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Unusual Pathways for Metal-Assisted C−C and C−P Coupling Reactions Using Allenylidenerhodium Complexes as Precursors

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Abstract: The rhodium allenylidenes *trans*-[RhCl{=C=C=C(Ph)R}(P*i*Pr$_3$)$_2$] [R = Ph (**1**), *p*-Tol (**2**)] react with NaC_5H_5 to give the half-sandwich type complexes [(η^5-C_5H_5)Rh{=C=C=C(Ph)R}(P*i*Pr$_3$)] (**3**, **4**). The reaction of **1** with the Grignard reagent CH_2=CHMgBr affords the η^3-pentatrienyl compound [Rh(η^3-*C*H$_2$*C*H*C*=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (**6**), which in the presence of CO rearranges to the η^1-pentatrienyl derivative *trans*-[Rh{η^1-C(CH=CH$_2$)=C=CPh$_2$}(CO)(P*i*Pr$_3$)$_2$] (**7**). Treatment of **7** with acetic acid generates the vinylallene CH_2=CH−CH=C=CPh$_2$ (**8**). Compounds **1** and **2** react with HCl to give the five-coordinate allenylrhodium(III) complexes [RhCl$_2$(CH=C=C(Ph)R}(P*i*Pr$_3$)$_2$] (**10**, **11**). An unusual [C_3 + C_2 + P] coupling process takes place upon treatment of **1** with terminal alkynes HC≡CR′, leading to the formation of the η^3-allylic compounds [RhCl{η^3-*anti*-*C*H(P*i*Pr$_3$)*C*(R′)*C*=C=CPh$_2$}(P*i*Pr$_3$)] [R′ = Ph (**12**), *p*-Tol (**13**), SiMe$_3$ (**14**)]. From **12** and RMgBr the corresponding phenyl and vinyl rhodium(I) derivatives **15** and **16** have been obtained. The previously unknown unsaturated ylide *i*Pr$_3$PCHC(Ph)=C=C=CPh$_2$ (**17**) was generated from **12** and CO. A [C_3 + P] coupling process occurs on treatment of the rhodium allenylidenes **1**, **2**, and *trans*-[RhCl{=C=C=C(*p*-Anis)$_2$}(P*i*Pr$_3$)$_2$] (**20**) with either Cl_2 or $PhICl_2$, affording the ylide−rhodium(III) complexes [RhCl$_3$C(P*i*Pr$_3$)C=C(R)R′}(P*i*Pr$_3$)] (**21**−**23**). The butatrienerhodium(I) compounds *trans*-[RhCl{η^2-H$_2$*C*=*C*=C=C(R)R′}(P*i*Pr$_3$)$_2$] (**28**−**31**) were prepared from **1**, **20**, and *trans*-[RhCl{=C=C=C(Ph)R}(P*i*Pr$_3$)$_2$] [R = CF_3 (**26**), *t*Bu (**27**)] and diazomethane; with the exception of **30** (R = CF_3, R′ = Ph), they thermally rearrange to the isomers *trans*-[RhCl{η^2-H$_2$C=*C*=*C*=C(R)R′}(P*i*Pr$_3$)$_2$] (**32, 33**, and *syn/anti*-**34**). The new 1,1-disubstituted butatriene H$_2$C=C=C=C(*t*Bu)Ph (**35**) was generated either from **31** or **34** and CO. The iodo derivatives *trans*-[RhI(η^2-H$_2$C=*C*=*C*=CR$_2$)(P*i*Pr$_3$)$_2$] [R = Ph (**38**), *p*-Anis (**39**)] were obtained by an unusual route from **1** or **20** and CH_3I in the presence of KI. While the hydrogenation of **1** and **26** leads to the allenerhodium(I) complexes *trans*-[RhCl{η^2-H$_2$*C*=*C*=C(Ph)R}(P*i*Pr$_3$)$_2$] (**40**, **41**), the thermolysis of **1** and **20** produces the rhodium(I) hexapentaenes *trans*-[RhCl(η^2-R$_2$C=*C*=*C*=C=C=CR$_2$)(P*i*Pr$_3$)$_2$] (**44**, **45**) via C−C coupling. The molecular structures of **3**, **7**, **12**, **21**, and **28** have been determined by X-ray crystallography. (Abbreviations used: *p*-Tol = *p*-tolyl, 4-$C_6H_4CH_3$; *p*-Anis = *p*-anisyl, 4-$C_6H_4OCH_3$.)

Introduction

In the context of our investigations on metallacumulenes of the general composition *trans*-[RhCl{=(C=)$_n$CRR′}(P*i*Pr$_3$)$_2$] (*n* = 1−4), we recently described the preparation of the corresponding rhodium allenylidenes *trans*-[RhCl(=C=C=CRR′)-(P*i*Pr$_3$)$_2$] using propargylic alcohols or propargylic chlorides as precursors for the coordinated C_3 unit.[1] After we found that the chloride in these complexes cannot only be replaced by other halides but also by pseudohalides such as OCN^-, SCN^-, N_3^- and even by hydroxide and related O-donor ligands,[2,3] we became interested to find out whether similar substitution reactions could occur with C-donors as well. From work in our laboratory we already knew that the related rhodium vinylidenes *trans*-[RhCl(=C=CHR)(P*i*Pr$_3$)$_2$] react with Grignard reagents R′MgX to give the substitution products *trans*-[Rh(R′)(=C=CHR}(P*i*Pr$_3$)$_2$], which for R′ = CH_3 and CH=CH$_2$ rearrange, even in the absence of a Lewis base, by intramolecular C−C coupling to yield η^3-allyl and η^3-butadienyl rhodium compounds.[4]

In this paper we report that the reactivity of the rhodium allenylidenes toward carbanions in some cases is analogous and in some cases different from that of the vinylidene counterparts.

(1) (a) Werner, H.; Rappert, T. *Chem. Ber*. **1993**, *126*, 669−678. (b) Werner, H.; Rappert, T.; Wiedemann, R.; Wolf, J.; Mahr, N. *Organometallics* **1994**, *13*, 2721−2727.
(2) (a) Werner, H.; Wiedemann, R.; Laubender, M.; Wolf, J.; Windmüller, B. *Chem. Commun*. **1996**, 1413−1414. (b) Werner, H.; Wiedemann, R.; Laubender, M.; Windmüller, B.; Wolf, J. *Chem. Eur. J*. **2001**, *7*, 1959−1967.
(3) (a) Laubender, M.; Werner, H. *Angew. Chem*. **1998**, *110*, 158−160; *Angew. Chem., Int. Ed. Engl*. **1998**, *37*, 150−152. (b) Laubender, M.; Werner, H. *Chem. Eur. J*. **1999**, *5*, 2937−2946.
(4) (a) Wiedemann, R.; Steinert, P.; Schäfer, M.; Werner, H. *J. Am. Chem. Soc*. **1993**, *115*, 9864−9865. (b) Wiedemann, R.; Wolf, J.; Werner, H. *Angew. Chem*. **1995**, *107*, 1359−1361; *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 1244−1246. (c) Werner, H.; Wiedemann, R.; Steinert, P.; Wolf, J. *Chem. Eur. J*. **1997**, *3*, 127−137.

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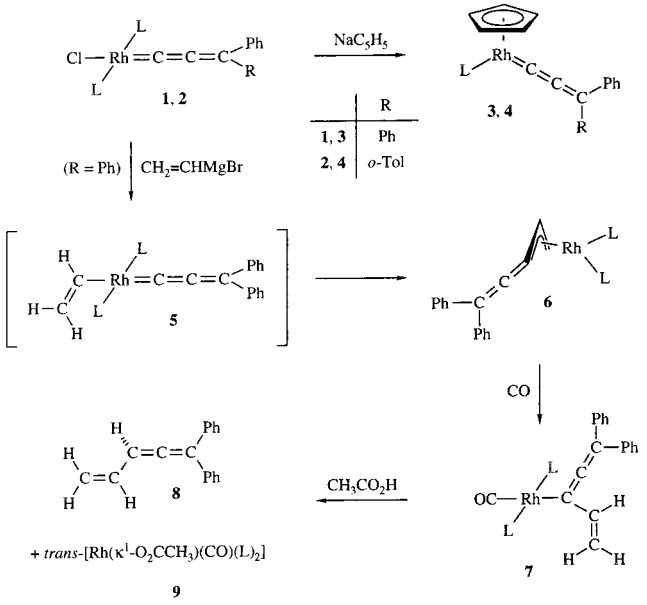
Moreover, we illustrate that the allenylidene ligand can be converted to allenes and, by two different pathways, also to 1,1-disubstituted butatrienes $CH_2{=}C{=}C{=}CRR'$, which because of their lability are otherwise hardly accessible. The most surprising result, however, is that the starting materials with a $Rh{=}C{=}C{=}CRR'$ chain undergo upon treatment with either 1-alkynes or phenyliodoniumdichloride an intramolecular C−P coupling reaction, thereby generating novel highly unsaturated phosphorus ylides unknown in the free state. Some results of these studies have already been communicated.[5]

Results and Discussion

Half-Sandwich-Type Allenylidenerhodium Complexes. To test the possibility of replacing the chloro ligand in compounds of the general composition *trans*-[RhCl(=C=C=CRR′}($PiPr_3$)$_2$] by carbanions, first the reactivity of **1** and **2** toward sodium cyclopentadienide was investigated. Both starting materials, if mixed with *solid* NaC_5H_5 and treated dropwise with THF, react at room temperature to give the half-sandwich-type complexes **3** and **4** in good yield (Scheme 1). They were isolated as green

Scheme 1. (L = P*i*Pr$_3$)



solids that are only moderately air-sensitive and readily soluble in most common organic solvents. The ^{13}C NMR spectra of **3** and **4** display three characteristic signals in the low-field region at about δ 228, 205−210, and 122 that, based on the different $^{103}Rh-^{13}C$ and $^{31}P-^{13}C$ coupling constants, are assigned to the α-, β-, and γ-carbon atoms of the allenylidene chain. The ^1H NMR spectrum of **3** exhibits only one set of resonances for the protons of the two phenyl groups, indicating that on the NMR time scale (in solution at room temperature) the rotation around the $Rh-C_{allenylidene}$ bond is not significantly hindered. It should be mentioned that the vinylidene analogues of **3** and **4** of the general composition [(η^5-C_5H_5)Rh(=C=CHR)(P*i*Pr$_3$)] were also prepared in our laboratory but by a different route.[6]

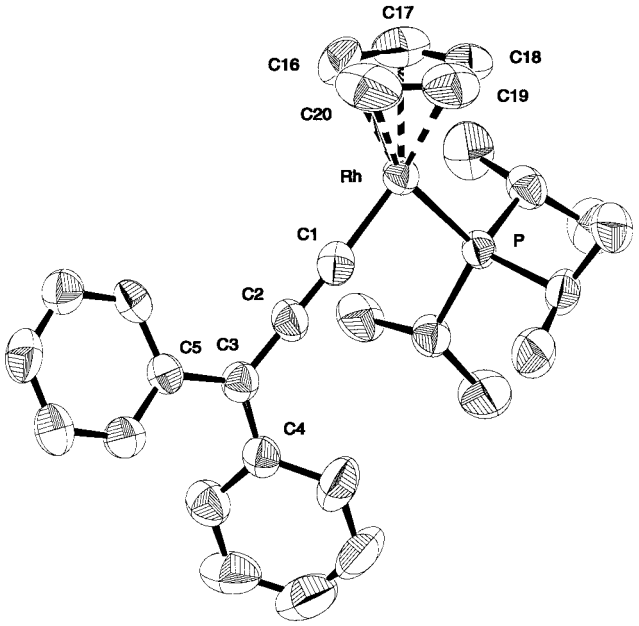


Figure 1. Molecular diagram of compound **3**. Selected bond distances (Å) and angles (deg): Rh−P, 2.2700(15); Rh−C1, 1.880(6); Rh−C16, 2.237-(6); Rh−C17, 2.253(7); Rh−C18, 2.242(6); Rh−C19, 2.231(7); Rh−C20, 2.198(7); C1−C2, 1.255(7); C2−C3, 1.350(7); C3−C4, 1.466(8); C3−C5, 1.465(7); P−Rh−C1, 89.48(17); Rh−C1−C2, 177.1(5); C1−C2−C3, 176.5(6); C2−C3−C4, 119.3(5); C2−C3−C5, 120.2(5); C4−C3−C5, 120.5(5).

The molecular structure of compound **3** is shown in Figure 1. The molecule possesses the expected two-legged piano-stool configuration with a Rh−C1 bond length of 1.880(6) Å, which is slightly longer (ca. 0.03 Å) compared to the square-planar complex **2**.[1b] It is almost identical to the bond length in the structurally related cyclopentadienylosmium(II) compound [(η^5-C_5H_5)OsCl(=C=C=CPh$_2$)(P*i*Pr$_3$)].[7] The two carbon−carbon distances in the RhC_3 chain differ by 0.10 Å, which suggests that besides the usual bond description Rh=C=C=C a second zwitterionic resonance structure has to be taken into consideration.[8] The Rh=C=C=C moiety is nearly linear, while the bond angles around the γ-carbon atom C3 are, as expected, about 120°.

Coupling of an Allenylidene and a Vinyl Group. Following the protocol for the preparation of the vinylidene complexes *trans*-[Rh(R′)(=C=CHR)(P*i*Pr$_3$)$_2$] (R′ = CH_3, $CH{=}CH_2$, C≡CPh, C_6H_4R),[4] the allenylidene compound **1** was treated under the same conditions with the corresponding Grignard reagent R′MgBr. However, in all cases, with the exception of R′ = $CH{=}CH_2$, a mixture of products was obtained that could not be separated by fractional crystallization or chromatographic techniques.

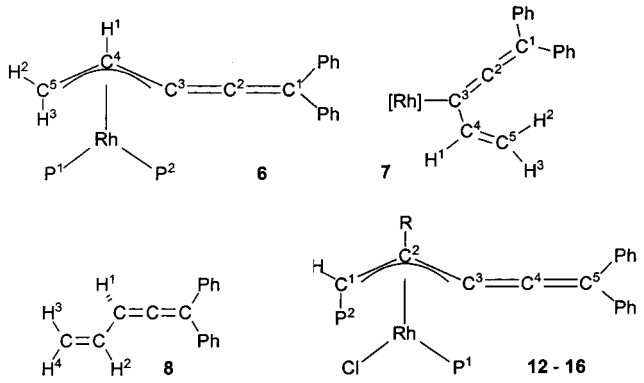
The attempt to prepare the vinylrhodium(I) derivative *trans*-[Rh($CH{=}CH_2$)(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] led to a surprising result. Treatment of the starting material **1** with $CH_2{=}CHMgBr$ in toluene/THF at −40 °C resulted not only in the substitution of chloride by the C-nucleophile but also by coupling of the vinyl and the allenylidene units to form a η^3-pentatrienyl ligand

(5) Wiedemann, R.; Steinert, P.; Gevert, O.; Werner, H. *J. Am. Chem. Soc*. **1996**, *118*, 2495−2496.
(6) (a) Wolf, J.; Werner, H.; Serhadli, O.; Ziegler, M. L. *Angew. Chem*. **1983**, *95*, 428−429; *Angew. Chem., Int. Ed. Engl*. **1983**, *22*, 414−415. (b) Werner, H.; Wolf, J.; Garcia Alonso, F. J.; Ziegler, M. L.; Serhadli, O. *J. Organomet. Chem*. **1987**, *336*, 397−411.
(7) Crochet, P.; Esteruelas, M. A.; López, A.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1998**, *17*, 3479−3486.
(8) (a) Bruce, M. I. *Chem. Rev*. **1991**, *91*, 197−257. (b) Le Bozec, H.; Dixneuf, P. H. *Russ. Chem. Bull*. **1995**, *44*, 801−812. (c) Werner, H. *Chem. Commun*. **1997**, 903−910. (d) Bruce, M. I. *Chem. Rev*. **1998**, *98*, 2797−2858. (e) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Eur. J. Inorg. Chem*. **2001**, 571−591.

(see Scheme 1). The ^{1}H spectrum of **6** displays three well-separated signals for the protons H^1, H^2 and H^3 of the π-bonded allylic unit at δ 4.79, 3.01, and 2.45, respectively. In agreement with previous data,[4,9] the resonance for the syn proton H^2 reveals a considerably smaller ^{31}P−^{1}H coupling constant (almost zero) than that of the anti proton H^3 (5.8 Hz). In the ^{13}C NMR spectrum of **6**, a significant difference in chemical shift for the signals of carbon atoms C^3 and C^5 is observed, indicating that the allylic fragment of the pentatrienyl ligand is unsymmetrically coordinated to the metal center. With regard to the mechanism of formation of **6**, we assume that initially the anticipated four-coordinate species **5** is generated that rapidly rearranges by migratory insertion to give the final product. The reason for the increased lability of **5** compared with the vinylidene counterparts *trans*-[Rh(CH═CH$_2$)(═C═CHR)(P*i*Pr$_3$)$_2$] (R = *t*Bu, Ph)[4] could be that the allenylidene is a weaker π-acceptor ligand than the related vinylidene and therefore less suitable to stabilize the bond between the metal and the *trans*-disposed vinyl group.[6,10] We note that upon treatment of [(η^5-C$_5$Me$_5$)RuCl(═C═C═CPh$_2$)(κ^1-P*i*Pr$_2$CH$_2$CO$_2$Me)] with CH$_2$═CHMgBr also a η^3-pentatrienyl complex is formed, and again in this case no M−CH═CH$_2$ intermediate could be detected spectroscopically.[11]

The reaction of **6** with CO in benzene at 10 °C leads instantaneously to a change of color from red to light yellow and finally to the isolation of yellow, moderately air-sensitive crystals of the carbonylrhodium(I) compound **7** in 65% yield (see Scheme 1). The addition of CO to the metal center is accompanied by a $\pi-\sigma$ conversion of the C$_5$ unit, possibly via an 18-electron intermediate [Rh(η^3-*C*H$_2$*C*H*C*═C═CPh$_2$)(CO)(P*i*Pr$_3$)$_2$]. The change in hapticity of the pentatrienyl ligand is clearly indicated by the ^{1}H NMR spectrum of **7**, which exhibits the resonances for the vinyl protons H^1, H^2, and H^3 at significantly lower field (δ 6.84, 5.97, and 5.11) compared to **6**. The ^{13}C NMR spectrum of **7** displays five signals for the carbon atoms C^1 to C^5 (see Chart 1), of which only that for the metal-bonded atom C^3 shows a ^{31}P−^{13}C and a ^{103}Rh−^{13}C coupling.

