and second with phenylacetylene (62 μL, 0.56 mmol). After the reaction mixture was stirred for 1 h at room temperature, the solvent was evaporated in vacuo and the white residue was washed three

times with pentane (2 mL each, 0 °C) and dried: yield 159 mg (86%). Method b: A solution of **2** (120 mg, 0.19 mmol) in pentane (5 mL) was treated with pyridine (0.5 mL, 6.0 mmol) and stirred for 1 h at room temperature. The reaction mixture was then worked up as described for method a: yield 120 mg (89%); mp 65 °C dec. Anal. Calcd for $C_{35}H_{58}NP_2Rh$: C, 66.37; H, 8.28; N, 1.98. Found: C, 66.24; H, 8.46; N, 1.96. IR (KBr): ν(RhH) 2177, ν(C≡C) 2080 cm^{-1}. ^{1}H NMR (90 MHz, C_6D_6): δ 10.02 (br m, 2 H, *ortho*-H of C_5H_5N), 7.70−6.70 (br m, 13 H, *meta*- and *para*-H of C_5H_5N and C_6H_5), 2.95 (m, 6 H, PC*H*CH$_3$), 1.25 [dvt, N = 13.3, J(H,H) = 6.6 Hz, 36 H, PCHC*H*$_3$], −18.00 [dt, J(Rh,H) = 15.0, J(P,H) = 15.0 Hz, 1 H, RhH]. ^{31}P NMR (36.2 MHz, C_6D_6): δ 41.3 [d, dd in off-resonance, J(Rh,P) = 98.5 Hz].

Preparation of [RhH(C≡CCO$_2$Me)$_2$(py)(P*i*Pr$_3$)$_2$] (14). This compound was prepared analogously as described for **11**, method b, using **13** (136 mg, 0.23 mmol) and pyridine (0.5 mL, 6.0 mmol) as starting materials. The time for the reaction was 20 min. A white microcrystalline solid was obtained: yield 105 mg (68%); mp 116 °C dec. Anal. Calcd for $C_{31}H_{54}NO_4P_2Rh$: C, 55.60; H, 8.14; N, 2.09. Found: C, 56.31; H, 8.37; N, 2.03. IR (KBr): ν(RhH) 2180, ν(C≡C) 2080, ν(C=O) 1670 cm^{-1}. ^{1}H NMR (90 MHz, C_6D_6): δ 9.72 (br m, 2 H, *ortho*-H of C_5H_5N), 6.68 (br m, 3 H, *meta*- and *para*-H of C_5H_5N), 3.41 (s, 6 H, CO_2Me), 2.95 (m, 6 H, PC*H*CH$_3$), 1.25 [dvt, N = 13.2, J(H,H) = 6.6 Hz, 36 H, PCHC*H*$_3$], −17.57 [dt, J(Rh,H) = 16.0, J(P,H) = 13.0 Hz, 1 H, RhH]. ^{31}P NMR (36.2 MHz, C_6D_6): δ 41.9 [d, dd in off-resonance, J(Rh,P) = 93.8 Hz].

Preparation of *trans*-[Rh(C≡CMe)(py)(P*i*Pr$_3$)$_2$] (15). A solution of **9** (116 mg, 0.20 mmol) in benzene (1.0 mL) was stirred for 3 days at 50 °C. The color gradually changed from yellow to orange-brown. The solvent was evaporated in vacuo, the residue was extracted with pentane (30 mL), and the extract was concentrated in vacuo until a precipitate began to be formed. After the solution was stored for 12 h at −78 °C, an orange microcrystalline solid was formed, which was identified by comparison of the ^{1}H and ^{31}P NMR data with those of an authentic sample:[10] yield 67 mg (62%).

Preparation of *trans*-[Rh(C≡C*t*Bu)(py)(P*i*Pr$_3$)$_2$] (16). A solution of **10** (112 mg, 0.17 mmol) in benzene (1 mL) was stirred for 2 days at 80 °C. A smooth change of color from yellow to orange-brown occurred. The solvent was evaporated in vacuo, the residue was extracted with pentane (30 mL), and the extract was brought to dryness in vacuo. After recrystallization of the oily residue from pentane at −78 °C, an orange microcrystalline solid was obtained: 51 mg (52%); mp 146 °C dec. Anal. Calcd for $C_{29}H_{56}NP_2Rh$: C, 59.68; H, 9.67; N, 2.40. Found: C, 60.02; H, 9.69; N, 2.48. IR (hexane): ν(C≡C) 2080 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 8.84 (br m, 2 H, *ortho*-H of C_5H_5N), 6.64 (br m, 1 H, *para*-H of C_5H_5N), 6.24 (br m, 2 H, *meta*-H of C_5H_5N), 2.31 (m, 6 H, PC*H*CH$_3$), 1.43 (s, 9 H, C(CH$_3$)$_3$), 1.39 [dvt, N = 12.6, J(H,H) = 6.8 Hz, 36 H, PCHC*H*$_3$]. ^{31}P NMR (81.0 MHz, C_6D_6): δ 41.1 [d, J(Rh,P) = 151.1 Hz].

Preparation of *trans*-[Rh(C≡CPh)(py)(P*i*Pr$_3$)$_2$] (17). This compound was prepared analogously as described for **15**, using **11** (141 mg, 0.20 mmol) as the starting material. A yellow microcrystalline solid was obtained, which was identified by comparison of the ^{1}H and ^{31}P NMR data with those of an authentic sample:[10] yield 66 mg (54%).

Reaction of Compound 17 with Phenylacetylene. A solution of **17** (78 mg, 0.11 mmol) in pentane (5 mL) was treated with phenylacetylene (14 μL, 0.13 mmol) and stirred for 30 min at room temperature. The solvent was evaporated in vacuo, and the remaining white solid was identified by NMR spectroscopy as **11**: yield 74 mg (81%).

Generation of *trans*-[Rh(C≡CMe)(HC≡CMe)(P*i*Pr$_3$)$_2$] (19). A slow stream of propyne was passed through a solution of **18** (136 mg, 0.27 mmol) in pentane (5 mL) for 10 s at −30 °C. The solution was warmed to −10 °C and stirred for 10 min. After the solvent was evaporated in vacuo, a brownish oily residue was obtained, which owing to the ^{31}P NMR spectrum consisted of a mixture of **6** (ca. 10%) and **19** (ca. 90%). Attempts to separate the mixture by fractional crystallization remained unsuccessful. Data for **19**: IR (hexane): ν(C≡C) 2100, ν(η^2-C≡C) 1895 cm^{-1}. ^{31}P NMR (36.2 MHz, C_6D_6): δ 38.5 [d, J(Rh,P) = 126.0 Hz].