Chart 1. Assignment of Protons, Carbon, and Phosphorus Atoms of Ligands in Compounds **6**−**8** and **12**−**16**

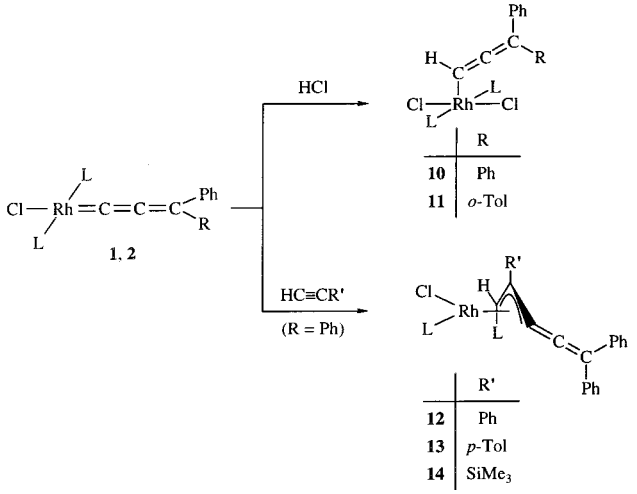


The proposed stereochemistry of **7** was substantiated by a single-crystal X-ray structural analysis (for a molecular diagram see ref 5). The rhodium is coordinated in a slightly distorted square-planar fashion with the two phosphine ligands in a trans disposition. The allene-like C═C═C chain is linear (177.5(5)°), with the two vinylic carbon atoms lying in the same plane. The plane containing the C$_3$ carbons and the ipso-carbon atoms of the phenyl groups is nearly perpendicular to the plane containing the metal and the vinylic carbon atoms, the dihedral angle being 95.5(2)°. The two C−C distances of the linear C$_3$ chain differ only slightly, which is in agreement with structural data for other transition-metal compounds containing η^1-allenyl ligands.[12]

The cleavage of the Rh−C σ-bond in **7** by an equimolar amount of acetic acid in benzene proceeds smoothly and gives, besides the acetatorhodium(I) complex **9**,[13] selectively the new vinylallene **8** (see Scheme 1). A characteristic feature of the ^{13}C NMR spectrum of **8** is the low-field signal at δ 210.2 for the central C═*C*═C carbon atom, the position of which is typical for organic allenes.[14]

Reactions of Rhodium Allenylidenes with HCl and Terminal Alkynes. In contrast to the iridium(I) compounds *trans*-[IrCl{═C═C═C(Ph)R}(P*i*Pr$_3$)$_2$] (R = *t*Bu, Ph), which react with HCl by oxidative addition to give the octahedral hydridoiridium(III) derivatives *trans*-[IrHCl$_2${═C═C═C(Ph)R}(P*i*Pr$_3$)$_2$],[15] treatment of the rhodium(I) precursors **1** and **2** with an equimolar amount of HCl in benzene affords the five-coordinate allenyl complexes **10** and **11** in nearly quantitative yields (Scheme 2). Typical spectroscopic data of **10** and **11** are

Scheme 2. (L = P*i*Pr$_3$)



the C═C═C stretching frequency in the IR spectra at about 1880 cm^{-1}, the doublet-of-triplet resonance for the RhCH proton in the ^{1}H NMR spectra at δ 7.44 (**10**) or 7.85 (**11**), and the three signals for the α-, β-, and γ-allenyl carbon atoms in the ^{13}C NMR spectra at about δ 69, 114, and 200, respectively. Although the spectroscopic data of **10** and **11** cannot show whether the configuration around the metal center corresponds to a square pyramid or a trigonal bipyramid, we assume, in

(9) (a) Vrieze, K.; Volger, H. C.; van Leeuwen, P. W. N. M. *Inorg. Chim. Acta Rev.* **1969**, 109−129. (b) Hughes, R. P. in *Comprehensive Organometallic Chemistry*, Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; 1st ed., Pergamon: Oxford, 1982; Vol. 5, p 492−540.
(10) (a) Antonova, A. B.; Ioganson, A. A. *Russ. Chem. Rev.* **1989**, *58*, 693−710. (b) Kovacik, I.; Gevert, O.; Werner, H.; Schmittel, M.; Söllner, R. *Inorg. Chim. Acta* **1998**, *275*−*276*, 435−439.
(11) Braun, T.; Meuer, P.; Werner, H. *Organometallics* **1996**, *15*, 4075−4077.
(12) (a) Huang, T.-M.; Hsu, R.-H.; Yang, C.-S.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *Organometallics* **1994**, *13*, 3657−3663. (b) Wouters, J. M. A.; Klein, R. A.; Elsevier: C. J.; Häming, L.; Stam, C. H. *Organometallics* **1994**, *13*, 4586−4593. (c) Werner, H.; Flügel, R.; Windmüller, B.; Michenfelder, A.; Wolf, J. *Organometallics* **1995**, *14*, 612−618.
(13) (a) Ohgomori, Y.; Yoshida, S.; Watanabe, Y. *J. Chem. Soc., Dalton Trans.* **1987**, 2969−2974. (b) Schäfer, M.; Wolf, J.; Werner, H. *J. Organomet. Chem.* **1995**, *476*, 85−91.
(14) Munson, J. W. *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; Wiley: New York, 1980; Vol. 1, Chapter 5.
(15) Ilg, K.; Werner, H. *Chem. Eur. J.* **2001**, *7*, 4633−4639.

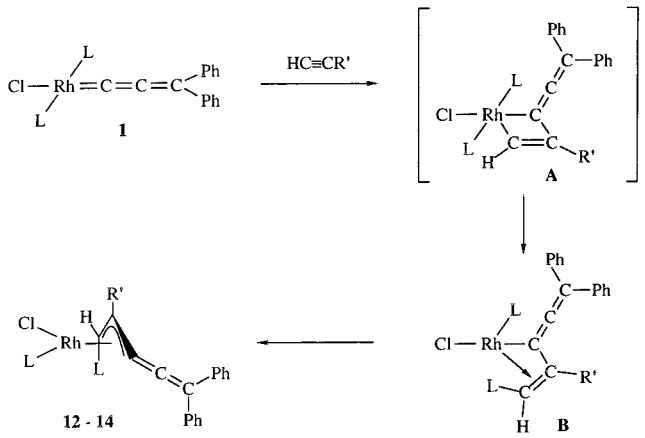
analogy to $[RhHCl_2(PiPr_3)_2]$,[16] that a square pyramidal geometry is preferred. We note that the ^1H NMR spectrum of **11** displays two signals (with a small difference in chemical shift) for the protons of the diastereotopic methyl groups of the isopropyl units, which is in agreement with the chirality of the molecule.

The reaction of the starting material **1** with the weakly acidic terminal alkynes HC≡CR′ (R′ = Ph, *p*-Tol, $SiMe_3$) proceeds by an unusual route. If a solution of **1** and the alkyne in benzene was stirred for 20 h (R′ = Ph, *p*-Tol) or 14 days (R′ = $SiMe_3$) at 10 °C, a gradual change of color from red to bright red occurred and, after removal of the solvent, the rhodium(I) complexes **12**−**14** were isolated in good to excellent yields. Both the elemental analyses as well as the mass spectrum of **12** confirmed that formally 1:1 adducts of **1** and the alkyne were formed that according to the ^{31}P NMR spectra contained two distinctly different $PiPr_3$ groups. The two ^{31}P NMR signals at about δ 48−53 and 38−40, corresponding to the AM part of an AMX pattern, show $^{103}Rh-^{31}P$ coupling constants of ca. 180 and 4 Hz, which indicates that only one of the phosphines is coordinated to the rhodium. The nonequivalence of the $PiPr_3$ units is also reflected in the ^1H NMR spectra of **12**−**14** in which four different resonances for the $PCHCH_3$ protons are observed.

The X-ray crystal structure analysis of **12** (for a molecular diagram see ref 5) confirmed that indeed only one of the phosphines is coordinated to the metal center while the other is part of a π-bonded unsaturated ylide. This novel ylide is built up from the allenylidene, the alkyne, and one $PiPr_3$ group. The PC_5 ligand is coordinated like a π-allyl unit, similarly to the C_5 moiety in compound **6**. The unsymmetric coordination is illustrated by the three Rh−C bond lengths, which differ by ca. 0.15 Å. Since the distance between rhodium and the C-bonded phosphorus atom is 3.367(1) Å, a direct interaction between these two atoms can be excluded. The P−C bond of the PC_5 ligand is significantly shorter than a P−C single bond but quite similar to that of $[RhCl\{\eta^3\text{-}anti\text{-}CH(PiPr_3)C(Ph)=O\}(PiPr_3)]$ (1.799(4) Å)[17] and of metal-substituted ylides.[18] Both the C−C distances and the C−C−C bond angle of the π-allylic moiety are nearly identical to those of the π-benzyl complex $[Rh(\eta^3\text{-}CH_2C_6H_5)(PiPr_3)_2]$ that was prepared from the dimer **24** (see Scheme 6) and $C_6H_5CH_2MgCl$.[19]

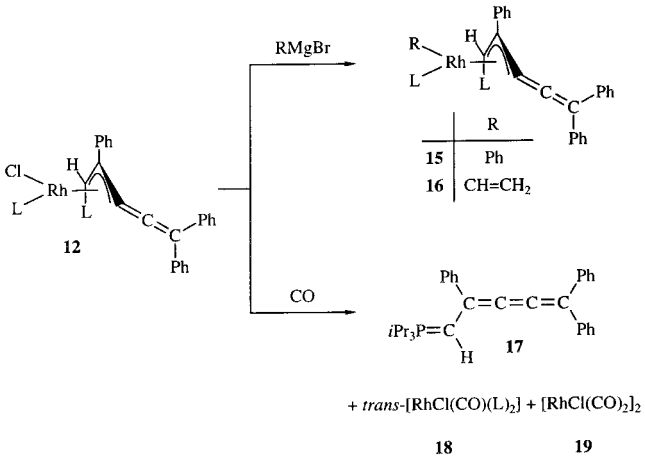
The proposed mechanism for the formation of compounds **12**−**14** is outlined in Scheme 3. We assume that in the initial step of the reaction a [2 + 2]-cycloaddition of the alkyne to the Rh=C bond of the RhC_3 chain to give intermediate **A** takes place, which is followed by a migration of one phosphine ligand from the metal to the RhCH carbon atom. Although the postulated intermediate **B** (like the product) is a 16-electron rhodium(I) species, the π-allylic isomer seems to be energetically preferred. We note that, to the best of our knowledge, there is no precedence for the metal-assisted C−C−P coupling process leading to the ligand system found in complexes **12**−**14**.

Scheme 3. (L = P*i*Pr$_3$)



Like in the rhodium vinylidenes *trans*-$[RhCl(=C=CHR)(PiPr_3)_2]$, the chloro ligand of **12** can easily be displaced by a phenyl or a vinyl group. Treatment of **12** with C_6H_5MgBr or $CH_2=CHMgBr$ in benzene/ether or benzene/THF results in the formation of the substitution products **15** and **16** (Scheme 4),

Scheme 4. (L = P*i*Pr$_3$)



which are isolated as black solids in 65−70% yield. As far as the π-bonded allylic ligand $anti\text{-}CH(PiPr_3)C(Ph)=C=C=CPh_2$ is concerned, the ^1H, ^{13}C, and ^{31}P NMR data of **15** and **16** are quite similar to those of **12** and thus deserve no further comment.

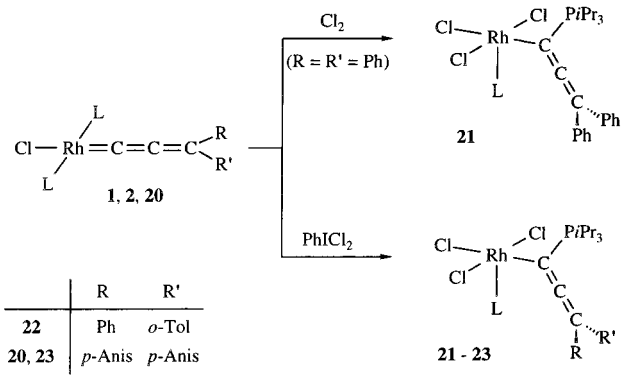
The free ylide **17**, the preparation of which as far as we know has not been reported as yet, can be generated on treatment of **12** with CO in benzene at 10 °C. The rhodium-containing products are **18**[20] and the well-known dimer **19**.[21] Ylide **17** was isolated upon extraction of the product mixture with pentane as a violet solid and characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopic data. The influence of the butatrienyl substituent on the electronic properties of the ylide carbon is reflected by the signal of the P=CH proton, which appears at δ 3.05 and is shifted ca. 4 ppm downfield compared with the $P=CH_2$ resonance of iPr_3PCH_2.[22]

Generation of Phosphacumulenes via Oxidatively Induced C−P Coupling. The reaction of the starting material **1** with

(16) Harlow, R. L.; Thorn, D. L.; Baker, R. T.; Jones, N. L. *Inorg. Chem.* **1992**, *31*, 993−997.
(17) Werner, H.; Mahr, N.; Frenking, G.; Jonas, V. *Organometallics* **1995**, *14*, 619−625.
(18) Inter alia: (a) Fachin, G.; Bertani, R.; Zanotto, L.; Galligaris, M.; Nardin, G. *J. Organomet. Chem.* **1989**, *366*, 409−420. (b) Werner, H.; Schippel, O.; Wolf, J.; Schulz, M. *J. Organomet. Chem.* **1991**, *417*, 149−162.
(19) Werner, H.; Schäfer, M.; Nürnberg, O.; Wolf, J. *Chem. Ber.* **1994**, *127*, 27−38.
(20) (a) Busetto, C.; D'Alfonso, A.; Maspero, F.; Perego, G.; Zazzetta, A. *J. Chem. Soc., Dalton Trans.* **1977**, 1828−1834. (b) Wang, K.; Rosini, G. P.; Nolan, S. P.; Goldman, A. S. *J. Am. Chem. Soc.* **1995**, *117*, 5082−5088.
(21) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1968**, *8*, 211−214.
(22) Köster, R.; Simic, D.; Grassberger, M. A. *Justus Liebigs Ann. Chem.* **1970**, *739*, 211−219.

chlorine in the molar ratio of 1:1 in THF/hexane under the exclusion of light proceeds by oxidative addition but does not give, in contrast to the analogous reactions of the carbonyl complexes *trans*-[RhCl(CO)(PR_3)$_2$] (PR_3 = PMe_3, PEt_3, P*n*Bu_3, PEt_2Ph, PPh_3) with Cl_2,[23] the expected trichlororhodium(III) compound [$RhCl_3$(=C=C=CPh_2)(P*i*Pr_3)$_2$]. The five-coordinate complex **21** is formed instead, which is equally obtained upon treatment of **1** with $PhICl_2$ in dichloromethane at −60 °C. By both routes the yield of **21**, being a red air-sensitive solid, is virtually quantitative (Scheme 5). The preparation of **22** and

Scheme 5. (L = P*i*Pr_3)



23 from **2** and **20** as precursors and $PhICl_2$ as the oxidizing reagent occurs analogously. The ^{1}H, ^{13}C, and ^{31}P NMR spectra of **21**−**23** display two completely different sets of signals for the hydrogen, carbon, and phosphorus atoms of the P*i*Pr_3 groups and, since only one of the ^{31}P NMR resonances shows a strong ^{103}Rh−^{31}P coupling, indicate that one of the phosphines is not linked to rhodium. The most typical feature of the ^{13}C NMR spectra of **21**−**23** is the resonance at δ 75−76 for the metal-bonded carbon of the phosphacumulene,[24] which is split into a doublet-of-doublet-of-doublets, due to coupling with rhodium and two different phosphorus atoms.