Preparation of [RhH(C≡C*t*Bu)$_2$(P*i*Pr$_3$)$_2$] (20). A solution of **18** (372 mg, 0.72 mmol) in pentane (10 mL) was treated with *tert*-butylacetylene (178 μL, 1.45 mmol) and stirred for 15 min at room temperature. After the solution was stored for 12 h at −78 °C, orange-brown crystals precipitated, which were separated from the mother liquor, washed twice with pentane (2 mL each, 0 °C), and dried: yield 229 mg (54%); mp 40 °C dec. Anal. Calcd for $C_{30}H_{61}P_2Rh$: C, 61.42; H, 10.48. Found: C, 61.31; H, 10.47. IR (hexane): ν(RhH) 2120, ν(C≡C) 2080 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 2.97 (m, 6 H, PC*H*CH$_3$), 1.31 [dvt, N = 13.9, J(H,H) = 6.8 Hz, 36 H, PCHC*H*$_3$], 1.30 (s, C(CH$_3$)$_3$), −30.45 [dt, J(Rh,H) = 49.6, J(P,H) = 13.6 Hz, 1 H, RhH]. ^{13}C NMR (100.6 MHz, C_6D_6): δ 124.5 [dt, J(Rh,C) = 8.7, J(P,C) = 1.2 Hz, RhC≡*C*], 103.9 [dt, J(Rh,C) = 37.1, J(P,C) = 15.5 Hz, Rh*C*≡C], 32.6 (s, C*C*H$_3$), 29.8 (s, *C*CH$_3$), 24.7 (vt, N = 22.6 Hz, P*C*HCH$_3$), 20.3 (s, PCHC*H*$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ 53.6 [d, dd in off-resonance, J(Rh,P) = 100.8 Hz].

Preparation of Compound 7 from 20 as the Precursor. A solution of **20** (98 mg, 0.17 mmol) in a 1:1 mixture of pentane and NEt$_3$ (3 mL) was stirred for 4 h at 40 °C. The reaction was worked up as described for the preparation of **7**: yield 87 mg (89%).

Preparation of *trans*-[Rh(C≡CMe)(C$_2$H$_4$)(P*i*Pr$_3$)$_2$] (21). A solution of **18** (169 mg, 0.33 mmol) in NEt$_3$ (4.0 mL) was treated under an ethene atmosphere (0.2 bar) at −78 °C with a 0.12 M solution of propyne in pentane (2.8 mL, 0.33 mmol). The solution was slowly warmed to 0 °C and stirred for 5 min. A gradual change of color from orange to orange-brown occurred. The solvent was evaporated in vacuo, the residue was extracted with pentane (30 mL), and the extract was brought to dryness in vacuo. After recrystallization of the residue from acetone at −78 °C an orange microcrystalline solid was obtained, which was identified by comparison of the ^{1}H and ^{31}P NMR data with those of an authentic sample:[5] yield 51 mg (52%).

Preparation of *trans*-[Rh(C≡C*t*Bu)(C$_2$H$_4$)(P*i*Pr$_3$)$_2$] (22). A solution of **18** (216 mg, 0.42 mmol) in pentane (15 mL) was treated under an ethene atmosphere at −30 °C with *tert*-butylacetylene (52 μL, 0.42 mmol). After the solution was warmed to room temperature, it was stirred for 15 min. The solvent was evaporated in vacuo, the residue was dissolved in acetone (8 mL), and the solution was stored for 20 h at −30 °C. An orange microcrystalline solid precipitated, which was separated from the mother liquor, washed three times with acetone (3 mL each, −20 °C), and dried: yield 183 mg (82%); mp 118 °C dec. Anal. Calcd for $C_{26}H_{55}P_2Rh$: C, 58.64; H, 10.59. Found: C, 58.75; H, 10.41. IR (hexane): ν(C≡C) 2070, ν(C=C) 1505 cm^{-1}. ^{1}H NMR (90 MHz, C_6D_6): δ 3.03 [dt, J(Rh,H) = 1.5, J(P,H) = 3.4 Hz, 4 H, C_2H_4], 2.45 (m, 6 H, PC*H*CH$_3$), 1.31 [dvt, N = 12.6, J(H,H) = 6.8 Hz, 36 H, PCHC*H*$_3$], 1.30 (s, C(CH$_3$)$_3$). ^{13}C NMR (22.5 MHz, C_6D_6): δ 108.6 [dt, J(Rh,C) = 47.6, J(P,C) = 21.2 Hz, Rh*C*≡C], 51.9 [dt, J(Rh,C) = 10.3, J(P,C) = 1.8 Hz, C_2H_4], 32.1 (s, C*C*H$_3$), 29.7 (s, *C*CH$_3$), 23.1 [dvt, N = 17.6, J(Rh,C) = 1.5 Hz, P*C*HCH$_3$], 20.7 (s, PCHC*H*$_3$); signal of RhC≡*C* not exactly located. ^{31}P NMR (36.2 MHz, C_6D_6): δ 39.3 [d, J(Rh,P) = 129.0 Hz].

Preparation of *trans*-[Rh(C≡CPh)(C$_2$H$_4$)(P*i*Pr$_3$)$_2$] (23). A solution of **18** (154 mg, 0.30 mmol) in pentane (15.0 mL) was treated under an ethene atmosphere with a solution of phenylacetylene (32 μL, 0.30 mmol) in pentane (5 mL) at −15 °C. The solution was slowly warmed to 0 °C and stirred for 5 min. The solvent was evaporated in vacuo, the residue was washed three times with pentane (2 mL each, 0 °C), and dried.

The orange solid was identified by comparison of the ^{1}H and ^{31}P NMR data with those of an authentic sample:[5] yield 119 mg (72%).

Preparation of Compound 16 from 22 as the Precursor. A solution of **22** (79 mg, 0.15 mmol) in pentane (5 mL) was treated with pyridine (0.1 mL, 1.24 mmol) and stirred for 10 min at room temperature. The reaction was worked up as described for the preparation of **16**: yield 54 mg (63%).