The proposed structure of **21** has been confirmed by an X-ray crystal structure analysis. The molecular diagram (Figure 2) reveals a square-pyramidal geometry around the metal center with the coordinated triisopropylphosphine in the apical position. The rhodium atom is situated somewhat above the basal plane manifested by the bending of the C1−Rh−Cl1 (165.43(1)°) and Cl2−Rh−Cl3 (165.47(4)°) axes. The bond length Rh−C1 is nearly identical to that in *trans*-[Rh{η^1-C(CH=CH_2)=CHPh}-(CO)(P*i*Pr_3)$_2$] (2.088(5) Å)[4] and *trans*-[Rh{η^1-C(C≡CCO_2Me)=$CHCO_2$Me}(CO)(P*i*Pr_3)$_2$] (2.099(4) Å)[25] but slightly shorter than in the η^1-pentatrienyl complex **7**. As expected, the C1−C2−C3 chain is linear (178.3(4)°), whereas the sum of the bond angles around C1 is almost exactly 360°. The two planes containing the substituents at C^1 (Rh and P2) and C^3 (ipso-carbons of C_6H_5) are orthogonal to each other (the dihedral angle being 89.7(2)°), in agreement with the allene-type structure of the molecule. Phosphacumulene ligands related to that found in **21** are known from [(η^5-C_5H_5)Mn{C(PPh_3)=C=CPh_2}(CO)$_2$] and

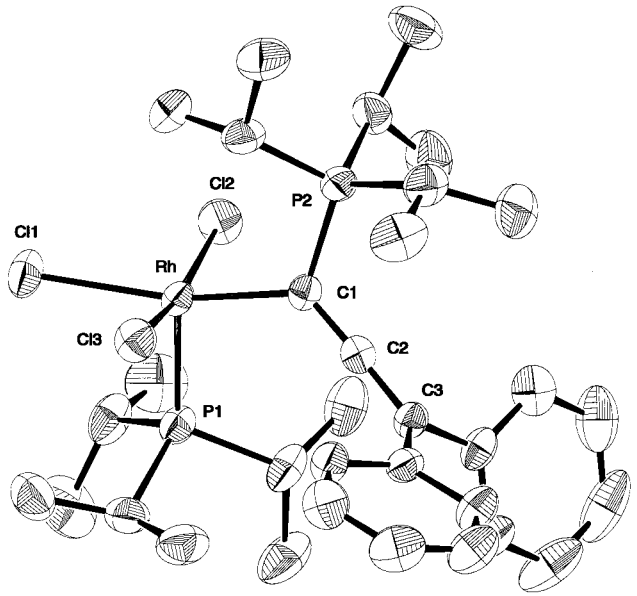


Figure 2. Molecular diagram of compound **21**. Selected bond distances (Å) and angles (deg): Rh−C1, 2.089(3); Rh−P1, 2.251(1); Rh−Cl1, 2.425-(1); Rh−Cl2, 2.321(1); Rh−Cl3, 2.339(1); C1−C2, 1.297(5); C2−C3, 1.328(5); C1−P2, 1.817(3); C1−Rh−P1, 102.73(8); C1−Rh−Cl1, 165.44-(8); C1−Rh−Cl2, 90.98(8); C1−Rh−Cl3, 86.08(8); P1−Rh−Cl1, 91.74-(4); P1−Rh−Cl2, 90.65(5); P1−Rh−Cl3, 103.88(4); Cl1−Rh−Cl2, 90.47-(4); Cl1−Rh−Cl3, 88.90(4); Cl2−Rh−Cl3, 165.47(3); Rh−C1−P2, 114.3(1); Rh−C1−C2, 130.1(2); P2−C1−C2, 114.7(3); C1−C2−C3, 178.2(3).

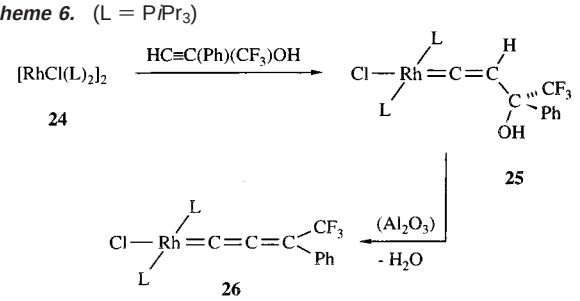
[Cr{C(PPh_3)=C=C*i*Pr_2}(CO)$_5$], but in these cases they have been generated by attack of free triphenylphosphine on allenylidene complexes.[26]

The mechanism of formation of **21**−**23** seems to be straightforward. We assume that the initial step of the reaction consists of the anticipated oxidative addition of chlorine at rhodium to form the six-coordinate species [$RhCl_3$(=C=C=CPh_2)(P*i*Pr_3)$_2$]. In this intermediate, the steric crowding around the metal center caused by the three chlorides and in particular by the two bulky phosphine ligands leads to a 1,2-shift of one P*i*Pr_3 group from the metal to the α-carbon of the allenylidene, yielding a molecule in which the two P*i*Pr_3 units are farther apart than in the intermediate. In this context we note that while the rhodium-(II) compound *trans*-[$RhCl_2$(P*i*Pr_3)$_2$] is known,[16,27] our attempts to prepare a rhodium(III) complex of the composition [$RhCl_3$-(P*i*Pr_3)$_2$] remained unsuccessful.

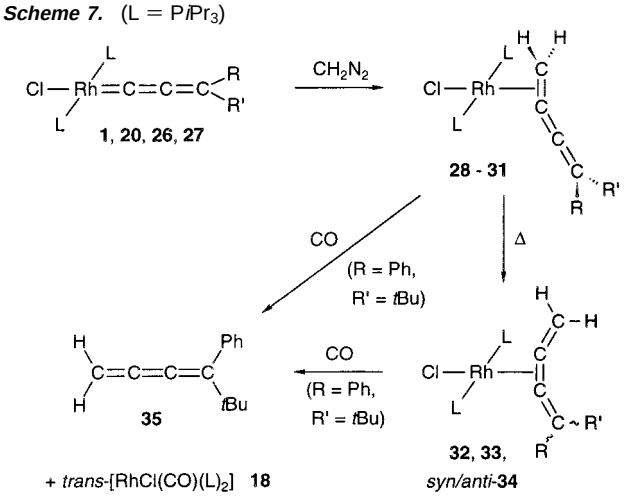
Rhodium Complexes with 1,1-Disubstituted Butatrienes as Ligands. After we found that the vinylidene compounds [(η^5-C_5H_5)Rh(=C=CHR)(P*i*Pr_3)] react with diazomethane to form the allene complexes [(η^5-C_5H_5)Rh(η^2-CH_2=*C*=CHR)(P*i*Pr_3)] (R = H, Me, Ph),[28] we became interested to find out whether a similar C−C coupling process would take place upon treatment of the allenylidene rhodium derivatives *trans*-[RhCl(=C=C=CRR′)(P*i*Pr_3)$_2$] with CH_2N_2. In addition to **1**, **20**, and **27** (see Scheme 7), we also prepared the new precursor **26** having, in contrast to the structurally related starting materials, a strong electron-withdrawing substituent at the terminal carbon of the allenylidene unit.

(23) (a) Heck, R. F. *J. Am. Chem. Soc*. **1964**, *86*, 2796−2799. (b) Chatt, J.; Shaw, B. L. *J. Chem. Soc. A* **1966**, 1537−1542. (c) Browning, J.; Goggin, P. L.; Goodfellow, R. J.; Norton, M. G.; Rattray, A. J. M.; Taylor, B. F.; Mink, J. *J. Chem. Soc., Dalton Trans*. **1977**, 2061−2067.
(24) For a review on phosphacumulenes: Bestmann, H. J. *Angew. Chem*. **1977**, *89*, 361−376; *Angew. Chem., Int. Ed. Engl*. **1977**, *16*, 349−367.
(25) Schäfer, M.; Mahr, N.; Wolf, J.; Werner, H. *Angew. Chem*. **1993**, *105*, 1377−1379; *Angew. Chem., Int. Ed. Engl*. **1993**, *32*, 1315−1318.
(26) (a) Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Khitrova, O. M.; Batsanov, A. S.; Struchkov, Y. T. *J. Organomet. Chem*. **1984**, *265*, 271−281. (b) Berke, H.; Härter, P.; Huttner, G., Zsolnai, L. *Z. Naturforsch. B* **1981**, *36*, 929−937.
(27) Rappert, T.; Wolf, J.; Schulz, M.; Werner, H. *Chem. Ber*. **1992**, *125*, 839−841.
(28) Wolf, J.; Zolk, R.; Schubert, U.; Werner, H. *J. Organomet. Chem*. **1988**, *340*, 161−178.

Scheme 6. (L = P*i*Pr$_3$)



Scheme 7. (L = P*i*Pr$_3$)



	R	R'
28, 32	Ph	Ph
29, 33	*p*-Anis	*p*-Anis
30	Ph	CF_3
27, 31, 34	Ph	*t*Bu

The synthetic procedure to obtain **26** is shown in Scheme 6. Treatment of the dimer **24**[29] with the alkynol in ether in the presence of NEt_3 led in the first step to the formation of the vinylidene compound **25**, which after column chromatography (with *neutral* Al_2O_3) was isolated as a blue solid in 91% yield. Although we assume that the π-alkyne complex *trans*-[RhCl-{η^2-HC≡CC(Ph)(CF$_3$)OH}(P*i*Pr$_3$)$_2$] is initially formed,[1] this intermediate is probably very labile and rearranges rapidly to the vinylidene isomer. The conversion of **25** to the rhodium allenylidene **26** occurs by passing a solution of the vinylidene compound in benzene through a column filled with *acidic* Al_2O_3. During this procedure a change of color from blue to yellow-green takes place and, if chromatography is continued, the product **26** is eluted in virtually quantitative yield. The IR and NMR spectroscopic data of **26** are similar to those of **27**[3] and deserve no further comment.

The reactions of **1**, **20**, **26**, and **27** with excess diazomethane in benzene at room temperature are completed within a few minutes. After removal of the solvent and recrystallization from pentane, the coupling products **28**−**31** were isolated as red or orange solids, only moderately sensitive to air and water, in 91−96% yield. The proposed structure (see Scheme 7) is particularly supported by the ^{13}C NMR spectra, which display four signals between δ 184 and 12 for the carbon nuclei of the butatriene ligand. Two of these signals show a relatively large ^{103}Rh−^{13}C coupling and are therefore assigned to the two carbon atoms of the C$_4$ unit bonded to the metal. The chemical shift of the *C*H$_2$ resonance of **28** at δ 13.0 as well as the ^1J(CH) coupling constant of 161.4 Hz indicates the predominant sp^3 character of this C atom, which implies that the bonding between rhodium and the C═CH$_2$ fragment of the butatriene is related to that of a metallacyclopropane. Since the ^{1}H NMR spectra of **28** and **29** exhibit two signals and the spectrum of **30** four signals for the PCHC*H*$_3$ protons, we assume that in contrast to *trans*-[Rh(C≡CMe)(η^2-*C*H$_2$═*C*═CH$_2$)(P*i*Pr$_3$)$_2$][30] the rotation of the butatriene ligand around the rhodium−olefin bond in **28**−**30** is slow on the NMR time scale.

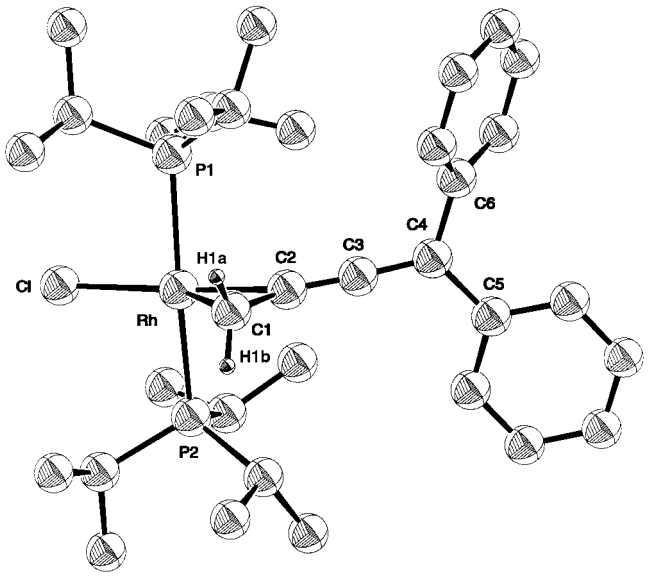


Figure 3. Molecular diagram of compound **28**. Selected bond distances (Å) and angles (deg): Rh−P1, 2.365(1); Rh−P2, 2.355(1); Rh−Cl, 2.349-(1); Rh−C1, 2.060(2); Rh−C2, 2.063(2); C1−C2, 1.408(3); C2−C3, 1.272-(3); C3−C4, 1.335(3); P1−Rh−P2, 166.45(2); P1−Rh−Cl, 88.16(3); P1−Rh−C1, 96.70(7); P1−Rh−C2, 90.56(6); P2−Rh−Cl, 87.42(2); P2−Rh−C1, 94.35(7); P2−Rh−C2, 92.89(6); Cl−Rh−C1, 144.36(7); Cl−Rh−C2, 175.65(6); C1−Rh−C2, 39.96(9); Rh−C1−C2, 70.1(1); Rh−C2−C1, 69.9-(1); C1−C2−C3, 144.7(2); C2−C3−C4, 174.8(2).

With regard to the formation of the coordinated C$_4$ cumulene from the rhodium allenylidenes and CH_2N_2, it is conceivable that the attack of the nucleophilic diazomethane occurs either at the metal or the α-carbon atom of the RhC$_3$ chain. In the course of their studies on the reactivity of carbene tungsten and rhenium complexes toward RCHN$_2$, both Casey[31] and Gladysz[32] supposed that the first step in these reactions consists of an attack of the C-nucleophile at the carbene carbon, generating an olefin. Although these authors as well as we have no evidence for an initial C−C interaction, theoretical work seems to be in favor of this proposal.[33]

The X-ray crystal structure analysis of **28** (Figure 3) confirmed a distorted square-planar coordination around the metal center with the Cl, Rh, and C1−C4 atoms lying in one plane. Although the C═CH$_2$ unit is bonded unsymmetrically

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

(30) Schäfer, M. Ph.D. Thesis, Universität Würzburg, **1994**.
(31) Casey, C. P.; Bertz, S. H.; Burkardt, T. J. *Tetrahedron Lett.* **1973**, *12*, 1421−1424.
(32) Wang, Y.; Gladysz, J. A. *Chem. Ber.* **1995**, *128*, 213−220.
(33) (a) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585−591. (b) Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974−982. (c) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Modrego, J.; Onate, E. *Organometallics* **1997**, *16*, 5826−5835.

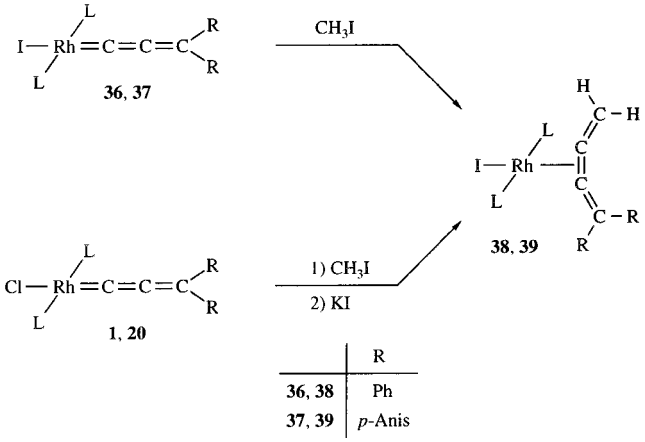
to rhodium, as is shown by the linearity of the Cl−Rh−C2 axis (175.65(6)°), the distances Rh−C1 and Rh−C2 are nearly identical. This is in contrast to the structurally similar compound *trans*-[RhCl(η^2-*C*H_2═*C*═CHCO$_2$Et)(P*i*Pr$_3$)$_2$], in which the Rh−C1 and Rh−C2 bond lengths are 2.120(5) and 1.991(5) Å.[34] The P1−Rh−P2 axis is somewhat bent (166.45(2)°) and directed toward the chloride, which is probably due to the steric requirements of the isopropyl and phenyl groups.

The butatrienerhodium(I) compounds **28**, **29**, and **31** are thermally labile and upon heating in toluene at 80−95 °C rearrange to the thermodynamically more stable complexes **32**−**34** (see Scheme 7). The isomerization can easily be followed by a change of color from red to yellow. In the case of **34**, a mixture of two isomers is formed that differ in the relative position of the phenyl and *tert*-butyl groups to the metal center. If the rearrangement of **31** is monitored by ^{31}P NMR spectroscopy, a ratio *syn*-**34**:*anti*-**34** of 2:1 is observed initially. After 6 h in toluene at 95 °C, the ratio changes to 10:1. However, even after stirring for 12 h, a complete conversion of *anti*-**34** to *syn*-**34** does not occur. Nevertheless, compound *syn*-**34** has been isolated analytically pure upon fractional crystallization from acetone and, by comparison of the ^{1}H NMR data with those of *anti*-**34**, identified as the isomer in which the phenyl group at C^4 is directed toward the metal. The assignment of the resonances for the H_{endo} and H_{exo} protons at C^1 follows from the work of Gladysz et al., who assigned the signals of the CH_2 protons of the allene complex [(η^5-C_5H_5)Re(η^2-CH_2═C═CH_2)-(NO)(PPh_3)]BF_4 on the basis of NOE measurements.[35] Owing to the presence of an unsymmetrical butatriene, the ^{13}C NMR spectra of **32**, **33**, and *cis*-**34** display four resonances in the region between δ 144 and 97 for the carbon atoms of the C_4 chain. Two of these signals show a ^{31}P−^{13}C coupling and thus belong to the butatriene C atoms linked to the metal. We note that in all of the previously described 1,1,4,4-tetrasubstituted butatrienerhodium(I) compounds *trans*-[Rh(η^2-R_2C═C═C═CR′$_2$)(PPh_3)$_2$], which were prepared from [RhCl(PPh_3)$_3$] and corresponding butatrienes,[36] the central C═C bond is coordinated to the metal. The linkage of a terminal R_2C═C bond not to rhodium(I) but to platinum(0) was recently reported by Stang.[37]

Similarly to the allylic type complex **12**, compounds **28**−**31** and **32**−**34** also react rapidly with CO in benzene at room temperature to yield the carbonyl complex **18** by ligand exchange. Of the butatrienes formed in these processes, those with C(aryl)$_2$ and C(Ph)CF_3 as the terminal unit are rather labile and undergo secondary reactions. The hitherto unknown cumulene **35** was characterized by GC/MS and by comparison of the spectroscopic data with those of other butatrienes.[38,39]

Quite unexpectedly, there is also an alternative route to convert a metal-bonded allenylidene moiety into a butatriene ligand (see Scheme 8). During attempts to oxidatively add CH_3I to the metal center of the rhodium(I) complexes **1** and **20**,

Scheme 8. (L = P*i*Pr$_3$)



thereby anticipating that they may react analogously to the Vaska-type compounds *trans*-[IrCl(CO)(PR_3)$_2$] with methyl iodide,[40] we observed that CH_3I can behave as a CH_2 source. While in the absence of a basic substrate the reaction of **1** with methyl iodide proceeds very slowly and gives a mixture of products, the butatriene complex **38** is formed as the major species together with **32** in the presence of Na_2CO_3. Subsequent treatment of the reaction mixture with KI yields **38** nearly quantitatively. The bis(*p*-anisyl) derivative **20** behaves similarly and affords **39**. Both compounds **38** and **39** are also obtained by treating the allenylidene(iodo)rhodium(I) complexes **36** and **37** with CH_3I and Na_2CO_3. Regarding the mechanism of formation of **38** and **39**, we assume that in the initial step the anticipated oxidative addition of methyl iodide at the rhodium center takes place, which is followed by an insertion of the allenylidene unit into the Rh−CH_3 bond. The so-formed intermediate with the Rh−C(CH_3)═C═CPh_2 linkage then reacts by a β-H shift to give an octahedral butatriene(hydrido)rhodium-(III) species, which upon reductive elimination of HI or HCl (the latter being facilitated by Na_2CO_3) generates the final product. There is precedence for the first two steps (oxidative addition and methyl migration) insofar as both we[41] and Fryzuk et al.[42] found that the vinylidene compounds *trans*-[IrCl(═C═CH_2)(P*i*Pr$_3$)$_2$] and [Ir(═C═CH_2){κ^3-N(Si$Me_2$$CH_2PPh_2$)$_2$}] react with methyl iodide to give the vinyl complexes [IrCl(I)-{C(CH_3)═CH_2}(P*i*Pr$_3$)$_2$] and [IrI{C(CH_3)═CH_2)}{κ^3-N(SiMe_2-CH_2PPh_2)$_2$}], respectively. However, in these cases a subsequent β-H shift does not occur.

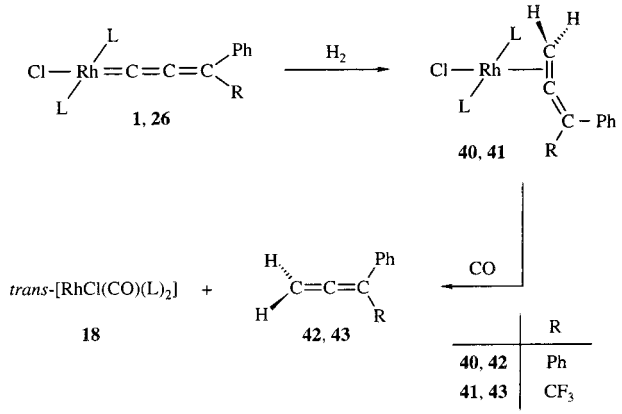
The assumption that both terminal hydrogen atoms of the allenylidene ligand in **38** stem from the methyl iodide has been confirmed by the preparation of **38**-d_2 from **36** and CD_3I. Both substrates react in acetone/THF in the presence of Na_2CO_3 to give **38**-d_2 as a yellow solid in 73% yield. While the ^{1}H NMR spectrum of **38**-d_2 displays no signals in the region around δ 4.5−5.5, the ^{2}H NMR spectrum exhibits two resonances at δ 5.35 and 4.86 assigned to the exo- and endo-D atoms of the ═CD_2 group.

Formation of Allenes and Hexapentaenes from Rhodium Allenylidenes as Precursors. The allenylidene ligand of both **1** and **26** can be converted not only to a butatriene but also to

(34) Werner, H.; Schneider, D.; Schulz, M. *J. Organomet. Chem.* **1993**, *451*, 175−182.
(35) Pu, J.; Peng, T.-S.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1992**, *11*, 3232−3241.
(36) (a) Hagelee, L.; West, R.; Calabrese, J.; Norman, J. *J. Am. Chem. Soc.* **1979**, *101*, 4888−4892. (b) Stang, P. J.; White, M. R.; Maas, G. *Organometallics* **1983**, *2*, 720−725.
(37) White, M. R.; Stang, P. J.; *Organometallics* **1983**, *2*, 1654−1658.
(38) Runge, W.; Brady, W. T. *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; Wiley: New York, 1980; Vol. 1.
(39) Westmijze, H.; Nap, I.; Meijer, J.; Kleijn, H.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 154−157, and references therein.
(40) Review: Collman, J. P.; Roper, W. R. *Adv. Organomet. Chem.* **1968**, *7*, 54−94.
(41) Höhn, A.; Werner, H. *J. Organomet. Chem.* **1990**, *382*, 255−277.
(42) Fryzuk, M. D.; Huang, L.; McManus, N. T.; Paglia, P.; Rettig, S. J.; White, G. S. *Organometallics* **1992**, *11*, 2979−2990.

an allene. The reaction of **1** with H_2 in benzene at room temperature is rather slow, but after 40 h the four-coordinate rhodium(I) complex **40** is quantitatively formed (see Scheme 9). In contrast, compound **26** reacts significantly faster with H_2 and affords after 30 min (benzene, 25 °C) the corresponding product **41**. Quite remarkably, under the chosen conditions no hydrogenation of the allene ligand occurs. Only after increasing the time of the reaction to 10 days and raising the temperature to 60 °C is the formation of a new rhodium complex observed. It is, according to the NMR data, the chloro(dihydrido) derivative $[RhH_2Cl(PiPr_3)_2]$.[16,29] Since the ^1H NMR spectra of **40** and **41** display only one signal for the CH_2 protons, we assume that the unsubstituted double bond of the allene is coordinated to the metal center. A slippage of the $[RhCl(PiPr_3)_2]$ fragment along the axis of the cumulene, as has been observed for some allene iron and platinum complexes,[43,44] could not be detected.

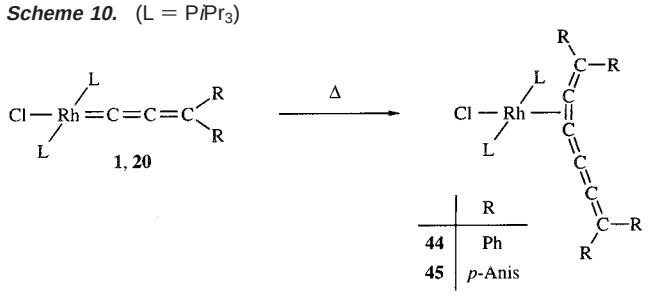
Scheme 9. (L = P*i*Pr$_3$)



In the same way as for **31** and **34**, treatment of **40** and **41** with CO in benzene at 10 °C leads to a replacement of the olefinic ligand. While 1,1-diphenylallene **42** is known,[45] the CF_3-substituted derivative **43** has not been reported as yet; it has been characterized by NMR spectroscopy. Typical features are the quartet for the CH_2 protons in the ^1H NMR at δ 4.75, the three resonances for the α-, β-, and γ-carbon atoms of the C_3 chain in the ^{13}C NMR at δ 83.1, 102.0, and 210.2 (the two latter showing a $^{13}C-^{19}F$ coupling), and the singlet at δ −60.7 in the ^{19}F NMR spectrum. The metal-containing product of the reactions of **40** and **41** with CO is the carbonyl complex **18**.

Not only the hydrogenation but also the thermolysis of the starting materials **1** and **20** leads to the cleavage of the Rh=C bond. After stirring of a solution of **1** or **20** in toluene at 95 °C for 5 days, besides the generation of free P*i*Pr$_3$, the formation of the hexapentaene complexes **44** and **45** is observed (Scheme 10). Both are bright red, slightly air-sensitive solids that are readily soluble in dichloromethane, but less soluble in pentane and ether. Compound **44** is known and has been recently prepared in our laboratory by treatment of *trans*-$[Rh(C{\equiv}CPh_2OH)(=C=CHCPh_2OH)(PiPr_3)_2]$ with acidic alumina.[46] The ^{13}C NMR spectrum of **45** displays, similarly to that of **44**, six resonances for the C atoms of the C_6 unit, of which two at δ

Scheme 10. (L = P*i*Pr$_3$)



128.0 and 113.4 show a relatively large $^{103}Rh-^{13}C$ coupling and are thus assigned to the carbons linked to rhodium. The assumption that the $C_\beta-C_\gamma$ and not the central $C_\gamma-C_\delta$ bond is coordinated to the metal center is supported by the X-ray crystal structure analysis of **44**.[46] It is worth mentioning that there is precedence for the linkage of two allenylidene fragments to give a tetrasubstituted hexapentaene, as on the heating of $[(\eta^5\text{-}C_5H_5)\text{-}Mn(=C=C=CtBu_2)(CO)_2]$ to give small quantities of $tBu_2C=C=C=C=CtBu_2$.[47] A related rhodium-mediated coupling of two vinylidene ligands to generate a coordinated butatriene is also known.[48]

Concluding Remarks

The present investigations have shown that square-planar rhodium allenylidenes of the general composition *trans*-$[RhCl(=C=C=CRR')(PiPr_3)_2]$ offer a multifaceted chemistry indeed. They react not only with C-nucleophiles by replacement of the chloride but also undergo reactions with H_2, Cl_2, HCl, methyl iodide, and phenylacetylene to give products in which the allenylidene unit is preserved as part of a newly formed ligand. The potential of the starting materials *trans*-$[RhCl(=C=C=CRR')(PiPr_3)_2]$ (**1**, **2**, **20**, **26**) to generate cumulenes such as allenes, butatrienes, hexapentaenes, and even unsaturated phosphorus ylides is clearly illustrated by the preparation of compounds **8**, **17**, **35**, and **43**, which are hardly accessible on conventional routes. Taking these results into consideration, it seems at least conceivable that rhodium allenylidenes, possibly formed in situ from appropriate propargylic alcohols following the classical Selegue method,[49] can be used as precursors for presently unknown unsaturated hydrocarbons and ylides. On the basis of this idea, current work in our laboratory is focused on reaction conditions that allow the conversion, e.g. of the butatriene complexes **31**, **34**, or **39**, upon treatment with the corresponding alkynol HC≡CCR(R′)OH to the starting materials **20** and **27** and free butatrienes. Another possibility is that compounds such as **1**, **2**, **20**, **26**, and **27**, similarly to their iridium counterparts *trans*-$[IrCl(=C=C=CRR')(PiPr_3)_2]$,[15] may serve as building blocks for the generation of rhodium carbenes and carbynes, the catalytic activity of which is still unexplored.

Experimental Section

All reactions were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **1**,[1a] **2**,[1b] **20**,[3b] **24**,[29] **27**,[3b] **36**, and **37**[2b] were prepared as described in the literature. NMR spectra were recorded at room temperature on Bruker AC 200 and Bruker AMX 400 instruments, IR spectra on a IFS 25 FT-IR infrared spectrometer,

(43) Ben-Shoshan, R.; Pettit, R. *J. Am. Chem. Soc.* **1967**, *89*, 2231−2232.
(44) Vrieze, K.; Volger, H. C.; Praat, A. P. *J. Organomet. Chem.* **1970**, *21*, 467−475.
(45) Beltrame, P.; Pitea, D.; Marzo, A.; SimOnetta, M. *J. Chem. Soc. B* **1967**, 71−75.
(46) Werner, H.; Wiedemann, R.; Mahr, N.; Steinert, P.; Wolf, J. *Chem. Eur. J.* **1996**, *2*, 561−569.
(47) Berke, H. *Angew. Chem.* **1976**, *88*, 684−685; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 624−625.
(48) Rappert, T.; Nürnberg, O.; Werner, H. *Organometallics* **1993**, *12*, 1359−1364.
(49) Selegue, J. P. *Organometallics* **1982**, *1*, 217−218.

and mass spectra on a Finnigan MAT 90 (70 eV) or on a Hewlett-Packard G 1800 GCD instrument. Coupling constants are given in hertz. Abbreviations used: s, singlet; d, doublet; t, triplet; m, multiplet; v, virtual coupling; br, broadened signal; $N = {}^3J(PH) + {}^5J(PH)$ or ${}^1J(PC) + {}^3J(PC)$. Melting points were measured by differential thermal analysis (DTA).

Preparation of [(η^5-C_5H_5)Rh(=C=C=CPh$_2$)(P*i*Pr$_3$)] (3). A mixture of **1** (140 mg, 0.22 mmol) and NaC_5H_5 (39 mg, 0.44 mmol) was treated dropwise with THF (3 mL) under stirring at room temperature. A rapid change of color from red to dark green occurred. After the solution was stirred for 5 min, the solvent was removed in vacuo and the residue extracted with pentane (30 mL). The extract was concentrated to ca. 3 mL and then chromatographed on Al_2O_3 (neutral, activity grade V, height of column 7 cm). With hexane, a green fraction was eluted that was concentrated to ca. 2 mL in vacuo. After storing the solution for 3 d at −78 °C, dark green crystals precipitated that were separated from the mother liquor, washed three times with 1-mL portions of pentane (0 °C), and dried in vacuo. Yield: 69 mg (62%). Mp: 124 °C dec. IR (KBr): ν(C=C=C) 1940 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.98 (m, 4H, ortho-H of C_6H_5), 7.28 (m, 2H, para-H of C_6H_5), 7.03 (m, 4H, meta-H of C_6H_5), 5.01 (s, 5H, C_5H_5), 2.09 (m, 3H, PC*H*CH$_3$), 1.00 (dd, J(PH) = 13.5, J(HH) = 6.9 Hz, 18H, PCHC*H*$_3$). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 228.6 (dd, J(RhC) = 71.2, J(PC) = 30.5 Hz, Rh=*C*=C=C), 208.9 (dd, J(RhC) = 16.5, J(PC) = 7.0 Hz, Rh=C=*C*=C), 148.0 (s, br, ipso-C of C_6H_5), 128.3, 127.8, 126.0 (all s, C_6H_5), 121.1 (dd, br, J(RhC) = 1.9, J(PC) = 5.7 Hz, Rh=C=C=*C*), 83.7 (dd, J(RhC) = 3.8, J(PC) = 2.5 Hz, C_5H_5), 26.8 (dd, J(RhC) = 1.9, J(PC) = 22.9 Hz, P*C*HCH$_3$), 19.9 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 68.5 (d, J(RhP) = 200.8 Hz). Anal. Calcd for $C_{29}H_{36}PRh$: C, 67.18; H, 7.00. Found: C, 67.49; H, 6.83.

Preparation of [(η^5-C_5H_5)Rh{=C=C=C(*o*-Tol)Ph}(P*i*Pr$_3$)] (4). This compound was prepared as described for **3** from **2** (176 mg, 0.27 mmol) and NaC_5H_5 (48 mg, 0.54 mmol) to give a dark green solid. Yield: 106 mg (75%). Mp: 146 °C dec. IR (KBr): ν(C=C=C) 1930 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.79, 7.11 (both m, 9H, C_6H_4 and C_6H_5), 5.09 (s, 5H, C_5H_5), 2.00 (s, 3H, $C_6H_4CH_3$), 1.98 (m, 3H, PC*H*CH$_3$), 0.92 (dd, J(PH) = 13.6, J(HH) = 6.9 Hz, 18H, PCHC*H*$_3$). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 227.2 (dd, J(RhC) = 71.0, J(PC) = 31.0 Hz, Rh=*C*=C=C), 204.5 (dd, J(RhC) = 16.9, J(PC) = 6.3 Hz, Rh=C=*C*=C), 146.2 (d, J(PC) = 2.5 Hz, ipso-C of C_6H_5 or C_6H_4), 146.0 (d, J(PC) = 3.8 Hz, ipso-C of C_6H_5 or C_6H_4), 132.9, 129.9, 129.5, 126.5, 125.8, 125.6, 125.4, 124.8 (all s, C_6H_5 and C_6H_4), 122.3 (d, br, J(PC) = 5.3 Hz, Rh=C=C=*C*), 83.4 (dd, J(RhC) = 2.7, J(PC) = 2.7 Hz, C_5H_5), 26.4 (d, J(PC) = 22.9 Hz, P*C*HCH$_3$), 19.9 (s, $C_6H_4CH_3$), 19.6 (s, PCH*C*H$_3$). ^{31}P NMR ($CDCl_3$, 162.0 MHz): δ 66.7 (d, J(RhP) = 197.3 Hz). Anal. Calcd for $C_{30}H_{38}PRh$: C, 67.67; H, 7.19. Found: C, 67.64; H, 7.23.

Preparation of [Rh(η^3-CH$_2$CHC=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (6). A solution of **1** (173 mg, 0.27 mmol) in toluene (4 mL) was treated dropwise at −40 °C with a 1.00 M solution of CH$_2$=CHMgBr in THF (0.30 mL, 0.30 mmol). After warming to 0 °C, the solution was stirred for 1 h, which led to a gradual change of color from red to dark red. The solvent was removed in vacuo and the residue extracted with pentane (25 mL). The extract was brought to dryness in vacuo, the oily residue was dissolved in acetone (2 mL), and the solution was stored for 24 h at −78 °C. Red crystals precipitated, which were washed twice with 1-mL portions of acetone (−20 °C) and dried in vacuo. Yield: 104 mg (61%). Mp: 62 °C dec. IR (C_6H_6): ν(C=C=C) 1970 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.84, 7.15 (both m, 10H, C_6H_5), 4.79 (dd, $J(H^1H^3)$ = 12.1, $J(H^1H^2)$ = 6.8 Hz, 1H, H^1), 3.01 (d, $J(H^1H^2)$ = 6.8 Hz, 1H, H^2), 2.45 (dd, $J(P^2H^3)$ = 5.8, $J(H^1H^3)$ = 12.1 Hz, 1H, H^3), 2.33, 2.07 (both m, 6H, PC*H*CH$_3$), 1.18 (dd, J(PH) = 12.0, J(HH) = 7.6 Hz, 18H, PCHC*H*$_3$), 1.11 (m, 18H, PCHC*H*$_3$).^{13}C NMR (C_6D_6, 100.6 MHz): δ 183.1 (s, C^2), 141.1, 140.4 (both s, ipso-C of C_6H_5), 130.1, 129.2, 127.5, 125.8, 125.2, 122.9 (all s, C_6H_5), 113.2 (ddd, J(RhC) = 54.0, J(PC) = 17.1 and 16.7 Hz, C^3), 106.9 (m, C^4), 79.7 (s, C^1), 50.3 (m, C^5), 28.3 (d, J(PC) = 9.3 Hz, P*C*HCH$_3$), 28.0 (d, J(PC) = 10.0 Hz, P*C*HCH$_3$), 20.8, 20.7, 20.5, 20.4 (all s, br, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): partly resolved AB pattern of ABX spectrum with signals at δ 52.4 (A part) and 51.4, 51.3, 51.2, 51.1 (B part). Anal. Calcd for $C_{35}H_{55}P_2Rh$: C, 65.62; H 8.65. Found: C 65.40; H 8.17. For assignment for protons H^1 to H^3 and carbon atoms C^1 to C^5, see Chart 1.