Preparation of *trans*-[Rh(C≡CH)(py)(P*i*Pr$_3$)$_2$] (25). A solution of **24** (72 mg, 0.15 mmol) in pentane (5 mL) was treated with pyridine (0.1 mL, 1.24 mmol) and stirred for 10 min at room temperature. The solvent and the olefin were evaporated in vacuo, and the orange residue was washed three times with pentane (1 mL each, 0 °C) and dried: yield 67 mg (84%); mp 96 °C dec. Anal. Calcd for $C_{25}H_{48}NP_2Rh$: C, 56.92; H, 9.17; N, 2.66. Found: C, 56.59; H, 9.06; N, 2.53. IR (benzene): ν(≡CH) 3280, ν(C≡C) 1920 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 8.81 (br m, 2 H, *ortho*-H of C_5H_5N), 6.64 (br m, 1 H, *para*-H of C_5H_5N), 6.25 (br m, 2 H, *meta*-H of C_5H_5N), 2.42 [dt, J(Rh,H) = 2.3, J(P,H) = 2.1 Hz, 1 H, ≡CH], 2.35 (m, 6 H, PC*H*CH$_3$), 1.39 [dvt, N = 12.6, J(H,H) = 6.9 Hz, 36 H, PCHC*H*$_3$]. ^{13}C NMR (50.3 MHz, C_6D_6): δ 155.8 (s, *ortho*-C of C_5H_5N), 133.7 (s, *para*-C of C_5H_5N), 122.7 (s, *meta*-C of C_5H_5N), 113.6 [dt, J(Rh,C) = 46.5, J(P,C) = 22.5 Hz, Rh*C*≡C], 100.5 [dt, J(Rh,C) = 14.5, J(P,C) = 3.0 Hz, RhC≡*C*], 24.9 [dvt, N = 16.4, J(Rh,C) = 2.3 Hz, P*C*HCH$_3$], 20.9 (s, PCHC*H*$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 40.3 [d, J(Rh,P) = 150.9 Hz].

Preparation of *trans*-[Rh(C≡CH)(PhC≡CMe)(P*i*Pr$_3$)$_2$] (26). A solution of **24** (67 mg, 0.14 mmol) in hexane (5 mL) was treated with PhC≡CMe (18 μL, 0.14 mmol) and stirred for 30 min at room temperature. The solvent and the olefin were evaporated in vacuo, and the orange microcrystalline residue was washed three times with pentane (1 mL each, 0 °C) and dried: yield 69 mg (88%); mp 90 °C dec. Anal. Calcd for $C_{29}H_{51}P_2Rh$: C, 61.70; H, 9.10. Found: C, 61.70; H, 9.09. IR (KBr): ν(≡CH) 3280, ν(η^2-C≡C) 1958, ν(C≡C) 1925 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 7.94 (m, 2 H, *ortho*-H of C_6H_5), 7.15 (m, 2 H, *meta*-H of C_6H_5), 6.98 (m, 1 H, *para*-H of C_6H_5), 2.96 [dt, J(Rh,H) = 1.8, J(P,H) = 1.7 Hz, 1 H, ≡CH], 2.42 (m, 6 H, PC*H*CH$_3$), 2.30 (s, 3 H, ≡CCH$_3$), 1.33, 1.25 [both dvt, N = 13.2, J(H,H) = 6.8 Hz, 18 H each, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, C_6D_6): δ 131.6, 131.2, 127.8, 125.9 (all s, C_6H_5), 115.5 [dt, J(Rh,C) = 47.8, J(P,C) = 20.2 Hz, Rh*C*≡C], 109.3 [dt, J(Rh,C) = 13.8, J(P,C) = 1.7 Hz, RhC≡*C*], 86.7 [dt, J(Rh,C) = 9.1, J(P,C) = 2.5 Hz, Ph*C*≡CMe], 76.0 [dt, J(Rh,C) = 10.4, J(P,C) = 1.5 Hz, PhC≡*C*Me], 25.0 [dvt, N = 17.6, J(Rh,C) = 1.1 Hz, P*C*HCH$_3$], 21.2, 20.5 (both s, PCHC*H*$_3$), 13.9 [d, J(Rh,C) = 1.2 Hz, ≡C*C*H$_3$]. ^{31}P NMR (162.0 MHz, C_6D_6): δ 39.6 [d, J(Rh,P) = 126.2 Hz].

Preparation of *trans*-[Rh(C≡CPh)(MeC≡CPh)(P*i*Pr$_3$)$_2$] (27). A solution of **23** (83 mg, 0.15 mmol) in benzene (5 mL) was treated with PhC≡CMe (19 μL, 0.15 mmol) and stirred for 30 min at room temperature. After the reaction was worked up as described for **26**, an orange microcrystalline solid was obtained: yield 89 mg (92%); mp 96 °C dec. Anal. Calcd for $C_{35}H_{55}P_2Rh$: C, 65.62; H, 8.65. Found: C, 66.04; H, 8.77. IR (hexane): ν(C≡C) 2090, ν(η^2-C≡C) 1965 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 7.98, 7.48 (both m, 2 H each, *ortho*-H of C_6H_5), 7.17, 7.15 (both m, 2 H each, *meta*-H of C_6H_5), 7.00, 6.94 (both m, 1 H each, *para*-H of C_6H_5), 2.35 (m, 6 H, PC*H*CH$_3$), 2.32 (s, 3 H, ≡CCH$_3$), 1.33, 1.22 [both dvt, N = 13.2, J(H,H) = 6.8 Hz, 18 H each, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, C_6D_6): δ 131.7, 131.2, 129.9, 129.8, 128.5, 127.9, 126.0, 124.5 (all s, C_6H_5), 125.6 [dt, J(Rh,C) = 13.5, J(P,C) = 1.0 Hz, RhC≡*C*], 125.4 [dt, J(Rh,C) = 47.9, J(P,C) = 20.7 Hz, Rh*C*≡C], 87.5 [dt, J(Rh,C) = 8.7, J(P,C) = 2.3 Hz, Ph*C*≡CMe], 76.9 [dt, J(Rh,C) = 10.4, J(P,C) = 1.0 Hz, PhC≡*C*Me], 24.9 (vt, N = 17.7 Hz, P*C*HCH$_3$), 21.1, 20.3 (both s, PCHC*H*$_3$), 13.8 (s, ≡C*C*H$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ 40.2 [d, J(Rh,P) = 126.2 Hz].