Preparation of *trans*-[Rh{η^1-C(CH=CH$_2$)=C=CPh$_2$}(CO)(P*i*Pr$_3$)$_2$] (7). A slow stream of CO was passed through a solution of **6** (90 mg, 0.14 mmol) in benzene (3 mL) at 10 °C. A change of color from red to light yellow occurred. After the solution was stirred for 5 min at room temperature, the solvent was evaporated in vacuo. The yellow residue was dissolved in acetone (2 mL) and the solution was stored for 10 h at −78 °C. Yellow crystals precipitated which were separated from the mother liquor, washed three times with 2-mL portions of acetone (0 °C) and dried in vacuo: yield 61 mg (65%); mp 98 °C dec. IR (C_6H_6): ν(C≡O) 1930, ν(C=C=C) 1850 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.63, 7.00 (both m, 10H, C_6H_5), 6.84 (dd, $J(H^1H^2)$ = 17.0, $J(H^1H^3)$ = 9.5 Hz, 1H, H^1), 5.97 (dd, $J(H^1H^2)$ = 17.0, $J(H^2H^3)$ = 3.1 Hz, 1H, H^2), 5.11 (dd, $J(H^1H^3)$ = 9.5, $J(H^2H^3)$ = 3.1 Hz, 1H, H^3), 2.01 (m, 6H, PC*H*CH$_3$), 1.06 (dvt, N = 13.3, J(HH) = 6.8 Hz, 36H, PCHC*H*$_3$). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 209.9 (t, J(PC) = 3.2 Hz, C^2), 195.1 (dt, J(RhC) = 55.8, J(PC) = 22.3 Hz, Rh−CO), 144.5 (s, br, C^4), 141.3 (s, ipso-C of C_6H_5), 129.0, 128.1, 125.3 (all s, C_6H_5), 118.8 (dt, J(RhC) = 27.0, J(PC) = 11.4 Hz, C^3), 117.8 (s, C^5), 98.4 (s, C^1), 26.1 (vt, N = 19.7 Hz, P*C*HCH$_3$), 20.5, 20.0 (both s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 47.3 (d, J(RhP) = 135.1 Hz). Anal. Calcd for $C_{36}H_{55}OP_2Rh$: C, 64.66; H, 8.29. Found: C, 64.42; H, 8.39. For assignment for protons H^1 to H^3 and carbon atoms C^1 to C^5 see Chart 1.

Reaction of 7 with CH$_3$CO$_2$H. A solution of **7** (35 mg, 0.05 mmol) in C_6D_6 (0.5 mL) was treated at 10 °C with acetic acid (3.1 μL, 0.05 mmol), which led to a gradual change of color from yellow to pale-yellow. After the solution was stirred for 5 min, the NMR spectra confirmed the formation of both *trans*-[Rh(κ^1-O$_2$CCH$_3$)(CO)(P*i*Pr$_3$)$_2$] (**9**)[13] and the vinylallene CH$_2$=CH−CH=C=CPh$_2$ (**8**) as the organic product. NMR data for **8**: ^{1}H NMR (C_6D_6, 400 MHz): δ 7.40 (m, 4H; ortho-H of C_6H_5), 7.15 (m, 4H, meta-H of C_6H_5), 7.05 (m, 2H, para-H of C_6H_5), 6.22 (m, 2H, H^1 and H^2), 5.09 (m, 1H, H^3), 4.87 (m, 1H, H^4). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 210.2 (s,=*C*=CPh$_2$), 136.8 (s, ipso-C of C_6H_5), 132.5 (s, *C*H=CH$_2$), 129.0, 128.8, 127.7 (all s, C_6H_5), 117.0 (s, CH=*C*H$_2$), 112.0 (s, =*C*Ph$_2$), 97.9 (s, =*C*H−CH=CH$_2$). For assignment for protons H^1 to H^4 see Chart 1.

Preparation of [RhCl$_2$(CH=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (10). A solution of **1** (97 mg, 0.15 mmol) in toluene (5 mL) was treated at 0 °C first with acetone (1 mL) and then dropwise with a 0.05 M solution of HCl in benzene (3 mL, 0.15 mmol). A quick change of color from red to green occurred. After the solution was stirred for 10 min at room temperature, the solvent was evaporated in vacuo. The residue was dissolved in acetone (3 mL) and the solution was stored at −20 °C for 24 h. Green crystals precipitated that were separated from the mother liquor, washed twice with 1-mL portions of acetone (0 °C), and dried in vacuo. Yield: 90 mg (88%). Mp: 164 °C dec. IR (C_6H_6): ν(C=C=C) 1875 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.52 (m, 4H, ortho-H of C_6H_5), 7.44 (dt, J(RhH) = 6.4, J(PH) = 3.6 Hz, 1H, RhCH), 7.23 (m, 6H, C_6H_5), 2.93 (m, 6H, PC*H*CH$_3$), 1.24 (dvt, N = 13.3, J(HH) = 7.1 Hz, 36H, PCHC*H*$_3$). ^{13} C NMR (C_6D_6, 50.3 MHz): δ 199.9 (dt, J(RhC) = 1.9, J(PC) = 3.2 Hz, Rh−CH=*C*), 141.0 (s, br, ipso-C of C_6H_5), 129.6, 127.8, 127.1 (all s, C_6H_5), 114.2 (s, br, Rh−CH=C=*C*), 68.5 (dt, J(RhC) = 36.2, J(PC) = 8.9 Hz, RhCH), 23.0 (vt, N = 19.1 Hz, P*C*HCH$_3$), 19.9 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 25.4 (d, J(RhP) = 97.3 Hz). Anal. Calcd for $C_{33}H_{53}Cl_2P_2Rh$: C, 57.82; H, 7.79. Found: C, 57.82; H, 8.42.

Preparation of [RhCl$_2${CH=C=C(*o*-Tol)Ph}(P*i*Pr$_3$)$_2$] (11). This compound was prepared as described for **10** from **2** (92 mg, 0.14 mmol) and a 0.05 M solution of HCl in benzene (2.8 mL, 0.14 mmol) to give

a green air-stable solid. Yield: 83 mg (86%). Mp: 132 °C dec. IR (C_6H_6): ν(C═C═C) 1885 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.85 (dt, J(RhH) = 6.4, J(PH) = 3.6 Hz, 1H, RhCH), 7.40 (m, 9H, C_6H_4 and C_6H_5), 2.93 (m, 6H, PC*H*CH$_3$), 2.14 (s, 3H, $C_6H_4CH_3$), 1.20 (dvt, N = 13.6, J(HH) = 7.0 Hz, 18H, PCHC*H*$_3$), 1.19 (dvt, N = 13.2, J(HH) = 6.7 Hz, 18H, PCHC*H*$_3$). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 198.9 (s, Rh−CH═*C*), 141.8, 139.4 (both s, ipso-C of C_6H_4R), 133.9, 130.6, 128.6, 128.3, 127.6, 126.7, 125.8 (all s, C_6H_4 and C_6H_5), 113.2 (s, Rh−CH═C═*C*), 69.3 (dt, J(RhC) = 36.7, J(PC) = 8.9 Hz, RhCH), 23.0 (vt, N = 18.9 Hz, P*C*HCH$_3$), 20.8 (s, $C_6H_4CH_3$), 20.0 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 25.2 (d, J(RhP) = 96.9 Hz). Anal. Calcd for $C_{34}H_{55}Cl_2P_2Rh$: C, 58.37; H, 7.92. Found: C, 58.53; H, 7.78.

Preparation of [RhCl{η^3-*anti*-CH(P*i*Pr$_3$)C(Ph)C═C═CPh$_2$}-(P*i*Pr$_3$)] (12). A solution of **1** (191 mg, 0.29 mmol) in benzene (4 mL) was treated at 10 °C with phenylacetylene (32 μL, 0.29 mmol) and then stirred for 20 h at room temperature. The solvent was evaporated in vacuo, and the remaining red solid was washed twice with 1-mL portions of pentane (−20 °C) and dried in vacuo. Yield: 203 mg (92%). Mp: 189 °C. IR (C_6H_6): ν(C═C═C) 1885 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 8.00, 7.61, 7.51, 7.09 (all m, 15H, C_6H_5), 2.52, 2.04 (both m, 3H each, PC*H*CH$_3$), 2.36 (dd, J(P^{2}H) = 9.6, J(P^{1}H) = 5.6 Hz, 1H, C*H*P*i*Pr$_3$), 1.33 (dd, J(PH) = 13.2, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$), 1.18 (dd, J(PH) = 15.2, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$), 1.12 (dd, J(PH) = 12.8, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$), 0.71 (dd, J(PH) = 14.8, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 187.5 (s, C^4), 143.7 (s, ipso-C of C−C_6H_5), 139.9, 139.2 (both s, ipso-C of ═C(C_6H_5)$_2$), 128.7, 128.2, 128.1, 128.0, 127.2, 126.6, 126.2, 126.0, 125.2 (all s, C_6H_5), 108.9 (s, C^5), 106.7 (m, C^3), 71.8 (d, J(PC) = 6.8 Hz, C^2), 24.2 (d, J(PC) = 17.7 Hz, P*C*HCH$_3$), 21.6 (d, J(PC) = 44.8 Hz, P*C*HCH$_3$), 20.9 (ddd, J(RhC) = 65.8, J(P^{2}C) = 25.8, J(P^{1}C) = 10.6 Hz, C^1), 20.0, 19.1 (both s, br, PCH*C*H$_3$), 18.3 (d, J(PC) = 2.4 Hz, PCH*C*H$_3$), 17.0 (d, J(PC) = 1.8 Hz, PCH*C*H$_3$). ^{31}P NMR ($CDCl_3$, 162.0 MHz): δ 52.9 (dd, J(RhP) = 179.6, J(PP) = 14.3 Hz, P^1), 39.3 (dd, J(RhP) = 4.2, J(PP) = 14.3 Hz, P^2). MS (70 eV): m/z 750 (M$^+$). Anal. Calcd for $C_{41}H_{58}ClP_2Rh$: C, 65.55; H, 7.78. Found: C, 65.76; H, 7.72. For assignment for carbon atoms C^1 to C^5 and phosphorus atoms P^1 and P^2, see Chart 1.

Preparation of [RhCl{η^3-*anti*-CH(P*i*Pr$_3$)C(p-Tol)C═C═CPh$_2$}-(P*i*Pr$_3$)] (13). This compound was prepared as described for **12** from **1** (123 mg, 0.19 mmol) and *p*-tolylacetylene (24 μL, 0.19 mmol) to give a red solid after a 40 h reaction time. Yield: 127 mg (88%). Mp: 190 °C. IR (C_6H_6): ν(C═C═C) 1925 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52, 7.05 (both m, br, 14H, C_6H_4 and C_6H_5), 2.26, 2.24 (both m, 3H each, PC*H*CH$_3$), 2.22 (m, 1H, C*H*P*i*Pr$_3$), 2.14 (s, 3H, $C_6H_4CH_3$), 1.35 (dd, J(PH) = 15.2, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$), 1.03 (dd, J(PH) = 13.2, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$), 0.93 (dd, J(PH) = 15.2, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$), 0.81 (dd, J(PH) = 11.2, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 187.3 (s, C^4), 140.5 (s, ipso-C of C_6H_4), 139.8, 139.0 (both s, ipso-C of ═C(C_6H_5)$_2$), 135.6, 128.7, 128.5, 128.0, 127.8, 126.8, 126.5, 125.9, 125.0 (all s, C_6H_4 and C_6H_5), 108.6 (s, C^5), 106.7 (ddd, J(RhC) = 26.2, J(PC) = 8.0 and 1.9 Hz, C^3), 71.9 (d, J(PC) = 6.0 Hz, C^2), 24.0 (d, J(PC) = 17.6 Hz, P*C*HCH$_3$), 21.4 (d, J(PC) = 43.3 Hz, P*C*HCH$_3$), 21.2 (s, $C_6H_4CH_3$), 20.2 (ddd, J(RhC) = 65.9, J(P^{2}C) = 41.2, J(P^{1}C) = 10.1 Hz, C^1), 19.8, 19.0 (both s, br, PCH*C*H$_3$), 18.1 (d, J(PC) = 2.2 Hz, PCH*C*H$_3$), 16.9 (d, J(PC) = 2.0 Hz, PCH*C*H$_3$). ^{31}P NMR ($CDCl_3$, 162.0 MHz): δ 52.4 (dd, J(RhP) = 179.3, J(PP) = 14.2 Hz, P^1), 38.7 (dd, J(RhP) = 4.0, J(PP) = 14.2 Hz, P^2). Anal. Calcd for $C_{42}H_{60}ClP_2Rh$: C, 65.92; H, 7.90. Found: C, 65.76; H, 7.80. For assignment for carbon atoms C^1 to C^5 and phosphorus atoms P^1 and P^2, see Chart 1.

Preparation of [RhCl{η^3-*anti*-CH(P*i*Pr$_3$)C(SiMe$_3$)C═C═CPh$_2$}-(P*i*Pr$_3$)] (14). A solution of **1** (245 mg, 0.38 mmol) in benzene (10 mL) was treated at 10 °C with trimethylsilylacetylene (150 μL, 1.06 mmol) and then stirred for 14 days at room temperature. The solvent was evaporated in vacuo, the remaining oily residue dissolved in pentane (15 mL), and the solution stored for 2 days at −78 °C. Red crystals precipitated that were separated from the mother liquor, washed twice with 1-mL portions of pentane (−20 °C), and dried in vacuo. Yield: 203 mg (72%). Mp: 63 °C. IR (C_6H_6): ν(C═C═C) 1915 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.56, 7.40, 7.12 (all m, 10H, C_6H_5), 2.55, 2.21 (both m, 3H each, PC*H*CH$_3$), 2.06 (dd, J(P^{2}H) = 14.4, J(P^{1}H) = 5.2 Hz, 1H, C*H*P*i*Pr$_3$), 1.36 (dd, J(PH) = 12.4, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$), 1.35 (dd, J(PH) = 12.3, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$), 1.22 (dd, J(PH) = 14.8, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$), 0.75 (dd, J(PH) = 15.2, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$), 0.46 (s, 9H, SiMe$_3$). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 187.7 (s, C^4), 142.1, 141.4 (both s, ipso-C of C_6H_5), 129.0, 128.5, 128.3, 127.5, 125.8, 125.5 (all s, C_6H_5), 108.4 (s, C^5), 106.7 (ddd, J(RhC) = 25.2, J(P^{1}C) = J(P^{2}C) = 4.5 Hz, C^3), 69.2 (dd, J(P^{1}C) = J(P^{2}C) = 5.2 Hz, C^2), 25.1 (d, J(PC) = 17.1 Hz, P*C*HCH$_3$), 23.4 (ddd, J(RhC) = 66.1, J(P^{2}C) = 27.2, J(P^{1}C) = 10.4 Hz, C^1), 21.5 (d, J(PC) = 43.3 Hz, P*C*HCH$_3$), 20.4, 20.3 (both s, PCH*C*H$_3$), 18.3 (d, J(PC) = 2.8 Hz, PCH*C*H$_3$), 17.4 (d, J(PC) = 2.1 Hz, PCH*C*H$_3$), 0.46 (s, SiMe$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 48.0 (dd, J(RhP) = 180.5, J(PP) = 15.7 Hz, P^1), 40.3 (dd, J(RhP) = 4.5, J(PP) = 15.7 Hz, P^2). ^{29}Si NMR (C_6D_6, 39.8 MHz): δ −1.9 (m). Anal. Calcd for $C_{38}H_{62}ClP_2RhSi$: C, 61.08; H, 8.36. Found: C, 60.83; H, 8.42. For assignment for carbon atoms C^1 to C^5 and phosphorus atoms P^1 and P^2, see Chart 1.

Preparation of [Rh(C_6H_5){η^3-*anti*-CH(P*i*Pr$_3$)C(Ph)C═C═CPh$_2$}-(P*i*Pr$_3$)] (15). A solution of **12** (105 mg, 0.14 mmol) in benzene (3 mL) was treated at 5 °C with a 1.0 M solution of C_6H_5MgBr in ether (0.50 mL, 0.50 mmol) and then stirred for 3 h at 50 °C. After the solution was cooled to room temperature, the solvent was evaporated in vacuo and the residue extracted with pentane (25 mL). The extract was brought to dryness in vacuo, the remaining oily residue was dissolved in ether (5 mL), and the solution stored for 24 h at −78 °C. Black crystals precipitated, which were separated from the mother liquor, washed twice with 1-mL portions of acetone (−20 °C), and dried in vacuo. Yield: 72 mg (65%). Mp: 160 °C. IR (C_6H_6): ν(C═C═C) 1925 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 8.09, 7.94, 7.72, 7.58, 7.17 (all m, 20H, C_6H_5), 2.16, 1.89 (both m, 3H each, PC*H*CH$_3$), 2.08 (dd, J(P^{2}H) = 8.3, J(P^{1}H) = 5.4 Hz, 1H, C*H*P*i*Pr$_3$), 1.22 (dd, J(PH) = 12.9, J(HH) = 7.1 Hz, 9H, PCHC*H*$_3$), 1.06 (dd, J(PH) = 13.0, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$), 0.99 (dd, J(PH) = 15.3, J(HH) = 7.1 Hz, 9H, PCHC*H*$_3$), 0.55 (dd, J(PH) = 14.9, J(HH) = 7.1 Hz, 9H, PCHC*H*$_3$). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 53.7 (dd, J(RhP) = 198.1, J(PP) = 14.2 Hz, P^1), 38.2 (dd, J(RhP) = 4.6, J(PP) = 14.2 Hz, P^2). Anal. Calcd for $C_{47}H_{63}P_2Rh$: C, 71.20; H, 8.01. Found: C, 70.90; H, 8.31. For assignment of phosphorus atoms P^1 and P^2, see Chart 1.

Preparation of [Rh(CH═CH$_2$){η^3-*anti*-CH(P*i*Pr$_3$)C(Ph)C═C═CPh$_2$}(P*i*Pr$_3$)] (16). A solution of **12** (203 mg, 0.27 mmol) in benzene (4 mL) was treated at 5 °C with a 1.0 M solution of CH_2═CHMgBr in THF (0.50 mL, 0.50 mmol) and then stirred for 24 h at room temperature. After the solvent was evaporated in vacuo, the oily residue was worked up as described for **15**. A black solid was obtained. Yield: 143 mg (71%). Mp: 141 °C. IR (C_6H_6): ν(C═C═C) 1930 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 8.64 (m, 1H, RhC*H*═CH$_2$), 7.93, 7.56−6.98 (both m, 15H, C_6H_5), 6.47 (m, 1H, one H of RhCH═C*H*$_2$), 5.76 (m, 1H, one H of RhCH═C*H*$_2$), 2.25, 1.98 (both m, 3H each, PC*H*CH$_3$), 1.28 (dd, J(PH) = 14.4, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$), 1.15 (dd, J(PH) = 13.1, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$), 1.06 (dd, J(PH) = 13.2, J(HH) = 7.1 Hz, 9H, PCHC*H*$_3$), 0.62 (dd, J(PH) = 12.2, J(HH) = 7.1 Hz, 9H, PCHC*H*$_3$), signal of C*H*P*i*Pr$_3$ probably covered by resonances of PC*H*CH$_3$. ^{13}C NMR (C_6D_6, 100.6 MHz): δ 177.4 (s, C^4), 173.4 (dd, J(RhC) = 42.3, J(PC) = 16.1, RhCH), 146.2 (s, ipso-C of C−C_6H_5), 142.0, 141.1 (both s, ipso-C of ═C(C_6H_5)$_2$), 129.4, 128.5, 128.4, 128.3, 127.3, 126.5, 126.2, 125.3, 124.1 (all s, C_6H_5), 119.5 (s, ═CH$_2$), 106.5 (dd, J(RhC) = 12.1, J(PC) = 6.0 Hz, C^3), 101.3 (s, C^5), 76.7 (d, J(PC) = 6.1 Hz, C^2), 26.2 (d, J(PC) = 17.4 Hz, P*C*HCH$_3$), 21.6 (d, J(PC) = 43.2, P*C*HCH$_3$), 20.0 (ddd, J(RhC) = 65.4, J(P^{2}C) = 36.3, J(P^{1}C) = 12.1 Hz, C^1), 20.4, 19.7, 18.2, 17.1 (all s, br, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 55.6 (dd, J(RhP) = 199.6, J(PP) =

13.0 Hz, P^1), 37.5 (dd, J(RhP) = 3.2, J(PP) = 13.0 Hz, P^2). Anal. Calcd for $C_{43}H_{61}P_2Rh$: C, 69.53; H, 8.28. Found: C, 67.84; H, 8.52. For assignment for carbon atoms C^1 to C^5 and phosphorus atoms P^1 and P^2, see Chart 1.

Reaction of 12 with CO. A slow stream of CO was passed for 30 s through a solution of **12** (70 mg, 0.10 mmol) in C_6D_6 (1 mL) at 10 °C. A change of color from red to violet occurred. The IR spectrum of the solution confirmed the formation of *trans*-[RhCl(CO)(P*i*Pr$_3$)$_2$] (**18**)[20] and [RhCl(CO)$_2$]$_2$ (**19**).[21] The solution was evaporated in vacuo and the residue extracted with pentane (15 mL). The extract was concentrated to ca. 5 mL and the solution stored for 2 h at −78 °C. A violet solid (18 mg) precipitated that was separated from the mother liquor, washed twice with pentane (−20 °C), and dried in vacuo. The IR and NMR spectra indicated that the violet solid contained, besides the phosphorus ylide *i*Pr$_3$PCHC(Ph)═C═C═CPh$_2$ (**17**) as the main product, small quantities of **18** that could not be completely separated by fractional crystallization. NMR data for **17**. ^{1}H NMR (C_6D_6, 400 MHz): δ 8.06, 7.77, 7.14 (all m, 15H, C_6H_5), 3.05 (d, J(PH) = 15.2 Hz, 1H, C*H*P*i*Pr$_3$), 2.15 (m, 3H, PC*H*CH$_3$), 0.85 (dd, J(PH) = 15.2, J(HH) = 7.6 Hz, 18H, PCHC*H*$_3$). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 174.2, 171.2 (both s, *C*═C═CPh$_2$ and C═*C*═CPh$_2$), 143.8, 140.9, 140.1, 139.1, 129.3, 128.7, 128.6, 128.5, 128.4, 127.9, 127.8, 126.0, 125.9 (all s, *C*Ph$_2$ and C_6H_5), 93.4 (s, br, CH*C*Ph) 45.9 (d, J(PC) = 100.8 Hz, *i*Pr$_3$P*C*H), 23.5 (d, J(PC) = 49.0 Hz, P*C*HCH$_3$), 17.4 (d, J(PC) = 2.7 Hz, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz): δ 33.57 (s).

Preparation of [RhCl$_3${C(P*i*Pr$_3$)C═CPh$_2$}(P*i*Pr$_3$)] (21). Method a. A solution of **1** (91 mg, 0.14 mmol) in THF (3 mL) was treated dropwise at room temperature under the exclusion of light with a freshly prepared solution of Cl_2 in hexane. The addition was stopped when the ^{31}P NMR spectrum of the solution confirmed the complete conversion of **1** to the product. A pink-red precipitate was formed that was separated from the mother liquor, washed three times with 2-mL portions of acetone (−20 °C), and dried. The solid was dissolved in CH_2Cl_2 (2 mL), and the solution was carefully layered with pentane (10 mL) and then stored for 24 h at 8 °C. Dark red crystals precipitated that were washed twice with 1-mL portions of pentane (−10 °C) and dried in vacuo. Yield: 92 mg (91%).

Method b. A solution of **1** (78 mg, 0.12 mmol) in CH_2Cl_2 (3 mL) was treated at −60 °C with $PhICl_2$ (21 mg, 0.12 mmol). After the solvent was evaporated in vacuo, the residue was washed twice with 1-mL portions of acetone (−20 °C) and worked up as described for method a. yield: 79 mg (92%). mp 136 °C dec. IR (CH_2Cl_2): ν(C═C═C) 1865 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.55, 7.31 (both m, 10H, C_6H_5), 3.34, 2.75 (both m, 3H each, PC*H*CH$_3$), 1.44 (dd, J(PH) = 15.5, J(HH) = 7.1 Hz, 18H, PCHC*H*$_3$), 1.21 (dd, J(PH) = 15.7, J(HH) = 6.9 Hz, 18H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 209.7 (s, *C*═CPh$_2$), 136.4, 136.3 (both s, ipso-C of C_6H_5), 128.9, 128.8, 128.5, 128.4, 127.3, 127.2 (all s, C_6H_5), 105.3 (d, J(RhC) = 18.1 Hz, *C*Ph$_2$), 75.8 (ddd, J(RhC) = 35.6, J(P^{1}C) = 19.2, J(P^{2}C) = 5.5 Hz, *C*P*i*Pr$_3$), 30.8 (d, J(PC) = 25.6 Hz, P*C*HCH$_3$), 24.5 (d, J(PC) = 40.3 Hz, P*C*HCH$_3$), 19.9 (d, J(PC) = 3.3 Hz, PCH*C*H$_3$), 18.9 (d, J(PC) = 2.2 Hz, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, $CDCl_3$): δ 110.9 (dd, J(RhP) = 144.9, J(PP) = 2.9 Hz, RhP*i*Pr$_3$), 48.2 (dd, J(RhP) = 6.5, J(PP) = 2.9 Hz, CP*i*Pr$_3$). Anal. Calcd for $C_{33}H_{52}Cl_3P_2Rh$: C, 55.05; H, 7.28; Rh 14.29. Found: C, 54.89; H, 7.43; Rh, 13.75.

Preparation of [RhCl$_3${C(P*i*Pr$_3$)C═C(o-Tol)Ph}(P*i*Pr$_3$)] (22). This compound was prepared as described for **21** (route b) from **2** (83 mg, 0.12 mmol) and $PhICl_2$ (21 mg, 0.12 mmol) to give dark red crystals. Yield: 81 mg (92%). Mp: 104 °C dec. IR (CH_2Cl_2): ν(C═C═C) 1868 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.72, 7.47, 7.25 (all m, 9H, C_6H_4 and C_6H_5), 3.37, 2.77 (both m, 3H each, PC*H*CH$_3$), 1.87 (s, 3 H, $C_6H_4CH_3$), 1.40, 1.37 (both dd, br, J(PH) = 15.5, J(HH) = 7.4 Hz, 9H each, PCHC*H*$_3$), 1.30 (dd, J(PH) = 15.7, J(HH) = 7.0 Hz, 9H, PCHC*H*$_3$), 1.18 (dd, J(PH) = 15.9, J(HH) = 7.1 Hz, 9H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 210.1 (s, *C*═C(*o*-Tol)Ph), 136.9 (d, J(PC) = 8.0 Hz, ipso-C of C_6H_4 or C_6H_5), 134.5 (d, J(PC) = 7.0 Hz, ipso-C of C_6H_4 or C_6H_5), 131.4, 130.8, 128.6, 128.5, 128.2, 126.7, 126.0 (all s, C_6H_4 and C_6H_5), 105.5 (d, J(PC) = 17.1 Hz, *C*(*o*-Tol)Ph), 75.5 (ddd, J(RhC) = 35.0, J(P^{1}C) = 20.8, J(P^{2}C) = 5.7 Hz, *C*P*i*Pr$_3$), 29.8 (d, J(PC) = 25.5 Hz, P*C*HCH$_3$), 24.5 (d, J(PC) = 40.2 Hz, P*C*HCH$_3$), 21.4, 18.1 (both s, PCH*C*H$_3$), 15.3 (s, $C_6H_4CH_3$). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 108.6 (d, J(RhP) = 144.2 Hz, RhP*i*Pr$_3$), 47.6 (s, CP*i*Pr$_3$). Anal. Calcd for $C_{33}H_{54}Cl_3P_2Rh$: C, 55.64; H, 7.42. Found: C, 55.21; H, 7.25.

Preparation of [RhCl$_3${C(P*i*Pr$_3$)C═C(p-C$_6$H$_4$OMe)$_2$}(P*i*Pr$_3$)] (23). This compound was prepared as described for **21** (route b) from **20** (78 mg, 0.11 mmol) and $PhICl_2$ (19 mg, 0.11 mmol) tp give dark red crystals. Yield: 76 mg (88%). Mp: 108 °C. IR (C_6H_6): ν(C═C═C) 1871 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.49, 6.88 (both d, J(HH) = 8.8 Hz, 4H each, C_6H_4), 3.80 (s, 6H, OCH$_3$), 3.30, 2.75 (both m, 3H each, PC*H*CH$_3$), 1.43, 1.21 (both dd, J(PH) = 15.6, J(HH) = 7.2 Hz, 18H each, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 210.1 (s, *C*═C(*p*-C_6H_4OMe)$_2$), 159.4 (s, *C*OMe), 130.6 (d, J(PC) = 3.0 Hz, C_6H_4), 129.0 (d, J(PC) = 8.0 Hz, ipso-C of C_6H_4), 114.2 (s, C_6H_4), 105.5 (d, J(PC) = 17.1 Hz, ═C(*p*-C_6H_4OMe)$_2$), 75.2 (ddd, J(RhC) = 35.4, J(P^{1}C) = 19.8, J(P^{2}C) = 5.8 Hz, *C*P*i*Pr$_3$), 55.7 (s, OCH$_3$), 31.0 (d, J(PC) = 26.0 Hz, P*C*HCH$_3$), 24.8 (d, J(PC) = 40.0 Hz, P*C*HCH$_3$), 20.2 (d, J(PC) = 2.5 Hz, PCH*C*H$_3$), 19.2 (d, J(PC) = 2.3 Hz, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 108.9 (d, J(RhP) = 145.8 Hz, RhP*i*Pr$_3$), 47.3 (d, J(RhP) = 5.2 Hz, CP*i*Pr$_3$). Anal. Calcd for $C_{35}H_{56}Cl_3O_2P_2Rh$: C, 53.89; H, 7.24. Found: C, 53.67; H, 7.46.

Preparation of *trans*-[RhCl{═C═CHC(Ph)(CF$_3$)OH}(P*i*Pr$_3$)$_2$] (25). A solution of **24** (86 mg, 0.13 mmol) in ether (5 mL) was treated dropwise with a solution of HC≡CC(Ph)(CF_3)OH (47 mg, 0.26 mmol) in ether (2 mL) at room temperature. A change of color from red to yellow occurred. After NEt_3 (3 mL) was added, the reaction mixture was stirred for 10 h at 20 °C, which led again to a change of color from yellow to blue. The solvent was evaporated in vacuo, the residue was dissolved in benzene (2 mL), and the solution was chromatographed on Al_2O_3 (activity grade V, neutral, height of column 10 cm). With benzene a blue fraction was eluted, which was brought to dryness in vacuo. A blue, moderately air-sensitive solid was obtained that was washed twice with 2-mL portions of acetone (0 °C) and dried. Yield: 153 mg (91%). Mp: 140 °C dec. IR (C_6H_6): ν(OH) 3580, ν(C═C) 1650 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.36 (m, 5H, C_6H_5), 2.76 (s, 1H, OH), 2.64 (m, 6H, PC*H*CH$_3$), 1.27 (dvt, N = 25.2, J(HH) = 11.7 Hz, 18H, PCHC*H*$_3$), 1.19 (dvt, N = 13.5, J(HH) = 6.6 Hz, 18H, PCHC*H*$_3$), 0.69 (t, J(PH) = 3.3 Hz, 1H, Rh═C═C*H*R). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 281.0 (dt, J(RhC) = 62.4, J(PC) = 15.1 Hz, Rh═*C*═CHR), 138.7 (s, ipso-C of C_6H_5), 128.4, 127.9, 126.0 (all s, C_6H_5), 125.5 (q, J(CF) = 286.8 Hz, CF_3), 110.3 (dt, br, J(RhC) = 16.1, J(PC) = 5.2 Hz, Rh═C═*C*HR), 65.0 (q, J(CF) = 29.7 Hz, *C*Ph(CF$_3$)OH), 23.3 (vt, N = 20.5 Hz, P*C*HCH$_3$), 19.8 (s, PCH*C*H$_3$). ^{31}P NMR ($CDCl_3$, 81.0 MHz): δ 41.9 (d, J(RhP) = 130.2 Hz). ^{19}F NMR ($CDCl_3$, 188.3 MHz): δ −82.3 (s). Anal. Calcd for $C_{28}H_{49}ClF_3OP_2Rh$: C, 51.03; H, 7.49. Found: C, 50.85; H, 7.58.

Preparation of *trans*-[RhCl{═C═C═C(CF$_3$)Ph}(P*i*Pr$_3$)$_2$] (26). A solution of **25** (153 mg, 0.23 mmol) in benzene (3 mL) was passed through a column with Al_2O_3 (activity grade I, acid, height of column 8 cm). While eluting with benzene, a change of color from blue to green-yellow was observed. The eluted solution was brought to dryness in vacuo, the remaining yellow solid was washed three times with 1-mL portions of pentane and dried. Yield: 139 mg (93%). Mp: 124 °C dec. IR (C_6H_6): ν(C═C═C) 1855 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.98 (m, 2H, ortho-H of C_6H_5), 7.43 (m, 1H, para-H of C_6H_5), 6.63 (m, 2H, meta-H of C_6H_5), 2.96 (m, 6H, PC*H*CH$_3$), 1.28 (dvt, N = 13.6, J(HH) = 7.1 Hz, 36H, PCHC*H*$_3$). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 277.3 (m, Rh═C═*C*═C), 210.3 (m, Rh═*C*═C═C), 152.5 (s, ipso-C of C_6H_5), 134.3 (q, J(CF) = 276.6 Hz, CF_3), 130.2, 127.3, 120.7 (all s, C_6H_5), 121.8 (q, J(CF) = 33.2 Hz, Rh═C═C═*C*), 24.1 (vt, N = 20.4 Hz, P*C*HCH$_3$), 20.2 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 162.0 MHz):

δ 36.0 (d, J(RhP) = 127.0 Hz). ^{19}F NMR (C_6D_6, 376.5 MHz): δ −66.7 (s). MS (70 eV): m/z 640 (M^+), 184 (C═C═C(Ph)CF_3^+). Anal. Calcd for $C_{28}H_{47}ClF_3P_2Rh$: C, 52.47; H, 7.39. Found: C, 52.11; H, 7.21.