Preparation of *trans*-[Rh(C≡CPh)(PhC≡CPh)(P*i*Pr$_3$)$_2$] (28). A solution of **23** (61 mg, 0.11 mmol) in hexane (5 mL) was treated with PhC≡CPh (20 mg, 0.11 mmol) and stirred for 30 min at room temperature. The solvent and the olefin were evaporated in vacuo, and the oily residue was layered with a small amount of pentane to initiate crystallization. After the mixture was stored for 6 h at 0 °C, an orange microcrystalline solid was formed, which was separated from the mother liquid, washed three times with pentane (1 mL each, 0 °C), and dried: yield 69 mg (89%); mp 136 °C dec. Anal. Calcd for $C_{40}H_{57}P_2Rh$: C, 68.37; H, 8.18. Found: C, 68.62; H, 8.18. IR (hexane): ν(C≡C) 2070, ν(η^2-C≡C) 1895 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 8.17, 7.51 (both m, 6 H, *ortho*-H of C_6H_5), 7.22, 7.17 (both m, 6 H, *meta*-H of C_6H_5), 7.05, 6.95 (both m, 3 H, *para*-H of C_6H_5), 2.35 (m, 6 H, PC*H*CH$_3$), 1.24 [dvt, N = 13.1, J(H,H) = 6.9 Hz, 36 H, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, C_6D_6): δ 131.4, 130.9, 129.8, 129.5, 128.5, 128.1, 126.7, 124.8 (all s, C_6H_5), 126.8 [dt, J(Rh,C) = 13.4, J(P,C) = 1.9 Hz, RhC≡*C*], 124.3 [dt, J(Rh,C) = 48.1, J(P,C) = 20.9 Hz, Rh*C*≡C], 91.6 [dt, J(Rh,C) = 10.5, J(P,C) = 2.3 Hz, Ph*C*≡*C*Ph], 25.2 (vt, N = 18.0 Hz, P*C*HCH$_3$), 20.9 (s, PCHC*H*$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ 38.7 [d, J(Rh,P) = 122.8 Hz].

Preparation of *trans*-[Rh(C≡CH)(CO)(P*i*Pr$_3$)$_2$] (29). A slow stream of CO was passed for 30 s through a solution of **24** (67 mg, 0.14 mmol) in pentane (5 mL) at room temperature. A rapid change of color from orange to pale yellow occurred. The solvent and the olefin were evaporated in vacuo, and the pale yellow microcrystalline residue was washed three times with pentane (1 mL each, 0 °C) and dried: yield 65 mg (97%); mp 126 °C dec. Anal. Calcd for $C_{21}H_{43}OP_2Rh$: C, 52.94; H, 9.10. Found: C, 53.38; H, 9.62. IR (hexane): ν(≡CH) 3280, ν(C≡C) and ν(CO) 1975, 1930 cm^{-1}. ^{1}H NMR (90 MHz, C_6D_6): δ 2.57 (m, 6 H, PC*H*CH$_3$), 2.55 [dt, J(Rh,H) = 1.6, J(P,H) = 2.3 Hz, 1 H, ≡CH], 1.32 [dvt, N = 13.7, J(H,H) = 7.0 Hz, 36 H, PCHC*H*$_3$]. ^{13}C NMR (22.5 MHz, C_6D_6): δ 196.0 [dt, J(Rh,C) = 58.6, J(P,C) = 13.7 Hz, RhCO], 116.7 [dt, J(Rh,C) = 41.0, J(P,C) = 21.5 Hz, Rh*C*≡C], 104.7 [dt, J(Rh,C) = 11.7, J(P,C) = 2.9 Hz, RhC≡*C*], 26.2 (vt, N = 21.5 Hz, P*C*HCH$_3$), 20.6 (s, PCHC*H*$_3$). ^{31}P NMR (36.2 MHz, C_6D_6): δ 52.9 [d, J(Rh,P) = 127.5 Hz].

Preparation of *trans*-[Rh(C≡CMe)(CO)(P*i*Pr$_3$)$_2$] (30). This compound was prepared analogously as described for **29**, using **21** (51 mg, 0.10 mmol) and CO as starting materials. A pale yellow microcrystalline solid was obtained: yield 42 mg (82%). Anal. Calcd for $C_{22}H_{45}OP_2Rh$: C, 53.88; H, 9.25. Found: C, 53.76; H, 9.16. IR (hexane): ν(CO) 1945 cm^{-1}. ^{1}H NMR (90 MHz, C_6D_6): δ 2.42 (m, 6 H, PC*H*CH$_3$), 1.93 [t, J(P,H) = 2.6 Hz, 3 H, ≡CCH$_3$], 1.33 [dvt, N = 14.0, J(H,H) = 7.0 Hz, 36 H, PCHC*H*$_3$]. ^{31}P NMR (36.2 MHz, C_6D_6): δ 50.0 [d, J(Rh,P) = 126.0 Hz].

Preparation of *trans*-[Rh(C≡CPh)(CO)(P*i*Pr$_3$)$_2$] (31). This compound was prepared analogously as described for **29**, using **23** (55 mg, 0.10 mmol) and CO as starting materials. The pale yellow microcrystalline product was characterized by comparison of the NMR data with those of an authentic sample:[5] yield 51 mg (93%).

Preparation of *trans*-[Rh(=C=CH$_2$)(py)(P*i*Pr$_3$)$_2$]BF$_4$ (32). A solution of **24** (96 mg, 0.20 mmol) in diethyl ether (5 mL) was treated at 0 °C with a solution of [pyH]BF$_4$ (33 mg, 0.20 mmol) in acetone (5 mL). The solution was slowly warmed to room temperature, which led to a change of color from orange to violet. After the solution was stirred for 15 min, it was concentrated in vacuo to ca. 2 mL and hexane (15 mL) was added. A violet microcrystalline solid precipitated, which was characterized by comparison of the ^{1}H and ^{31}P NMR data with those of an authentic sample:[9] yield 112 mg (91%).

Preparation of [(η^5-C$_5$H$_5$)Rh(=C=CH$_2$)(P*i*Pr$_3$)] (33). A solution of **24** (52 mg, 0.11 mmol) in benzene (5 mL) was treated with freshly distilled cyclopentadiene (9 μL, 0.11 mmol) and stirred for 2 h at room temperature. The solvent was evaporated in vacuo, and the residue was recrystallized from

pentane to give an orange microcrystalline solid. This was characterized by comparison of the ^{1}H and ^{13}C NMR data with those of an authentic sample:[10] yield 33 mg (85%).

Preparation of Compound 5 from 24 as the Precursor. A slow stream of acetylene was passed for 10 s at −10 °C through a solution of **24** (127 mg, 0.27 mmol) in a 1:1 mixture of pentane and NEt_3 (4 mL). After the solution was warmed to room temperature, it was stirred for 5 min and then worked up as described for **5**: yield 99 mg (78%).

Preparation of *trans*-[Rh(C≡C*t*Bu)(=C=CHCO$_2$Me)(P*i*Pr$_3$)$_2$] (34). A solution of **22** (158 mg, 0.30 mmol) in a 1:1 mixture of pentane and NEt_3 (6 mL) was treated at −78 °C with HC≡CCO$_2$Me (26 μL, 0.30 mmol). After the solution was warmed to room temperature, it was stirred for 30 min, which led to a change of color from orange to dark green. The solvent was evaporated in vacuo, the residue was extracted with pentane (30 mL), and the extract was concentrated to ca. 10 mL in vacuo. After the solution was stored for 6 h at −78 °C, blue-green crystals precipitated, which were separated from the mother liquor, washed twice with pentane (2 mL each, 0 °C), and dried: yield 117 mg (67%); mp 76 °C dec. Anal. Calcd for $C_{28}H_{55}O_2P_2Rh$: C, 57.14; H, 9.42. Found: C, 56.81; H, 9.36. IR (benzene): ν(C≡C) 2105, ν(C=O) 1680, ν(C=C) 1585 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 3.47 (s, 3 H, CO_2Me), 2.77 (m, 6 H, PC*H*CH$_3$), 1.32 [dvt, N = 13.7, J(H,H) = 7.2 Hz, 36 H, PCHC*H*$_3$], 1.28 [t, J(P,H) = 3.1 Hz, 1 H, =C*H*CO$_2$CH$_3$], 1.19 (s, 9 H, CCH$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 299.3 [dt, J(Rh,C) = 52.9, J(P,C) = 14.6 Hz, Rh=C], 158.0 [t, J(P,C) = 2.0 Hz, *C*O$_2$Me], 145.1 [dt, J(Rh,C) = 9.0, J(P,C) = 1.8 Hz, RhC≡*C*], 108.6 [dt, J(Rh,C) = 12.7, J(P,C) = 4.7 Hz, =*C*HCO$_2$Me], 108.5 [dt, J(Rh,C) = 36.6, J(P,C) = 19.3 Hz, Rh*C*≡C], 50.3 (s, CO$_2$*C*H$_3$), 32.1 (s, C*C*H$_3$), 29.6 (s, *C*CH$_3$), 25.4 (vt, N = 21.3 Hz, P*C*HCH$_3$), 20.5 (s, PCHC*H*$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 48.5 [d, J(Rh,P) = 135.2 Hz].

Preparation of *trans*-[Rh(C≡CPh)(=C=CHCO$_2$Me)(P*i*Pr$_3$)$_2$] (35). A solution of **23** (96 mg, 0.17 mmol) in a 1:1 mixture of pentane and NEt_3 (4 mL) was treated at −78 °C with HC≡CCO$_2$Me (15 μL, 0.17 mmol). After the solution was warmed to room temperature, it was stirred for 1 h and then worked up as described for **34**. A blue microcrystalline solid was obtained: yield 80 mg (76%); mp 104 °C dec. Anal. Calcd for $C_{30}H_{51}O_2P_2Rh$: C, 59.21; H, 8.45. Found: C, 59.38; H, 8.84. IR (benzene): ν(C≡C) 2080, ν(C=O) 1685, ν(C=C) 1585 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 7.34 (m, 2 H, *ortho*-H of C_6H_5), 7.08 (m, 1 H, *para*-H of C_6H_5), 6.90 (m, 2 H, *meta*-H of C_6H_5), 3.48 (s, 3 H, CO_2Me), 2.73 (m, 6 H, PC*H*CH$_3$), 1.40 [t, J(P,H) = 3.1 Hz, 1 H, =C*H*CO$_2$CH$_3$], 1.33 [dvt, N = 13.8, J(H,H) = 7.1 Hz, 36 H, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, C_6D_6): δ 300.7 [dt, J(Rh,C) = 53.1, J(P,C) = 14.7 Hz, Rh=C], 157.8 (br s, *C*O$_2$Me), 136.1 [d, J(Rh,C) = 9.4 Hz, RhC≡*C*], 130.2, 128.7, 128.4, 125.6 (all s, C_6H_5), 125.4 [dt, J(Rh,C) = 36.8, J(P,C) = 18.9 Hz, Rh*C*≡C], 109.0 [dt, J(Rh,C) = 13.0, J(P,C) = 5.0 Hz, =*C*HCO$_2$Me], 50.4 (s, CO$_2$*C*H$_3$), 25.7 (vt, N = 21.5 Hz, P*C*HCH$_3$), 20.4 (s, PCHC*H*$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ 48.4 [d, J(Rh,P) = 133.6 Hz].

Preparation of *trans*-[Rh(C≡CPh)(=C=CH$_2$)(P*i*Pr$_3$)$_2$] (36). Method a: A slow stream of acetylene was passed for 30 s through a solution of **23** (151 mg, 0.27 mmol) in a 1:1 mixture of pentane and NEt_3 (10 mL) at room temperature. The reaction was stirred for 10 min, which led to a change of color from orange to dark violet. The solvent was evaporated in vacuo, the residue was dissolved in pentane (30 mL), and the solution was stored for 12 h at −78 °C. A dark violet solid precipitated, which was separated from the mother liquor, washed twice with pentane (1 mL each, 0 °C), and dried: yield 117 mg (78%). Method b: A solution of **24** (138 mg, 0.29 mmol) in a 1:1 mixture of pentane and NEt_3 (8 mL) was treated at −15 °C with phenylacetylene (31 μL, 0.29 mmol). After the solution was warmed to room temperature, it was stirred for 10 min and then worked up as described for method a: yield 130 mg (81%); mp 89 °C dec. Anal. Calcd for $C_{28}H_{49}P_2Rh$: C, 61.09; H, 8.97. Found: C, 61.02; H, 9.27. IR (KBr): ν(C≡C) 2080, ν(C=C) 1620, 1580 cm^{-1}. ^{1}H NMR (90 MHz, C_6D_6): δ 7.42 (m, 2 H, *ortho*-H of C_6H_5), 7.25−6.97 (br m, 3 H, *para*- and *meta*-H of C_6H_5), 2.83 (m, 6 H, PC*H*CH$_3$), 1.37 [dvt, N = 13.5, J(H,H) = 7.1 Hz, 36 H, PCHC*H*$_3$], −0.03 [dt, J(Rh,H) = 0.7, J(P,H) = 3.4 Hz, 2 H, =CH$_2$]. ^{13}C NMR (100.6 MHz, C_6D_6): δ 309.2 [dt, J(Rh,C) = 48.1, J(P,C) = 15.8 Hz, Rh=C], 134.4 [d, J(Rh,C) = 9.4 Hz, RhC≡*C*], 130.2, 129.4, 128.3, 125.1 (all s, C_6H_5), 92.4 [dt, J(Rh,C) = 14.0, J(P,C) = 5.3 Hz, =CH$_2$], 25.2 (vt, N = 20.2 Hz, P*C*HCH$_3$), 20.5 (s, PCHC*H*$_3$); signal for Rh*C*≡C not exactly located. ^{31}P NMR (36.2 MHz, C_6D_6): δ 47.1 [d, J(Rh,P) = 136.3 Hz].