Preparation of *trans*-[RhCl(η^2-H$_2$*C*═*C*═C═CPh$_2$)(P*i*Pr$_3$)$_2$] (28). A solution of **1** (90 mg, 0.14 mmol) in benzene (3 mL) was treated dropwise with a 0.28 M solution of diazomethane in ether (1.5 mL, 0.42 mmol) at room temperature. An instantaneous evolution of gas (N_2) and a change of color from deep red to pale red occurred. After the solution was stirred for 5 min, the solvent was evaporated in vacuo. The residue was dissolved in pentane (10 mL) and the solution was stored for 12 h at −78 °C. Red crystals precipitated that were separated from the mother liquor, washed twice with 1-mL portions of pentane (−20 °C), and dried. Yield: 87 mg (95%). Mp: 113 °C dec. IR (C_6H_6): ν(C═C═C═C) 1950 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 7.48 (m, 4H, ortho-H of C_6H_5), 7.12 (m, 6H, meta- and para-H of C_6H_5), 2.61 (dt, J(PH) = 5.4, J(RhH) = 1.6 Hz, 2H, ═CH$_2$), 2.48 (m, 6H, PC*H*CH$_3$), 1.23 (dvt, N = 14.0, J(HH) = 7.2 Hz, 18H, PCHC*H*$_3$), 1.21 (dvt, N = 14.4, J(HH) = 7.2 Hz, 18H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 181.5 (s, *C*═CPh$_2$), 141.4 (s, ipso-C of C_6H_5), 128.8, 128.5, 126.5 (all s, C_6H_5), 111.4 (s, ═CPh$_2$), 108.5 (dt, J(RhC) = 22.1, J(PC) = 5.0 Hz, *C*═CH$_2$), 23.0 (vt, N = 18.1 Hz, P*C*HCH$_3$), 20.8, 20.2 (both s, PCH*C*H$_3$), 13.0 (d, J(RhC) = 13.6 Hz, ═CH$_2$). ^{31}P NMR (162.0 MHz, C_6D_6): δ 35.5 (d, J(RhP) = 115.7 Hz). Anal. Calcd for $C_{34}H_{54}ClP_2Rh$: C, 61.58; H, 8.21; Rh, 15.52. Found: C, 61.30; H, 8.37; Rh, 14.79.

Preparation of *trans*-[RhCl{η^2-H$_2$*C*═*C*═C═C(*p*-C$_6$H$_4$OMe)$_2$}-(P*i*Pr$_3$)$_2$] (29). This compound was prepared as described for **28** from **20** (83 mg, 0.12 mmol) and a 0.28 M solution of diazomethane in ether (1.5 mL, 0.42 mmol). After recrystallization from pentane at −78 °C, orange crystals were obtained. Yield: 81 mg (96%). Mp: 126 °C dec. IR (C_6H_6): ν(C═C═C═C) 1939 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 7.47, 6.81 (both d, J(HH) = 8.8 Hz, 4H each, C_6H_4), 3.34 (s, 6H, OCH$_3$), 2.64 (dt, J(PH) = 5.7, J(RhH) = 1.6 Hz, 2H, ═CH$_2$), 2.50 (m, 6H, PC*H*CH$_3$), 1.26 (dvt, N = 14.4, J(HH) = 7.2 Hz, 18H, PCHC*H*$_3$), 1.24 (dvt, N = 14.0, J(HH) = 7.2 Hz, 18H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 179.9 (s, *C*═C(*p*-C$_6$H$_4$OMe)$_2$), 159.0 (s, *C*OMe), 134.2 (s, ipso-C of C_6H_4), 129.9, 114.0 (both s, C_6H_4), 111.1 (s, ═C(*p*-C$_6$H$_4$-OMe)$_2$), 108.7 (dt, J(RhC) = 22.1, J(PC) = 4.0 Hz, *C*═CH$_2$), 54.8 (s, OCH$_3$), 23.1 (vt, N = 18.1 Hz, P*C*HCH$_3$), 20.8, 20.3 (both s, PCH*C*H$_3$), 12.0 (d, J(RhC) = 13.7 Hz, ═CH$_2$). ^{31}P NMR (162.0 MHz, C_6D_6): δ 35.5 (d, J(RhP) = 116.8 Hz). Anal. Calcd for $C_{36}H_{58}ClO_2P_2Rh$: C, 59.79; H, 8.08. Found: C, 59.64; H, 8.19.

Preparation of *trans*-[RhCl{η^2-H$_2$*C*═*C*═C═C(CF$_3$)Ph}(P*i*Pr$_3$)$_2$] (30). This compound was prepared as described for **28** from **26** (85 mg, 0.13 mmol) and a 0.28 M solution of diazomethane in ether (1.5 mL, 0.42 mmol). After recrystallization from pentane at −78 °C, red crystals were obtained. Yield: 83 mg (96%). Mp: 118 °C dec. IR (C_6H_6): ν(C═C═C═C) 2020 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (m, 5H, C_6H_5), 2.87, 2.78 (both dddd, J(HH) = J(P^{1}H) = J(P^{2}H) = 5.6, J(RhH) = 1.6 Hz, 1H each, ═CH$_2$), 2.56, 2.33 (both m, 3H each, PC*H*CH$_3$), 1.37 (dvt, N = 14.0, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$), 1.30 (dvt, N = 12.8, J(HH) = 6.8 Hz, 9H, PCHC*H*$_3$), 1.18 (dvt, N = 12.8, J(HH) = 6.4 Hz, 9H, PCHC*H*$_3$), 1.04 (dvt, N = 13.6, J(HH) = 6.8 Hz, 9H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 183.8 (s, *C*═C(Ph)CF_3), 135.2 (s, ipso-C of C_6H_5), 128.3, 127.4, 127.1 (all s, C_6H_5), 125.0 (q, J(FC) = 272.2 Hz, CF_3), 109.9 (dt, J(RhC) = 22.1, J(PC) = 4.0 Hz, *C*═CH$_2$), 99.3 (q, J(FC) = 34.0 Hz, ═C(Ph)CF_3), 22.2 (vt, N = 18.9 Hz, P*C*HCH$_3$), 22.1 (vt, N = 18.7 Hz, P*C*HCH$_3$), 20.5, 20.1, 19.8, 19.6 (all s, PCH*C*H$_3$), 16.1 (d, J(RhC) = 14.7 Hz, ═CH$_2$). ^{19}F NMR (376.5 MHz, $CDCl_3$): δ −58.6 (s). ^{31}P NMR (162.0 MHz, $CDCl_3$): Partly resolved AB pattern of ABX spectrum with signals at δ 34.8 and 34.2. MS (70 eV): m/z 654 (M^+), 458 ([M − Cl − P*i*Pr$_3$]$^+$). Anal. Calcd for $C_{29}H_{49}ClF_3P_2Rh$: C, 53.18; H, 7.54. Found: C, 52.98; H, 7.51.

Preparation of *trans*-[RhCl{η^2-H$_2$*C*═*C*═C═C(tBu)Ph}(P*i*Pr$_3$)$_2$] (31). This compound was prepared as described for **28** from **27** (86 mg, 0.14 mmol) and a 0.28 M solution of diazomethane in ether (1.5 mL, 0.42 mmol). After recrystallization from pentane at −78 °C, orange crystals were obtained. Yield: 80 mg (92%). Mp: 105 °C. IR (C_6H_6): ν(C═C═C═C) 1945 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 7.22, 7.02 (both m, 5H, C_6H_5), 2.65−2.57 (m, 5H, ═CH$_2$ and PC*H*CH$_3$), 2.44 (m, 3H, PC*H*CH$_3$), 1.42 (m; d in ^{1}H{^{31}P}, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$), 1.26 (m; d in ^{1}H{^{31}P}, J(HH) = 7.2 Hz, 9H, PCHC*H*$_3$), 1.25 (s, 9H, C(CH$_3$)$_3$), 1.08 (m, 18H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 179.3 (s, *C*═C(*t*Bu)Ph), 141.6 (s, ipso-C of C_6H_5), 128.8, 127.4, 125.8 (all s, C_6H_5), 100.2 (s, ═C(*t*Bu)Ph), 109.4 (dt, J(RhC) = 23.1, J(PC) = 5.0 Hz, *C*═CH$_2$), 36.3 (s, *C*(CH$_3$)$_3$), 30.0 (s, C(*C*H$_3$)$_3$), 22.3 (vt, N = 24.2 Hz, P*C*HCH$_3$), 22.3 (vt, N = 24.0 Hz, P*C*HCH$_3$), 21.0, 20.6, 20.1, 19.8 (all s, PCH*C*H$_3$), 12.5 (d, J(RhC) = 13.4 Hz, ═CH$_2$). ^{31}P NMR (162.0 MHz, C_6D_6): AB part of a degenerated ABX spectrum with four signals at δ 36.3, 36.1, 35.6, and 35.4. Anal. Calcd for $C_{32}H_{58}ClP_2Rh$: C, 59.76; H, 9.09. Found: C, 59.64; H, 8.90.

Preparation of *trans*-[RhCl(η^2-H$_2$C═*C*═*C*═CPh$_2$)(P*i*Pr$_3$)$_2$] (32). A solution of **28** (83 mg, 0.13 mmol) in toluene (3 mL) was stirred for 2 h at 80 °C. A smooth change of color from red to yellow occurred. After the solution was cooled to room temperature, the solvent was evaporated in vacuo. The remaining yellow microcrystalline residue was washed twice with 1-mL portions of ether (0 °C) and dried. Yield: 81 mg (98%). Mp: 162 °C dec. IR (C_6H_6): ν(C═C═C═C) 1930 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.03, 7.39 (both m, 2H each, ortho-H of C_6H_5), 7.34, 7.29 (both m, 2H each, meta-H of C_6H_5), 7.14 (m, 2 H, para-H of C_6H_5), 5.46 (s, br, 1H, exo-H of ═CH$_2$), 5.00 (s, br, 1H, endo-H of ═CH$_2$), 2.46 (m, 6H, PC*H*CH$_3$), 1.30 (dvt, N = 14.0, J(HH) = 7.2 Hz, 18H, PCHC*H*$_3$), 1.14 (dvt, N = 12.8, J(HH) = 6.8 Hz, 18H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 142.7 (dt, J(RhC) = 17.1, J(PC) = 4.0 Hz, RhC), 141.6, 140.1 (both s, ipso-C of C_6H_5), 138.0 (dt, J(RhC) = 20.1, J(PC) = 5.0 Hz, RhC), 129.3, 128.8, 128.5, 128.1, 127.0, 126.6 (all s, C_6H_5), 127.6 (s, br, ═CPh$_2$), 98.4 (s, br, ═CH$_2$), 23.5 (vt, N = 19.4 Hz, P*C*HCH$_3$), 20.9, 19.8 (both s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 31.0 (d, J(RhP) = 116.3 Hz). Anal. Calcd for $C_{34}H_{54}ClP_2Rh$: C, 61.58; H, 8.21; Rh, 15.51. Found: C, 61.31; H, 8.45; Rh, 15.91.

Preparation of *trans*-[RhCl{η^2-H$_2$C═*C*═*C*═C(*p*-C$_6$H$_4$OMe)$_2$}-(P*i*Pr$_3$)$_2$] (33). This compound was prepared as described for **32** from **29** (94 mg, 0.13 mmol) to give a yellow microcrystalline solid. Yield: 91 mg (97%). Mp: 167 °C dec. IR (C_6H_6): ν(C═C═C═C) 2029 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 9.06, 7.02, 7.35, 6.89 (all d, J(HH) = 8.8 Hz, 2H each, C_6H_4), 5.47 (s, br, 1H, exo-H of ═CH$_2$), 5.00 (s, br, 1H, endo-H of ═CH$_2$), 3.38, 3.34 (both s, 3H each, OCH$_3$), 2.49 (m, 6H, PC*H*CH$_3$), 1.35 (dvt, N = 14.0, J(HH) = 7.2 Hz, 18H, PCHC*H*$_3$), 1.18 (dvt, N = 12.8, J(HH) = 6.8 Hz, 18H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 159.3, 158.6 (both s, *C*OMe), 142.8 (dt, J(RhC) = 15.1, J(PC) = 4.0 Hz, RhC), 134.4, 134.0 (both s, ipso-C of C_6H_4), 133.8 (dt, J(RhC) = 20.1, J(PC) = 6.0 Hz, RhC), 130.7, 129.8, 113.9, 113.6 (all s, C_6H_4), 126.9 (d, br, J(RhC) = 2.0 Hz, ═C(*p*-C$_6$H$_4$OMe)$_2$), 97.0 (s, br, ═CH$_2$), 54.8 (s, OCH$_3$), 23.5 (vt, N = 19.1 Hz, P*C*HCH$_3$), 21.0, 19.8 (both s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ 30.9 (d, J(RhP) = 116.9 Hz). Anal. Calcd for $C_{36}H_{58}ClO_2P_2Rh$: C, 59.79; H, 8.08; Rh, 14.23. Found: C, 59.78; H, 8.25; Rh, 14.44.

Preparation of *trans*-[RhCl{η^2-H$_2$C═*C*═*C*═C(*t*Bu)Ph}(P*i*Pr$_3$)$_2$] (*syn*- and *anti*-34). A solution of **27** (87 mg, 0.14 mmol) in toluene (3 mL) was stirred for 2 h at 95 °C. A change of color from orange to yellow occurred. After the solution was cooled to room temperature, the solvent was evaporated in vacuo and the residue washed twice with 1-mL portions of ether (0 °C). The NMR spectra of the yellow solid indicated that a mixture of *syn*-**34** and *anti*-**34** in the molar ratio of ca. 2:1 was formed. After the yellow solid was dissolved in toluene (3 mL) and the solution stirred again for 6 h at 95 °C, the ratio of *syn*-**34** and *anti*-**34** had changed to 10:1. The solvent was removed in vacuo, the residue was dissolved in acetone (6 mL), and the solution was stored for 20 h at −78 °C. Yellow crystals precipitated that were separated from the mother liquor, washed twice with 1-mL portions of pentane

(0 °C), and dried. The NMR spectra confirmed that a pure sample of *syn*-**34** was isolated. Yield: 61 mg (67%). Mp: 132 °C dec. IR (C_6H_6): ν(C=C=C=C) 1950 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33, 7.24 (both m, 5H, C_6H_5), 5.62 (t, J(PH) = 2.4 Hz, 1H, exo-H of =CH_2), 5.21 (s, br, 1H, endo-H of =CH_2), 2.43 (m, 6H, PC*H*CH_3), 1.26 (s, 9H, C(CH_3)$_3$), 1.23 (dvt, N = 14.0, J(HH) = 7.2 Hz, 18H, PCHC*H*$_3$), 1.18 (dvt, N = 13.2, J(HH) = 6.8 Hz, 18H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 143.6 (dt, J(RhC) = 16.1, J(PC) = 4.0 Hz, RhC), 142.4 (s, ipso-C of C_6H_5), 134.3 (d, J(RhC) = 3.0 Hz, =C(*t*Bu)Ph), 132.6 (dt, J(RhC) = 18.1, J(PC) = 4.0 Hz, RhC), 130.1, 127.1, 125.9 (all s, C_6H_5), 100.2 (s, =CH_2), 24.3 (vt, N = 20.0 Hz, P*C*HCH$_3$), 20.9, 20.5 (both s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 28.1 (d, J(RhP) = 119.2 Hz). Anal. Calcd for $C_{32}H_{58}ClP_2Rh$: C, 59.76; H, 9.09. Found: C, 60.06; H, 9.35. NMR data of *anti*-**34**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24, 6.92 (both m, 5H, C_6H_5), 4.65 (s, br, 1H, exo-H of =CH_2), 4.19 (s, br, 1H, endo-H of =CH_2), 2.55 (m, 6H, PC*H*CH_3), 1.50 (s, 9H, C(CH_3)$_3$), 1.38 (dvt, N = 13.2, J(HH) = 6.4 Hz, 18H, PCHC*H*$_3$), 1.32 (dvt, N = 12.8, J(HH) = 6.4 Hz, 18H, PCHC*H*$_3$). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 29.0 (d, J(RhP) = 119.5 Hz).

Generation of H_2C=C=C=C(*t*Bu)Ph (35). A slow stream of CO was passed for 30 s either through a solution of **31** (51 mg, 0.08 mmol) or of *syn*-**34** (58 mg, 0.09 mmol) in benzene (3 mL) at room temperature. A gradual change of color from yellow to pale yellow occurred. After the solvent was evaporated in vacuo, the NMR spectra of the residue showed that besides **18** the butatriene **35** was formed. It was identified by comparison with the NMR data of related butatrienes.[38,39] Data for **35**.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.22 (m, 5H, C_6H_5), 5.13, 5.05 (both d, 1H each, J(HH) = 7.6 Hz, =CH_2), 1.24 (s, C(CH_3)$_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 168.6, 158.7 (both s, *C*=CH_2 and *C*=CPh_2), 140.0 (s, ipso-C of C_6H_5), 135.3 (s, =CPh_2), 128.6, 127.8, 127.2 (all s, C_6H_5), 89.3 (s, =CH_2), 37.8 (s, *C*(CH_3)$_3$), 30.1 (s, C(*C*H$_3$)$_3$).

Preparation of *trans*-[RhI(η^2-H_2C=*C*=*C*=CPh_2)(P*i*Pr$_3$)$_2$] (38). Method a. A suspension of **36** (97 mg, 0.13 mmol) and Na_2CO_3 (500 mg, 4.72 mmol) in a 1:1 mixture of acetone and THF (4 mL) was treated dropwise with CH_3I (60 μL, 135 mg, 0.95 mmol) at room temperature. A change of color from red to yellow occurred. After the reaction mixture was stirred for 6 h, the solvent was evaporated in vacuo, and the residue extracted with cooled CH_2Cl_2 (3 mL, −30 °C). The extract was brought to dryness in vacuo, and the remaining yellow solid was washed three times with 2-mL portions of acetone and dried in vacuo. Yield: 75 mg (76%).