Preparation of [RhH(C≡CH)(C≡Ph)(py)(P*i*Pr$_3$)$_2$] (37). A solution of **36** (129 mg, 0.24 mmol) in pentane (4 mL) was treated with pyridine (0.5 mL, 6.0 mmol) and stirred for 20 min at room temperature. A change of color from blue to pale yellow occurred. The solvent was evaporated in vacuo, and the white residue was washed three times with pentane (1 mL each, 0 °C) and dried: yield 105 mg (72%); mp 106 °C dec. Anal. Calcd for $C_{33}H_{54}NP_2Rh$: C, 62.95; H, 8.64; N, 2.22. Found: C, 62.89; H, 9.13; N, 2.37. IR (KBr): ν(≡CH) 3280, ν(RhH) 2180, ν(C≡CPh) 2095, ν(C≡CH) 1945 cm^{-1}. ^{1}H NMR (90 MHz, C_6D_6): δ 9.90 (br m, 2 H, *ortho*-H of C_5H_5N), 7.63−6.65 (br m, 8 H, *meta*- and *para*-H of C_5H_5N and C_6H_5), 3.03 (m, 6 H, PC*H*CH$_3$), 2.34 [dt, J(Rh,H) = 1.6, J(P,H) = 1.6 Hz, 1 H, ≡CH], 1.26, 1.24 [both dvt, N = 13.4, J(H,H) = 6.8 Hz, 18 H each, PCHC*H*$_3$], −17.94 [dt, J(Rh,H) = 16.5, J(P,H) = 14.2 Hz, 1 H, RhH]. ^{31}P NMR (36.2 MHz, C_6D_6): δ 41.6 [d, dd in off-resonance, J(Rh,P) = 98.2 Hz].

Preparation of [RhH(C≡CPh)(C≡CCO$_2$Me)(py)(P*i*Pr$_3$)$_2$] (38). A solution of **35** (86 mg, 0.14 mmol) in diethyl ether (5 mL) was treated with pyridine (0.5 mL, 6.0 mmol) and stirred for 20 min at room temperature. A change of color from blue to pale yellow occurred. The reaction mixture was worked up as described for **37** to give a white microcrystalline solid: yield 64 mg (65%); mp 116 °C dec. Anal. Calcd for $C_{35}H_{56}NO_2P_2Rh$: C, 61.13; H, 8.21; N, 2.04. Found: C, 61.56; H, 7.91; N, 2.02. IR (KBr): ν(RhH) 2180, ν(C≡C) 2070 (br), ν(C=O) 1670 cm^{-1}. ^{1}H NMR (90 MHz, C_6D_6): δ 9.96 (br m, 2 H, *ortho*-H of C_5H_5N), 7.56−6.51 (br m, 8 H, *meta*- and *para*-H of C_5H_5N and C_6H_5), 3.48 (s, 3 H, CO_2CH_3), 2.90 (m, 6 H, PC*H*CH$_3$), 1.20 [dvt, N = 13.2, J(H,H) = 7.0 Hz, 36 H, PCHC*H*$_3$], −17.66 [dt, J(Rh,H) = 16.5, J(P,H) = 13.7 Hz, 1 H, RhH]. ^{31}P NMR (36.2 MHz, C_6D_6): δ 42.0 [d, dd in off-resonance, J(Rh,P) = 95.3 Hz].

Preparation of *trans*-[Rh(C≡CMe)(η^2-CH$_2$=C=CH$_2$)(P*i*Pr$_3$)$_2$] (39). Method a: To a solid sample of **1** (70 mg, 0.15 mmol), stored in a Schlenk tube at −50 °C, an excess of propyne (ca. 1 mL, ca. 17 mmol)) was condensed. An orange suspension was obtained to which pentane (2 mL, −50 °C) was added. After the reaction mixture was stirred for 5 min at −50 °C, it was slowly warmed to room temperature. The solvent was evaporated in vacuo and the residue was recrystallized from pentane (3 mL) at −78 °C to give a yellow microcrystalline solid: yield 60 mg (79%). Method b: The same procedure was applied as described for a using **18** (78 mg, 0.15 mmol) as starting material: yield 63 mg (83%); mp 68 °C dec. Anal. Calcd for $C_{24}H_{49}P_2Rh$: C, 57.36; H, 9.83. Found: C, 57.67; H, 9.95. IR (KBr): ν(C≡C) 2100, ν(C=C=C) 1740 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 5.45, 5.25 [both m, in ^{1}H{^{31}P} both ddt, J(Rh,H) = 1.0, ^2J(H,H) = 2.7, ^4J(H,H) = 3.5 Hz, 1 H each, =CH$_2$ uncoordinated], 2.48 [dtt, J(Rh,H) = 1.7, J(P,H) = 5.0, ^4J(H,H) = 3.5 Hz, 2 H, =CH$_2$ coordinated], 2.44 (m, 6 H, PC*H*CH$_3$), 2.00 [t, J(P,H) = 2.1 Hz, 3 H, ≡CCH$_3$], 1.35 [dvt, N = 13.0, J(H,H) = 6.9 Hz, 36 H, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, C_6D_6): δ 182.4 [dt, J(Rh,C) = 16.1, J(P,C) = 4.5 Hz, =C=], 117.2 [dt, J(Rh,C) = 12.7, J(P,C) = 2.1 Hz, RhC≡*C*], 108.5 [dt, J(Rh,C) = 45.8, J(P,C) = 21.0 Hz, Rh*C*≡C], 94.2 [dt, J(Rh,C) = 2.4, J(P,C) = 2.4 Hz, =CH$_2$ uncoordinated], 24.5 [dvt, N = 18.8, J(Rh,C) = 1.1 Hz, P*C*HCH$_3$], 20.8 (s, PCHC*H*$_3$), 17.2 [dt, J(Rh,C) = 8.1, J(P,C) = 1.9 Hz, =CH$_2$ coordinated],

6.8 [dt, J(Rh,C) = 1.0, J(P,C) = 1.0 Hz, ≡CCH_3]. ^{31}P NMR (162.0 MHz, C_6D_6): δ 38.5 [d, J(Rh,P) = 126.6 Hz].

Reaction of Compound 39 with CO. A slow stream of CO was passed for 10 s through a solution of **39** (50 mg, 0.10 mmol) in C_6D_6 (0.5 mL) at room temperature. The ^{1}H and ^{31}P NMR spectra revealed that besides allene the carbonyl complex **30** was formed: yield virtually quantitative.

Preparation of *trans*-[Rh(C≡CMe)$_2${C(CH$_3$)=CH$_2$}(P-*i*Pr$_3$)$_2$] (40). Method a: A slow stream of propyne was passed for 1 min through a solution of **1** (228 mg, 0.49 mmol) in a 1:1 mixture of pentane and NEt_3 (6 mL) at −20 °C. After the solution was warmed to room temperature, it was stirred for 10 h, which led to a smooth change of color from orange-yellow to red. The solvent was evaporated in vacuo, the residue was dissolved in pentane (10 mL), and the solution was concentrated to ca. 2 mL in vacuo. After the solution was stored for 48 h at −78 °C, a red microcrystalline solid precipitated, which was separated from the mother liquor, washed twice with pentane (2 mL each, −20 °C), and dried: yield 104 mg (39%). Method b: A slow stream of propyne was passed for 15 s through a solution of **18** (143 mg, 0.28 mmol) in pentane (5 mL) at −40 °C. After the solution was warmed to −20 °C, it was stirred for 10 min and then the solvent was evaporated in vacuo. The oily residue was dissolved in pentane (5 mL), and a stream of propyne was passed through the solution for 1 min at room temperature. The solution was stirred for 5 min, and the solvent was removed. The oily residue was dissolved in a 4:1 mixture of benzene/hexane (2 mL), and the solution was chromatographed on Al_2O_3 (basic, activity grade IV, height of column 7 cm). With benzene/hexane (4:1) a red fraction was eluted, which was brought to dryness in vacuo. After recrystallization of the residue from acetone at −78 °C, a red microcrystalline solid was obtained: yield 81 mg (54%); mp 74 °C dec. Anal. Calcd for $C_{37}H_{53}P_2Rh$: C, 59.77; H, 9.84. Found: C, 59.48; H, 9.93. IR (KBr): ν(C≡C) 2105, ν(C=C) 1575 cm^{-1}. ^{1}H NMR (90 MHz, C_6D_6): δ 5.54 [m, in ^{1}H{^{31}P} br d, J(Rh,H) = 2.4 Hz, 1 H, one H of =CH_2 *trans* to CH_3], 4.31 [m, in ^{1}H{^{31}P} br d, J(Rh,H) = 4.3 Hz, 1 H, one H of =CH_2 *cis* to CH_3], 2.98 (m, 6 H, PC*H*CH_3), 2.30 (m, 3 H, RhCCH_3), 2.06 [dt, J(Rh,H) = 0.6, J(P,H) = 1.7 Hz, 6 H, ≡CCH_3], 1.40 [dvt, N = 13.0, J(H,H) = 7.1 Hz, 36 H, PCHCH_3]. ^{31}P NMR (81.0 MHz, C_6D_6): δ 30.2 [d, J(Rh,P) = 104.6 Hz].

Preparation of *trans*-[Rh(C≡CMe){η^2-Me*C*≡*C*C(Me)=CH$_2$}(P*i*Pr$_3$)$_2$] (41). A solution of **40** (81 mg, 0.15 mmol) in benzene (1 mL) was stirred for 20 min at room temperature. A change of color from deep red to orange occurred. The solvent was evaporated in vacuo, and the remaining orange oil was dried in vacuo: yield 80 mg (98%). IR (hexane): ν(C≡C) 2090, ν(η^2-C≡C) 1930 cm^{-1}. ^{1}H NMR (90 MHz, C_6D_6): δ 5.91 (m, 1 H, one H of =CH_2), 5.27 (m, 1 H, one H of =CH_2), 2.35 (m, 6 H, PC*H*CH_3), 2.20 (br s, 3 H, η^2-RC≡CCH_3), 2.07 [dt, J(Rh,H) = 0.6, J(P,H) = 1.8 Hz, 3 H, RhC≡CCH_3], 2.00 (m, 3 H, CH_2=CCH_3), 1.38, 1.33 [both dvt, N = 13.1, J(H,H) = 7.1 Hz, 18 H each, PCHCH_3]. ^{13}C NMR (100.6 MHz, C_6D_6): δ 133.6 (s, *C*(CH$_3$)=CH$_2$), 117.4 (s, C(CH$_3$)=*C*H$_2$), 117.1 [dt, J(Rh,C) = 13.3, J(P,C) = 2.9 Hz, RhC≡*C*], 105.8 [dt, J(Rh,C) = 46.7, J(P,C) = 21.2 Hz, Rh*C*≡C], 89.3 [dt, J(Rh,C) = 9.1, J(P,C) = 2.9 Hz, one C of *C*≡*C*], 77.9 [dt, J(Rh,C) = 10.5, J(P,C) = 1.5 Hz, one C of *C*≡*C*], 25.2 [dvt, N = 17.5, J(Rh,C) = 1.2 Hz, PCHCH$_3$], 24.0 (s, C(*C*H$_3$)=CH$_2$), 21.0, 20.4 (both s, PCHCH_3), 13.7 [d, J(Rh,C) = 1.2 Hz, η^2-RC≡C*C*H$_3$], 7.1 [dt, J(Rh,C) = 0.9, J(P,C) = 0.9 Hz, RhC≡C*C*H$_3$]. ^{31}P NMR (36.2 MHz, C_6D_6): δ 40.1 [d, J(Rh,P) = 130.4 Hz].

Reaction of Compound 41 with CO. A slow stream of CO was passed for 10 s through a solution of **41** (49 mg, 0.09 mmol) in C_6D_6 (0.5 mL) at room temperature. The ^{1}H and ^{31}P NMR spectra revealed that besides the carbonyl complex **30** the enyne **42** was formed: yield virtually quantitative. Data for **42**: ^{1}H NMR (90 MHz, C_6D_6): δ 5.29 [dqq, ^2J(H,H) = 1.6, ^4J(H,H) = 1.0, ^6J(H,H) = 0.6 Hz, 1 H, one H of =CH_2 *cis* to CH_3], 5.01 [dqq, ^2J(H,H) = 1.6, ^4J(H,H) = 1.5, ^6J(H,H) = 0.4 Hz, 1 H, one H of =CH_2 *trans* to CH_3], 1.77 [dd, ^4J(H,H) = 1.5, ^4J(H,H) = 1.0 Hz, 3 H, =CCH_3], 1.57 [dd, ^6J(H,H) = 0.6, ^6J(H,H) = 0.4 Hz, 3 H, C≡CCH_3].