Method b. A suspension of **1** (88 mg, 0.14 mmol) and Na_2CO_3 (500 mg, 4.72 mmol) in a 1:1 mixture of acetone and THF (4 mL) was treated dropwise with CH_3I (60 μL, 135 mg, 0.95 mmol) at room temperature. A change of color from red to yellow occurred. After the reaction mixture was stirred for 6 h, the solvent was evaporated in vacuo and the residue extracted with CH_2Cl_2 (3 mL, 0 °C). The extract was brought to dryness in vacuo and the residue dissolved in THF (4 mL). The solution was treated with KI (300 mg, 1.81 mmol) and stirred for 3 h at room temperature. The solvent was removed and the yellow residue extracted with benzene (5 mL). After the extract was filtered, the solvent was evaporated in vacuo, and the remaining yellow solid was washed three times with 2-mL portions of acetone (0 °C) and dried. Yield: 83 mg (82%). Mp: 146 °C dec. IR (C_6H_6): ν(C=C=C=C) 1710 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62, 7.26 (both m, 10H, C_6H_5), 5.13 (s, br, 1H, exo-H of =CH_2), 4.78 (s, br, 1H, endo-H of =CH_2), 2.68 (m, 6H, PC*H*CH_3), 1.29 (dvt, N = 13.8, J(HH) = 7.0 Hz, 18H, PCHC*H*$_3$), 1.19 (dvt, N = 12.9, J(HH) = 6.6 Hz, 18H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 142.4 (dt, J(RhC) = 18.1, J(PC) = 3.0 Hz, RhC), 140.4, 140.0 (both s, ipso-C of C_6H_5), 135.9 (dt, J(RhC) = 20.1, J(PC) = 5.0 Hz, RhC), 128.8, 128.3, 128.1, 127.6, 126.5, 126.2 (all s, C_6H_5), 127.5 (s, br, =CPh_2), 98.3 (s, =CH_2), 24.3 (vt, N = 20.0 Hz, P*C*HCH$_3$), 20.9, 20.5 (both s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 28.9 (d, J(RhP) = 113.5 Hz). Anal. Calcd for $C_{34}H_{54}IP_2Rh$: C, 54.12; H, 7.21; Rh, 13.64. Found: C, 53.94; H, 7.49; Rh, 13.41.

Preparation of *trans*-[RhI(η^2-D_2C=*C*=*C*=CPh_2)(P*i*Pr$_3$)$_2$] (38-d_2). This compound was prepared as described for **38** from **36** (112 mg, 0.15 mmol) and CD_3I (60 μL, 138 mg, 0.95 mmol). A yellow microcrystalline solid was obtained. Yield: 83 mg (73%). Mp: 158 °C dec. IR (C_6H_6): ν(C=C=C=C) 1943 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54, 7.17 (both m, 10H, C_6H_5), 2.60 (m, 6H, PC*H*CH_3), 1.20 (dvt, N = 14.0, J(HH) = 6.4 Hz, 18H, PCHC*H*$_3$), 1.19 (dvt, N = 12.9, J(HH) = 6.6 Hz, 18H, PCHC*H*$_3$). ^{2}H NMR (61.4 MHz, C_6H_6): δ 5.35 (s, br, exo-D of =CD_2), 4.86 (s, br, endo-D of =CD_2). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 142.3 (dt, J(RhC) = 18.1, J(PC) = 5.0 Hz, RhC), 140.4, 140.1 (both s, ipso-C of C_6H_5), 136.0 (dt, J(RhC) = 20.1, J(PC) = 5.0 Hz, RhC), 128.8, 128.3, 128.1, 127.6, 126.5, 126.2 (all s, C_6H_5), 127.5 (m, =CPh_2), 24.3 (vt, N = 20.1 Hz, P*C*HCH$_3$), 20.9, 20.5 (both s, PCH*C*H$_3$); signal of =CD_2 not exactly located. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 29.0 (d, J(RhP) = 113.4 Hz). Anal. Calcd for $C_{34}H_{52}D_2IP_2Rh$: C, 53.98; H, 7.46. Found: C, 54.34; H, 7.82.

Preparation of *trans*-[RhI{η^2-H_2C=*C*=*C*=C(*p*-C_6H_4OMe)$_2$}(P*i*Pr$_3$)$_2$] (39). This compound was prepared as described for **38**, either according to method a from **37** (121 mg, 0.15 mmol), Na_2CO_3 (500 mg, 4.72 mmol), and CH_3I (60 μL, 135 mg, 0.95 mmol) or according to method b from **20** (134 mg, 0.18 mmol), Na_2CO_3 (550 mg, 5.20 mmol), and CH_3I (65 μL, 147 mg, 1.04 mmol) to give a yellow microcrystalline solid. Yield: 91 mg (74%) following method a and 122 mg (79%) following method b. Mp: 156 °C dec. IR (C_6H_6): ν(C=C=C=C) 1790 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50, 7.01, 6.80, 6.72 (all d, J(HH) = 8.8 Hz, 2H each, C_6H_4), 4.99 (s, br, 1H, exo-H of =CH_2), 4.64 (s, br, 1H, endo-H of =CH_2), 3.73, 3.69 (both s, 3H each, OCH_3), 2.59 (m, 6H, PC*H*CH_3), 1.20 (dvt, N = 13.6, J(HH) = 6.8 Hz, 18H, PCHC*H*$_3$), 1.10 (dvt, N = 12.8, J(HH) = 6.8 Hz, 18H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 158.4, 157.8 (both s, *C*OMe), 142.6 (dt, J(RhC) = 17.1, J(PC) = 4.0 Hz, RhC), 133.3, 132.9 (both s, ipso-C of C_6H_4), 132.0 (dt, J(RhC) = 20.1, J(PC) = 5.0 Hz, RhC), 130.1, 129.3, 113.3, 112.9 (all s, C_6H_4), 126.6 (s, br, =C(*p*-C_6H_4OMe)$_2$), 96.9 (s, br, =CH_2), 55.3, 55.2 (both s, OCH_3), 24.2 (vt, N = 19.8 Hz, P*C*HCH$_3$), 20.9, 20.4 (both s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 28.9 (d, J(RhP) = 113.9 Hz). Anal. Calcd for $C_{36}H_{58}IO_2P_2Rh$: C, 53.08; H, 7.18. Found: C, 52.84; H, 7.00.

Preparation of *trans*-[RhCl(η^2-H_2C=*C*=CPh_2)(P*i*Pr$_3$)$_2$] (40). A solution of **1** (160 mg, 0.25 mmol) in benzene (5 mL) was stirred for 40 h under an atmosphere of hydrogen at room temperature. A change of color from red to yellow occurred. After the solvent was evaporated in vacuo, the remaining yellow solid was washed twice with 1-mL portions of pentane and dried. Yield: 152 mg (95%). Mp: 201 °C. IR (C_6H_6): ν(C=C=C) 1690 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.03, 7.47, 7.36, 7.31, 7.13, 7.12 (all m, 10H, C_6H_5), 2.41 (dt, J(RhH) = 2.1, J(PH) = 5.1 Hz, 2H, =CH_2), 2.33 (m, 6H, PC*H*CH_3), 1.21 (dvt, N = 13.5, J(HH) = 7.0 Hz, 18H, PCHC*H*$_3$), 1.15 (dvt, N = 12.8, J(HH) = 6.7 Hz, 18H, PCHC*H*$_3$). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 173.3 (dt, J(RhC) = 23.1, J(PC) = 6.0 Hz, =C =), 143.9, 140.6 (both s, ipso-C of C_6H_5), 128.7, 128.2, 128.0, 127.4, 125.6, 125.4 (all s, C_6H_5), 123.1 (s, =CPh_2), 22.1 (vt, N = 18.6 Hz, P*C*HCH$_3$), 20.6, 19.6 (both s, PCH*C*H$_3$), 16.4 (d, J(RhC) = 13.1 Hz, =CH_2). ^{31}P NMR (C_6D_6, 81.0 MHz): δ 32.7 (d, J(RhP) = 116.3 Hz). Anal. Calcd for $C_{33}H_{54}Cl_1P_2Rh$: C, 60.88; H, 8.36. Found: C 60.76; H, 8.38.

Preparation of *trans*-[RhCl{η^2-H_2C=*C*=C(CF_3)Ph)(P*i*Pr$_3$)$_2$] (41). This compound was prepared as described for **40** from **26** (107 mg, 0.17 mmol) to give a yellow microcystalline solid. Yield: 103 mg (96%). Mp: 180 °C. IR (C_6H_6): ν(C=C=C) 1690 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.86, 7.25 (both m, 5H, C_6H_5), 2.62 (m, 2H, =CH_2), 2.31 (m, 6H, PC*H*CH_3), 1.23 (dvt, N = 13.5, J(HH) = 6.9 Hz, 18H, PCHC*H*$_3$), 1.12 (dvt, N = 12.8, J(HH) = 6.2 Hz, 18H, PCHC*H*$_3$). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 179.0 (m, =C =), 134.8 (s, ipso-C of C_6H_5), 127.8, 127.3, 126.3 (all s, C_6H_5), 122.5 (q, J(FC) = 277.4 Hz, CF_3), 112.9 (q, J(FC) = 27.3 Hz, =C(Ph)CF_3), 22.3 (vt, N = 19.4

Table 1. Crystallographic Data for **3**, **21**, and **28**

	3	**21**	**28**
formula	$C_{29}H_{36}PRh$	$C_{33}H_{51}Cl_3P_2Rh + {}^1/_2CH_2Cl_2$	$C_{34}H_{54}ClP_2Rh$
fw	518.46	761.40	663.07
crystal size, mm	0.50 × 0.35 × 0.30	0.20 × 0.23 × 0.40	0.30 × 0.30 × 0.40
crystal syst	orthorhombic	triclinic	monoclinic
space group	*Pcab* (No. 61)	*P*-1 (No. 2)	*P*21/*c* (No. 14)
cell dimens determn	23 rflns, 10° < θ < 14°	25 rflns, 8° < θ < 18°	23 rflns, 10° < θ < 14°
a, Å	16.305(3)	9.463(4)	18.52(1)
b, Å	17.315(4)	11.369(5)	11.193(3)
c, Å	18.344(4)	17.936(9)	16.523(9)
α, deg	90	92.00(3)	90
β, deg	90	97.90(2)	93.35(3)
γ, deg	90	108.25(2)	90
V, Å^3	5178.8(18)	1809(1)	3520(3)
Z	8	2	4
d_{calcd}, g cm^{-1}	1.330	1.398	1.29
temp, K	293(2)	293(2)	293(2)
μ, mm^{-1}	0.735	0.872	0.680
scan method	ω/θ	ω/θ	ω/θ
2θ(max), deg	52	48	48
total no. of rflns	5620	5618	5567
no. of unique rflns	5072 (*R*(int) = 0.0000)	5225 (*R*(int) = 0.0188)	5351 (*R*(int) = 0.0130)
no. of obsd rflns	2500 ($I > 2\sigma(I)$)	5225 ($I > 2\sigma(I)$)	4654 ($I > 2\sigma(I)$)
no. of rflns used for refinement	5072	4411	4654
no. of params refined	286	376	559
final *R* indices	$R_1 = 0.0523$	$R_1 = 0.0317$	$R_1 = 0.0214$
	$wR_2 = 0.1170^a$ ($I > 2\sigma(I)$)	$wR_2 = 0.0791^a$ ($I > 2\sigma(I)$)	$wR_2 = 0.0568^a$ ($I > 2\sigma(I)$)
R indices (all data)	$R_1 = 0.1597$	$R_1 = 0.0481$	$R_1 = 0.0305$
	$wR_2 = 0.1483^a$	$wR_2 = 0.0858^a$	$wR_2 = 0.0610^a$
resid electron density, e Å^3	0.999/0.406	0.707/0.798	0.296/0.170

[a] $w^{-1} = [\sigma^2F_o^2 + (0.0681P)^2 + 0.0000P]$ (**3**), $w^{-1} = [\sigma^2F_o^2 + (0.0422P)^2 + 1.8768P]$ (**21**), $w^{-1} = [\sigma^2F_o^2 + (0.0456P)^2 + 0.0000P]$ (**28**), where $P = (F_o^2 + 2F_c^2)/3$.

Hz, P*C*HCH$_3$), 20.5, 19.5 (both s, PCH*C*H$_3$), 18.9 (d, br, *J*(RhC) = 13.9 Hz, =CH$_2$). ^{31}P NMR (CDCl$_3$, 81.0 MHz): δ 33.5 (d, *J*(RhP) = 113.4 Hz). ^{19}F NMR (CDCl$_3$, 188.3 MHz): δ −59.44 (s). MS (70 eV): *m*/*z* 642 (M^+), 458 (RhCl(P*i*Pr$_3$)$_2^+$), 184 ($H_2C{=}C{=}C(Ph)CF_3^+$). Anal. Calcd for $C_{28}H_{49}ClF_3P_2Rh$: C, 52.30; H, 7.68; Rh, 16.00. Found: C, 52.21; H, 7.64; Rh, 15.53.

Reaction of 40 with CO. A slow stream of CO was passed for 1 min through a solution of **40** (35 mg, 0.05 mmol) in C_6D_6 (0.5 mL) at 10 °C. A gradual change of color from yellow to pale yellow occurred. The solution was stored for 5 h at room temperature and then investigated by NMR spectroscopy. The ^{1}H, ^{13}C, and ^{31}P NMR spectra indicated that besides **18** the 1,1-disubstituted allene $CH_2{=}C{=}CPh_2$ (**42**)[45] was formed.

Reaction of 41 with CO. This reaction was carried out analogously as described for **40** with **41** (40 mg, 0.06 mmol) as starting material. Besides the formation of **18**, only that of $CH_2{=}C{=}C(CF_3)Ph$ (**43**) was observed. NMR data for **43**. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.38, 7.06, 6.99 (all m, 5H, C_6H_5), 4.75 (q, *J*(FH) = 3.2 Hz, =CH$_2$). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 210.2 (q, *J*(FC) = 5.0 Hz, =C=), 138.0 (m, ipso-C of C_6H_5), 129.0, 128.4, 127.3 (all s, C_6H_5), 124.2 (q, *J*(FC) = 273.7 Hz, CF_3), 102.0 (q, *J*(FC) = 32.2 Hz, =C(Ph)CF$_3$), 83.1 (s, =CH$_2$). ^{19}F NMR (C_6D_6, 188.3 MHz): δ −60.70 (s).

Preparation of *trans*-[RhCl(η^2-Ph$_2$C=*C*=*C*=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] (44). A solution of **1** (180 mg, 0.28 mmol) in toluene (3 mL) was stirred for 5 days at 95 °C. After the solution was cooled to room temperature, the residue was washed three times with 2-mL portions of ether and then twice 1-mL portions of acetone (−20 °C). The remaining solid was dissolved in acetone (3 mL, 25 °C) and the solution was stored for 5 days at −78 °C. Bright red crystals precipitated, which were separated from the mother liquor, washed twice with 1-mL portions of acetone (−20 °C), and dried. Yield: 75 mg (88%). The IR and NMR data of the product were identical to those of **44**.[46]

Preparation of *trans*-[RhCl{η^2-(*p*-C$_6$H$_4$OMe)$_2$C=*C*=*C*=C=C=C(*p*-C$_6$H$_4$OMe)$_2$}-(P*i*Pr$_3$)$_2$] (45). This compound was prepared as described for **44** from **20** (190 mg, 0.27 mmol) to give bright red crystals. Yield: 75 mg (88%). Mp: 155 °C dec. IR (C_6H_6): ν(C=C=C=C) 1939 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 8.82, 7.53, 7.28, 7.26 (all d, *J*(HH) = 8.8 Hz, 2H each, C_6H_4), 3.91, 3.88 (both s, 3H each, OCH$_3$), 3.89 (s, 6H, OCH$_3$), 2.56 (m, 6H, P*C*HCH$_3$), 1.44 (dvt, *N* = 13.6, *J*(HH) = 6.8 Hz, 18H, PCHC*H*$_3$), 1.27 (dvt, *N* = 13.2, *J*(HH) = 6.4 Hz, 18H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 160.5 (s, =C=), 159.3, 159.1, 158.9, 158.4 (all s, *C*OMe), 134.0 (s, br, =C=), 134.1, 133.5, 132.4, 131.1 (all s, ipso-C of C_6H_4), 130.9, 130.1, 129.8, 129.6 (all s, C_6H_4), 128.0 (dt, *J*(RhC) = 20.1, *J*(PC) = 4.0 Hz, RhC), 127.2 (d, *J*(RhC) = 2.0 Hz, =C(*p*-C$_6$H$_4$OMe)$_2$), 115.3 (s, =C(*p*-C$_6$H$_4$-OMe)$_2$), 114.0, 113.9, 113.8, 113.4 (all s, C_6H_4), 113.4 (dt, *J*(RhC) = 16.1, *J*(PC) = 5.0 Hz, RhC), 55.6, 55.5, 55.4 (all s, OCH$_3$), 23.6 (vt, *N* = 19.2 Hz, P*C*HCH$_3$), 21.9, 19.7 (both s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ 32.4 (d, *J*(RhP) = 113.9 Hz). Anal. Calcd for $C_{52}H_{70}ClO_4P_2Rh$: C, 65.10; H, 7.35. Found: C, 64.89; H, 6.94.

X-ray Structure Determination of Compounds 3, 7, 12, 21, and 28. Single crystals of **3**, **7**, and **12** were grown by cooling a solution in acetone at −30 °C, those of **21** by slow diffusion of pentane into a saturated solution of **21** in CH_2Cl_2 at room temperature, and those of **28** by cooling a solution in pentane at −10 °C. Crystal data collection parameters are summarized in Table 1. The data were collected on an Enraf-Nonius CAD4 diffractometer using monochromated Mo Kα radiation (λ = 0.71073 Å). Crystal data were corrected by Lorentz and polarization effects, and empirical absorption corrections were applied (Ψ-scan method, minimum transmissions 91.97% (**3**), 95.4% (**7**), 97.07% (**12**), and 97.49% (**28**)). The structures were solved by direct methods (**3**, **7**, **12**, **21**) and the Patterson method (**28**) (SHELXS-86).[50] Atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least squares on F^2 (SHELXL-93).[51]

(50) Sheldrick, G. M. *Acta Crystallogr. Sect. A* **1990**, *46*, 467.
(51) Sheldrick, G. M. Program for Crystal Structure Refinement; Universität Göttingen, 1996.

Except for H1a and H1b of compound **28**, the positions of all hydrogen atoms were calculated according to ideal geometry and refined using the riding method. The asymmetric unit of **21** contains one-half of the solvent molecule CH_2Cl_2, which was disordered. Near to the center of symmetry there was one chlorine atom and one-half of the carbon atom, and the second half was generated by a symmetry operation.

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Supporting Information Available: Tables of data collection parameters, bond lengths and angles, positional and thermal parameters, and least-squares planes for **3**, **21**, and **28**; data for these compounds are also given in CIF format. (For the corresponding data of **7** and **12**, see ref 5.) This material is available free of charge via the Internet at http://pubs.acs.org.

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