Reaction of Compound 1 with Excess Phenylacetylene. A solution of **1** (87 mg, 0.19 mmol) in pentane (10 mL) was treated with phenylacetylene (1.0 mL, 9.11 mmol) and stirred for 1 h at room temperature. A change of color from yellow to orange-red occurred. The solvent and unreacted phenylacetylene were evaporated in vacuo, and the remaining orange oil was characterized by IR and NMR spectroscopy. Owing to the relative intensities of the signals in the ^{1}H NMR spectrum (in C_6D_6), the product contained **43** (ca. 15%), **44** (ca. 50%), **45** (ca. 10%), **46** (ca. 20%), and traces of some unknown substances. Compounds **44** and **46** were identified by comparison of the NMR data with those in the literature.[25] After the orange oil was dissolved in hexane (2 mL) and the solution chromatographed on Al_2O_3 (basic, activity grade III, height of column 5 cm), an orange fraction was eluted, from which **43** (41 mg) and **44** (25 mg) were isolated by fractional crystallization from pentane. Data for **45**: IR (hexane): ν(C≡C) 2080, ν(η^2-C≡C) 1860 cm^{-1}. ^{31}P NMR (36.2 MHz, C_6D_6): δ 39.2 [d, J(Rh,P) = 121.6 Hz].

Preparation of *trans*-[Rh(C≡CPh){η^2-(*E*)-PhC≡*C*CH=CHPh}(P*i*Pr$_3$)$_2$] (43). A solution of **23** (133 mg, 0.24 mmol) in diethyl ether (5 mL) was treated with a solution of **44** (49 mg, 0.24 mmol) in diethyl ether (3 mL) and stirred for 30 min at room temperature. The solvent was evaporated in vacuo, the residue was extracted with pentane (25 mL), and the extract was brought to dryness in vacuo. The remaining orange solid was washed twice with pentane (2 mL each, 0 °C) and dried: yield 136 mg (78%); mp 108 °C dec. Anal. Calcd for $C_{42}H_{59}P_2Rh$: C, 69.22; H, 8.43. Found: C, 69.08; H, 8.43. IR (hexane): ν(C≡C) 2080, ν(η^2-C≡C) 1885 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 8.12, 7.50, 7.46 (all m, 6 H, *ortho*-H of C_6H_5), 7.41 [d, J(H,H) = 15.7 Hz, 1 H, CH=C*H*Ph], 7.23, 7.16, 7.14 (all m, 6 H, *meta*-H of C_6H_5), 7.11 [d, J(H,H) = 15.7 Hz, 1 H, C*H*=CHPh], 7.05, 7.04, 6.95 (all m, 3 H, *para*-H of C_6H_5), 2.40 (m, 6 H, PC*H*CH_3), 1.34, 1.24 [both dvt, N = 13.5, J(H,H) = 6.8 Hz, 18 H each, PCHCH_3]. ^{13}C NMR (100.6 MHz, C_6D_6): δ 138.2 (s, CH=CH−C_{ipso}), 135.6 (br s, CH=*C*HPh), 131.5 [d, J(Rh,C) = 0.7 Hz, *ortho*-C of RC≡CC_6H_5], 131.3 [d, J(Rh,C) = 1.1 Hz, η^2-C≡C−C_{ipso}], 129.8 [t, J(P,C) = 0.8 Hz, *ortho*-C of RhC≡CC_6H_5], 129.5 [dt, J(Rh,C) = 1.0, J(P,C) = 1.3 Hz, RhC≡C−C_{ipso}], 129.2, 128.5, 128.1, 127.7, 126.9, 126.3, 124.8 (all s, C_6H_5), 126.8 [dt, J(Rh,C) = 12.5, J(P,C) = 1.8 Hz, RhC≡*C*], 124.8 [dt, J(Rh,C) = 48.2, J(P,C) = 20.5 Hz, Rh*C*≡C], 117.3 (br s, *C*H=CHPh), 96.7 [dt, J(Rh,C) = 11.4, J(P,C) = 2.9 Hz, RC≡*C*Ph], 90.2 [dt, J(Rh,C) = 9.5, J(P,C) = 1.8 Hz, R*C*≡CPh], 24.9 (vt, N = 18.0 Hz, P*C*HCH$_3$], 21.1, 20.4 (both s, PCHCH_3). ^{31}P NMR (36.2 MHz, C_6D_6): δ 38.8 [d, J(Rh,P) = 123.1 Hz].

Reaction of the Mixture of Compounds 43 and 45 with CO. This reaction was carried out under the same conditions as described for the reaction of **39** with CO. The color changed from orange to pale yellow. The ^{1}H NMR spectrum confirmed the formation of the carbonyl complex **31** and of the isomeric butenynes **44** and **46**. The latter were identified by comparison of their NMR data with those reported in the literature.[25]

Catalytic Dimerization of Phenylacetylene. A solution of **1** (52 mg, 0.11 mmol) in hexane (9 mL) was treated with phenylacetylene (1.2 mL, 11.0 mmol) and 1 mL of benzene (as reference for GC) and stirred at 40 °C. After 4 h, GC measurements revealed that ca. 50% of the alkyne had been reacted. Besides small amounts of a brownish solid (possibly an oligomer or polymer of PhC≡CH) a red solution was formed, which, after it was cooled to room temperature, was brought to dryness in vacuo. Owing to the ^{1}H NMR spectrum, the oily residue consisted of a mixture of **44** and **46** in the ratio of 70:30.

To isolate the main component **44**, the procedure was as follows: The oily residue was dissolved in benzene (3 mL) and the solution was chromatographed on Al_2O_3 (neutral, activity

grade I, 15 × 5 cm columns). With hexane, a pale brown fraction was eluted containing butenyne **46** as the major species. Subsequent elution with dichloromethane gave a yellow fraction, from which the solvent was evaporated in vacuo. The residue was extracted with hexane (45 mL), the extract was brought to dryness in vacuo, and the residue (276 mg) was recrystallized from pentane at 0 °C. A pale yellow solid was obtained, which by comparison of the NMR data was identified as **44**.[25] Yield: 171 mg (ca. 30%, based on PhC≡CH).

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